Chapter 11

Evaluating Environmental Performance of a Flowsheet

Detailed Environmental Assessment of
Chemical Process Flowsheets

Outline

The last step for improving the environmental performance of a chemical process design is a detailed environmental impact assessment of a process flowsheet

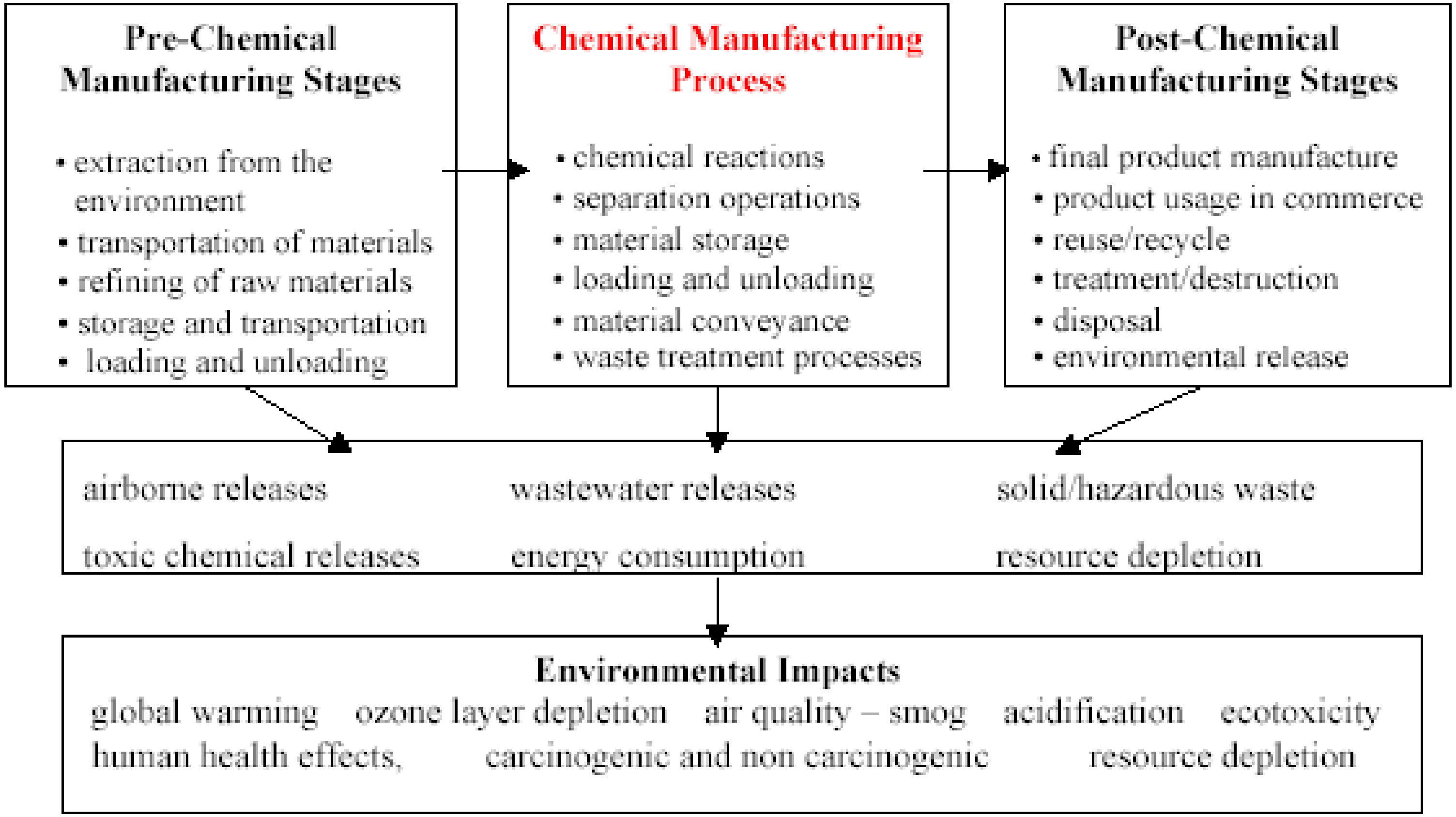
- Tier 3 assessment
  - » How to formulate environmental impact indicators
  - » How to "draw the boundaries" around the assessment - what to leave in - what to leave out
  - » A methodology to integrate emissions estimation, environmental fate and transport, and relative risk assessment
  - » Example application for VOC recovery/recycle

Educational goals and topics covered in the module

Students will:

- learn to apply a systematic risk assessment methodology to the evaluation of chemical process designs
- integrate emission estimation, environmental fate and transport calculations, and relative risk assessment to rank process design alternatives

Boundaries for impact assessment



Pre-Chemical Manufacturing Stages

- extraction from the environment
- transportation of materials
- refining of raw materials
- storage and transportation
- loading and unloading

Chemical Manufacturing Process

- chemical reactions
- separation operations
- material storage
- loading and unloading
- material conveyance
- waste treatment processes

Post-Chemical Manufacturing Stages

- final product manufacture
- product usage in commerce
- reuse/recycle
- treatment/destruction
- disposal
- environmental release

airborne releases
wastewater releases
solid/hazardous waste
toxic chemical releases
energy consumption
resource depletion

Environmental Impacts

global warming ozone layer depletion air quality – smog acidification ecotoxicity
human health effects, carcinogenic and non carcinogenic resource depletion

Chapter 11: chemical manufacturing stage only - Chapter 13: all stages

1. Introduction

Environmental Indexes (Metrics)

(it is appropriate for a detailed environmental impact evaluation)

- The end result of impact evaluation will be a set of environmental metrics (indexes) which represent the major environmental impact or risks of the entire process

- The indexes are used in process design applications such as
  (1) ranking of the technologies
  (2) optimizing in-process waste recycle/recovery processes
  (3) evaluation of the modes of reactor design

1. Introduction

- In quantitative risk assessment, it is shown that

  (1) impacts are a function of dose
  (2) that dose is a function of concentration
  (3) that concentration is a function of emission rate

Thus, emissions from a process design flowsheet are the primary piece of information required for impact assessment

- The concentrations in the relevant compartments of the environment (air, water, soil) are dependent upon the emissions, location, and physicochemical properties of the pollutants

- A suitable fate and transport model can transform the emissions into environmental concentrations.

1. Introduction

❁ Information regarding toxicity or inherent impact is required to convert concentration-dependent doses into probabilities of harm (risk). Based on this understanding of risk assessment, the steps for environmental impact assessment are grouped into three categories

(1) Estimates of the rates of release for all chemicals in the process
(2) Calculation of environmental fate and transport and environmental concentrations
(3) The accounting for multiple measures of risk using toxicology and inherent environmental impact information

11.2 Estimation of Environmental Fates of Emissions and Wastes

After a chemical is released into environment (either to air, surface water or soil), there are several transport and reaction processes that affect the ultimate concentrations in each of these compartments

Two Important Issues arise when choosing the type of environmental fate and transport model-accuracy and ease of use

1) accuracy depends on how rigorously the model incorporates environmental processes into its description of mass transport and reaction
2) Ease of use relates to the data requirement and computational demands which the model places on the environmental assessment

11.2 Estimation of Environmental Fates of Emissions and Wastes

Major Modeling Approaches

1) **Single-Compartmental Models (*SCMs*)**

2) **Multi-Compartmental Models (*MCMs*)**

11.2 Estimation of Environmental Fates of Emissions and Wastes

Single Compartmental Models (SCM)

-Focuses on transport and fate processes in only one compartment.

- Atmospheric dispersion models to predict air concentrations downwind from stationary sources
- Ground water dispersion models to predict concentrations in contaminated plumes downgrading from subsurface pollution sources)

A severe limitation when multiple environmental impacts are under consideration. To provide multi-compartmental insights into fate and transport, several SCMs can be linked together (Poor)

11.2 Estimation of Environmental Fates of Emissions and Wastes

Multi-Compartmental Models (MCMs)

The MCMs predict chemical concentrations in several environmental compartments simultaneously.

Advantage: They require modest data input, relatively simple and computationally efficient, and they account for several intermediate transport mechanisms and degradation.

Limitation: General lack of experimental data, and they can only be used to provide only order-of-magnitude estimates of environmental concentrations

11.2 Estimation of Environmental Fates of Emissions and Wastes

Example of Level III MCM Fugacity Model (Mackay, 2001)

This model predicts the steady-state concentrations of a chemical in 4 environmental compartments (air(1), surface water(2), soil(3) and sediment(4)) in response to a constant emission into an environmental region of defined volume

Problem Description

- surface area selected for the model is 10^5 km^2
- the 10% fraction of area covered by water and 90% is land.
- the surface area of sediment is the same as the water area

Problem Description

- The atmospheric height is set at 1000 m, which is the typical height affected by pollutants emitted at the earth's surface
- The depth of water is 20 m and those of the soil and sediment layers are assumed to be 10 cm and 1 cm.
- Atmospheric compartment contains a condensed (aerosol) phase having a volume fraction of 2×10^{-11} or 30 μg/m^3.
- Water compartment contains suspended sediments of volume fraction 5×10^{-6} or 5 m/L and organic carbon content of 20 %
- Fish are included at a volume fraction of 10^{-6} and are assumed to contain 5 % lipid into which hydrophobic chemical can partition
- The soil compartment is assumed to contain 20 % by volume of air, 30 % water and the remainder solids.
- The organic carbon content of soils is 2 %

All of these parameters could be modified, but these values are reasonable

Problem Description

Fig. 11.2-1 is the process occurring in the model domain which can affect the concentrations in each of the four compartments.

Chemical may directly enter compartments by emissions (**E_i** ,moles/hr) and advective inputs, (**$G_{Ai}C_{Bi}$** , moles/hr).

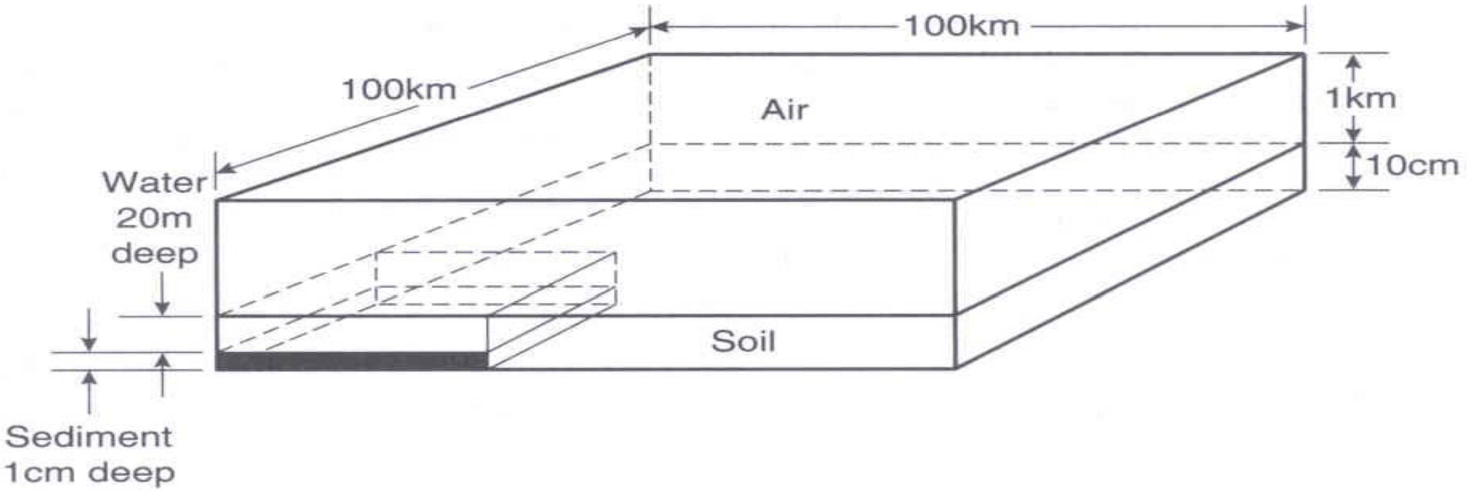
There is transfer of chemical between compartments by diffusive and non-diffusive processes characterized by intermediate transfer values (**D_{ij}** ,moles/Pa.hr).

Chemical may enter or exit compartments by advective (bulk flow) mechanisms having a transfer value **D_{Ai}**, and chemical may disappear by reaction within each compartment having a loss value **D_{Ri}**.

Problem Description

MCMs use the concept of fugacity in describing mass transfer and reaction processes. ***Fugacity is property of a chemical as the "escaping tendency" from a given environmental phase.***

Partitioning of a chemical between environmental phases can be described by the equilibrium criterion of equal fugacity **f** (Pa) in all phases. The fugacity is equal to partial pressure in the dilute limit typical of most environmental concentrations. The fugacity is proportional to concentration, C= **f**Z, where Z is termed the fugacity capacity (Pa.m^3/mole) and C is the concentration (mole/m^3)



Model Domain (not to scale)

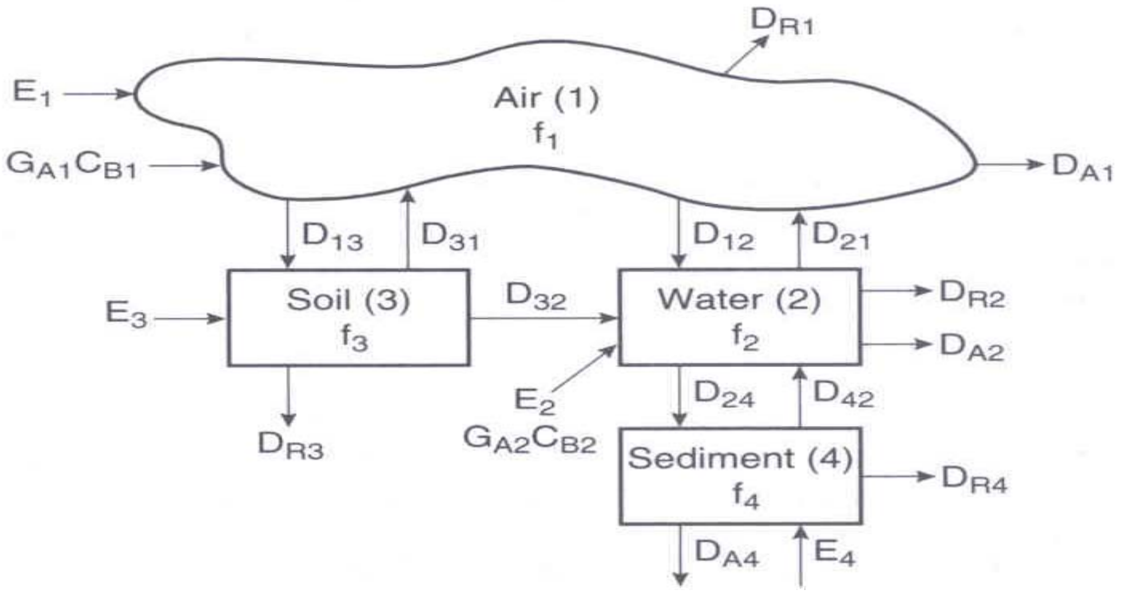
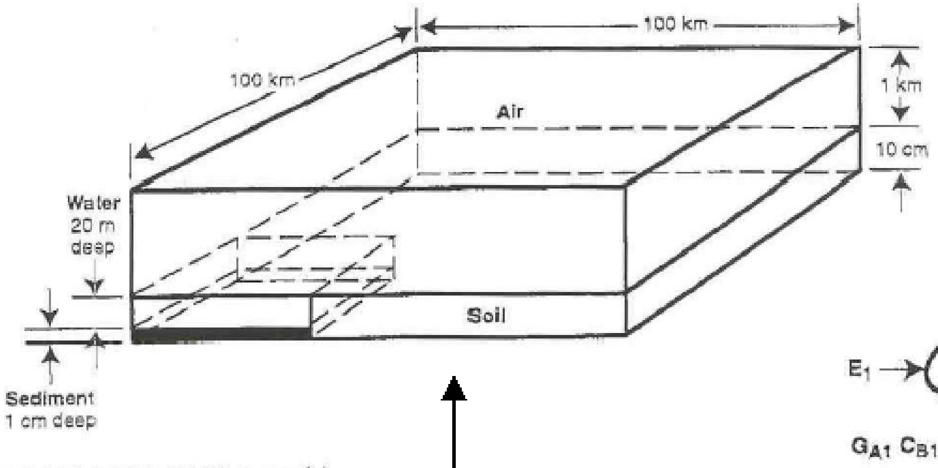


Fig. 11.2-1.

Schematic diagram of fugacity level III model domain and the intermedia transport mechanisms

Multimedia compartment model formulation - chapter 11.2

Multimedia compartment model



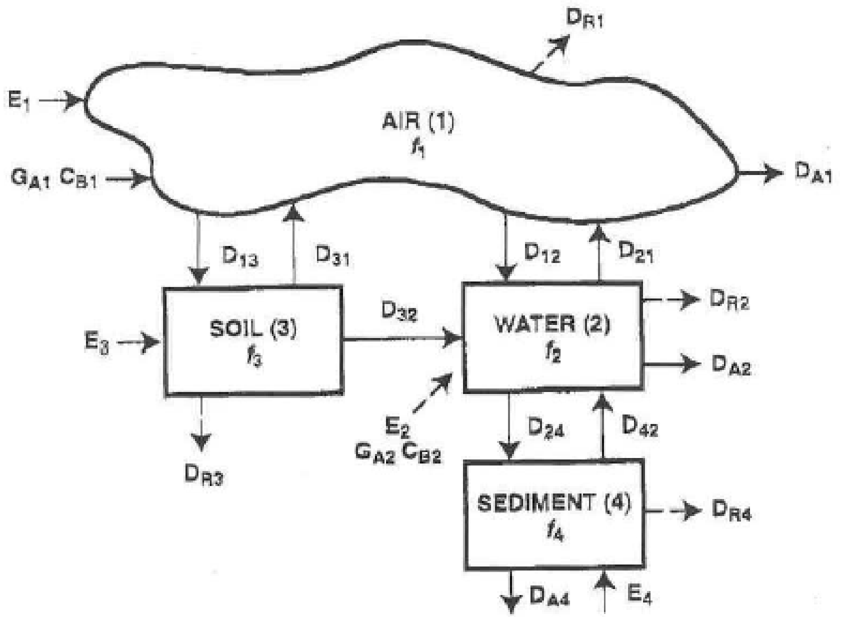
MODEL DOMAIN (Not to scale)

Model Domain Parameters

- surface area - 10^4 -10^5 km^2
- 90% land area, 10% water
- height of atmosphere - 1 km
- soil depth - 10 cm
- depth of sediment layer - 1 cm
- multiphase compartments

Processes modeled

- emission inputs, E
- advection in and out, D_A
- intercompartment mass transfer, $D_{i,j}$
- reaction loss, D_R



Mackay, D. 1991, "Multimedia Environmental Models", 1st edition,, Lewis Publishers, Chelsea, MI

Pursuing Answers

- expressions for relating fugacity to concentrations in different environmental phases (air, water, solids(soil, sediment, suspended sediment), fish, and aerosol)

- intermediate transport mechanisms and reaction expressions of inclusion in the model

- model equations for the fugacity and ultimate the molar concentration in each compartment

2.1 Fugacity and Fugacity Capacity

Air Phase (1)

- The fugacity in the air phase is rigorously defined as

$$\boxed{f = y\phi P_T \approx P}$$

Where P_T is the total pressure (Pa)

1. At the low pressure (1 *atm*), $\phi \approx 1$. Making the fugacity equal to partial pressure (P) of the chemical in air
2. The concentration is related to partial pressure by the ideal gas law

$$C_1 = n / V = P / RT = f / RT = fZ_1$$

Where n is moles of the chemical in a volume V (m^3), R is the gas constant (8.31 $Pa.m^3/mol.K$). T is absolute temperature, *the air Phase fugacity* Z_1 *is 1/RT and has a value* 4.04×10^{-4} *moles/*m^3*.Pa*. The fugacity capacity is independent of chemical, being a constant at the system temperature

Water Phase (2)

- In aqueous phase, the fugacity of a chemical is

$$\boxed{f = x\gamma P^s}$$

1. In most cases, the activity coefficient is a constant (not varying with x). Thus, there is a linear relation between f and concentration, **C_2** (moles.m^3)

$$C_2 = x / v_w = f / (v_w \gamma P^s) = f / H = fZ_2$$

Where v_w is the molar volume of solution (water, 1.8×10^{-5} m^3/mol. **H** is the Henry's law constant for the chemical (Pa.m^3/mol), and *Z_2 is the water fugacity capacity for each chemical, which is the inverse of the chemical's Henry's law constant.*

Soil Phase (3)

- Chemicals associated with the soil or sediment phases are almost always sorbed into the natural organic matter in the soil and are in equilibrium with the water phase concentration
- A linear relation has been observed between the sorbed concentration (C_s, moles/kg soil or sediment) and the aqueous concentration (C_2, moles/L solution)

$$\boxed{C_s = K_d C_2}$$

Where K_d is the equilibrium distribution coefficient (L solution/kg solids) and the slope of the linear sorption isotherm

- Because natural organic matter is composed mainly of carbon, the distribution coefficient is related to the fraction of organic carbon in the soil or sediment by

$$K_{OC} = K_d / \phi_3$$

Soil Phase (3)

$$K_{OC} = K_d / \phi_3$$

where **K_{OC}** is the organic carbon-based distribution coefficient (L/kg)
And ϕ_3 is the mass fraction of organic carbon in the soil phase (g organic carbon/g soil solids).

- The Octanol-Water Partition Coefficient has been correlated as $K_{OC} = 0.41\ K_{OW}$.
- It is convenient to relate the concentration per volume of sorbed phase (C_3 for soil solids) to the fugacity by multiplying Cs by the phase density (ρ_3, kg solid/m_3 solid) and by relating C_2 to partial pressure (fugacity) through the Henry's law constant.

$$\rho_3 C_s = [1/H] K_{OC} \phi_3 \rho_3 f / 1000 = Z_3 f$$

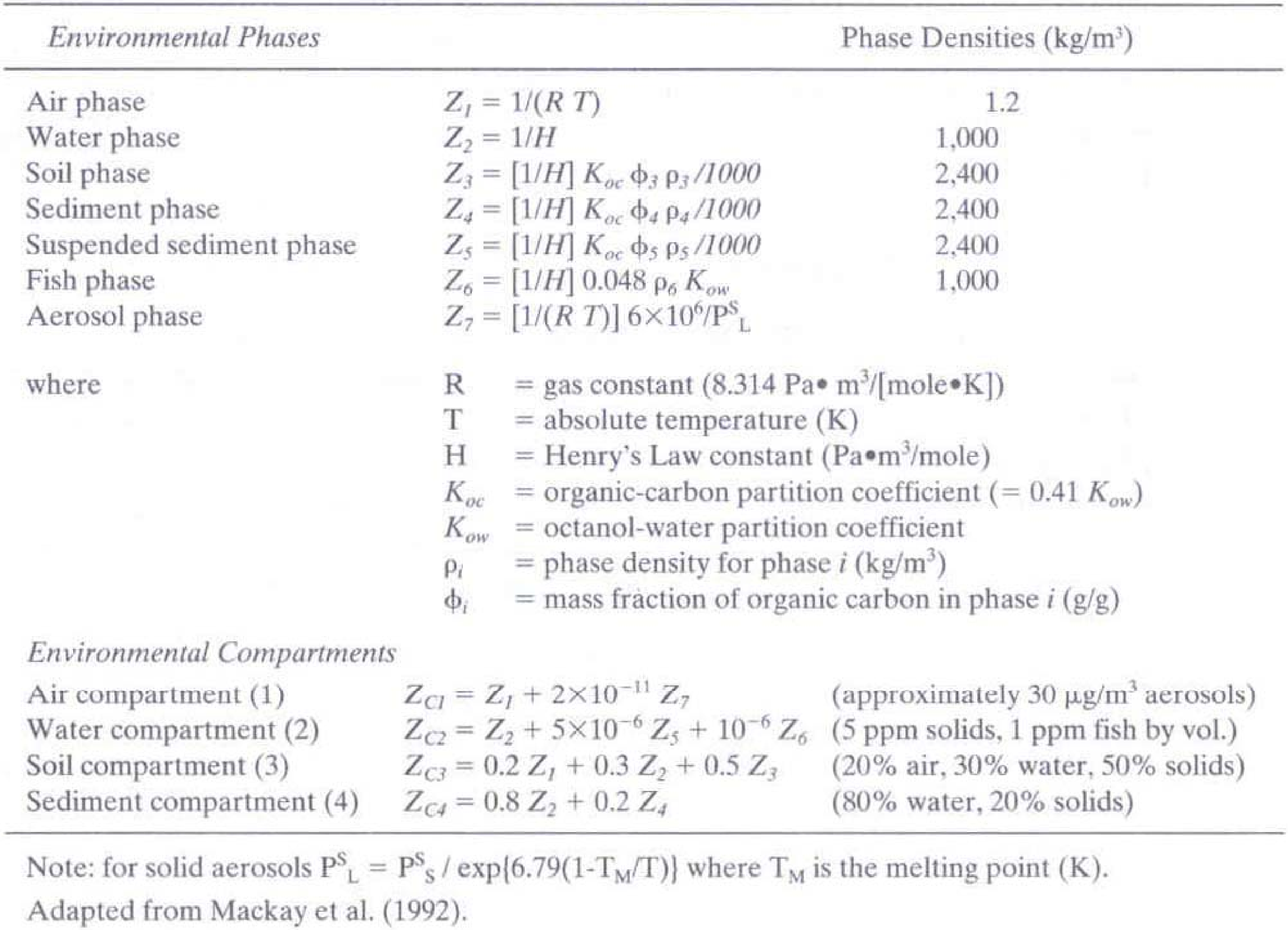
Where the factor 1000 is used to convert L to m^3.

Soil Phase (3)

- Similar expressions for fugacity capacities (Z) are obtained for the other environmental phases which make up the 4 environmental compartments. A summary of these equations is given in **Table 11.2-1**

- Included in **Table 11.2-1** are the fugacity capacities for each of the environmental compartments - the air, surface water, soil, and sediments – which are summations of individual phases Z values weighted by their respective volume fractions in the compartment.

Table 11.2-1. Fugacity capacity(Z) values for the various phases and compartments in the environment



Environmental Phases		Phase Densities (kg/m³)
Air phase	$Z_1 = 1/(R\ T)$	1.2
Water phase	$Z_2 = 1/H$	1,000
Soil phase	$Z_3 = [1/H]\ K_{oc}\ \phi_3\ \rho_3/1000$	2,400
Sediment phase	$Z_4 = [1/H]\ K_{oc}\ \phi_4\ \rho_4/1000$	2,400
Suspended sediment phase	$Z_5 = [1/H]\ K_{oc}\ \phi_5\ \rho_5/1000$	2,400
Fish phase	$Z_6 = [1/H]\ 0.048\ \rho_6\ K_{ow}$	1,000
Aerosol phase	$Z_7 = [1/(R\ T)]\ 6\times10^6/P^S_L$	

where

R = gas constant (8.314 Pa• m³/[mole•K])
T = absolute temperature (K)
H = Henry's Law constant (Pa•m³/mole)
K_{oc} = organic-carbon partition coefficient (= 0.41 K_{ow})
K_{ow} = octanol-water partition coefficient
ρ_i = phase density for phase *i* (kg/m³)
ϕ_i = mass fraction of organic carbon in phase *i* (g/g)

Environmental Compartments		
Air compartment (1)	$Z_{C1} = Z_1 + 2\times10^{-11}\ Z_7$	(approximately 30 μg/m³ aerosols)
Water compartment (2)	$Z_{C2} = Z_2 + 5\times10^{-6}\ Z_5 + 10^{-6}\ Z_6$	(5 ppm solids, 1 ppm fish by vol.)
Soil compartment (3)	$Z_{C3} = 0.2\ Z_1 + 0.3\ Z_2 + 0.5\ Z_3$	(20% air, 30% water, 50% solids)
Sediment compartment (4)	$Z_{C4} = 0.8\ Z_2 + 0.2\ Z_4$	(80% water, 20% solids)

Note: for solid aerosols $P^S_L = P^S_S / \exp\{6.79(1-T_M/T)\}$ where T_M is the melting point (K).

Adapted from Mackay et al. (1992).

2.2 Intermedia Transport

- Chemicals move between environmental compartments by diffusive and non-diffusive processes
- Diffusive processes (volatilization from water to air or soil to air) can proceed in more than one direction, depending on the sign of the fugacity difference between compartments.
- The diffusive rate of transfer N_{ij} (moles/h) from a component **i** to compartment **j** is defined

$$\boxed{N_{ij} = D_{ij}(f_i) \cdot (moles/h)}$$

Where D_{ij} (moles/Pa.hr) is an intermedia transport parameter for diffusion from compartment i to j and f_i is the fugacity in compartment i, serving to drive the chemical into adjoining compartments he he total pressure (Pa)

2.2 Intermedia Transport

- In parallel to diffusive transport is non-diffusive (one-way) transport between compartments, such as rain washout and wet/dry deposition of atmospheric particles to soil and water, and sediment deposition and re-suspension
- This transport can be described by

$$\boxed{N = GC = CZf \ = Df \ \cdot (moles / h)}$$

Where G (m^3/h) is a volumetric flow rate of the transported Material (rainwtaer, suspended sediment, etc.) and C (moles/m3) is its phase concentration.

- **Fig. 11.2-1** illustrates all of the intermediate diffusive and non-diffusive transport mechanisms within the model domain
- Tin the following discussion, each intermediate transport parameter will be derived.

Air/Water Transport (D_{12} and D_{21})

- 3 processes are included in air-to-water transport: diffusion (absorption), washout by rain, and wet/dry deposition of aerosols
- The conventional 2-film approach is taken for absorption from air to water compartments through the atmosphere/water interface using air-side (k_A = 5 m/h) and water-side (k_W = 0.05 m/h) mass transfer coefficients.
- for the sake of organization, we rename the mass transfer coefficients as $k_A = u_1$ and $k_W = u_2$
- the intermediate transport parameter for absorption is

$$\boxed{D_{VW} = 1/\{1/(u_1 A_W Z_1) + 1/(u_2 A_W Z_2)\}}$$

Where A_W is the interfacial area between the atmosphere and the Surface water. For rain washout, a rainfall rate u_3 of 0.876 m/yr (10^{-4} m/h) is assumed.

Air/Water Transport

- The ***D*** value for rain washout is

$$D_{RW} = u_3 A_W Z_2$$

- For wet and dry deposition of aerosols, the deposition velocity $\boldsymbol{u_4}$ is taken to be the sum of these parallel transport mechanisms *(6 ×10^{-10} m/h)* and therefore the ***D*** value becomes

$$D_{QW} = u_4 A_W Z_7$$

- Since these mechanisms operate in parallel, we can define a cumulative ***D*** value for the air-to-water transfer ($\boldsymbol{D_{12}}$) as

$$D_{12} = D_{VW} + D_{RW} + D_{QW}$$

- Water-to-air transport is just the reverse of the absorption mechanism
- And the ***D*** value for water-to-air transport ($\boldsymbol{D_{21}}$) is

$$D_{21} = D_{VW}$$

Air/Soil Transport (D_{13} and D_{31})

- For air-to-soil transport, identical treatments of rain washout (D_{RS}) and wet/dry deposition (D_{QS}) are taken as in the air-to-water transport case.
- The only difference is that the correct area term is the air/soil interface area A_S.
- For diffusion from air to soil, the chemical must traverse a thin mass transfer resistance film at the atmosphere/soil interface before diffusing through the soil air phase or the soil water phase, both of which have resistances of their own
- The value of this mass transfer coefficient at the soil surface u_5 is the same as the air-side mass transfer coefficient for the atmosphere-water interface u_1 (5 m/h)
- Diffusion through the soil-air or –water phases is hampered by the presence of the soil solids, and the molar diffusion coefficients of the chemical in either air or water decreases substantially

Air/Soil Transport

- The **Millington-Quirk relation** is employed to decrease the diffusion coefficients by a factor about 20
- Thus the effective air diffusion coefficient becomes 0.05*0.02 $m^2/h = 10^{-3}$ m^2/h and the effective water diffusion coefficient becomes $0.05*2\times10^{-6}$ $m^2/h = 10^{-7}$ m^2/h.
- The effective diffusion coefficients divided by the path length of diffusion in soil (half the soil depth, 0.05 m) yields the mass transfer coefficients for diffusion in the soil water $u_6 = 2\times10^{-6}$ m/h and soil air $u_7 = 0.02$ m/h
- Downward flow of water in the soil pores is likely to result in a water transport velocity of about 10^{-5} m/h. Thus, u_6 is taken to be a larger value in order to account for this, 10^{-5} m/h.
- The soil diffusion processes in the air and water occur in parallel but are in series with the air film at the soil surface

Air/Soil Transport

- The final equation for air-to-soil diffusion D value is

$$\boxed{D_{VS} = \frac{1}{1/D_s + 1/(D_{SW} + D_{SA})}}$$

where

$$D_S = u_5 A_S Z_1$$

$$D_{SW} = u_6 A_S Z_2$$

$$D_{SA} = u_7 A_S Z_1$$

- The total **D** value for all air-to-soil processes is given by

$$D_{13} = D_{VS} + D_{QS} + D_{RS}$$

- For soil-to-air diffusion transport, $\mathbf{D_{31}}$ value is equal to $\mathbf{D_{VS}}$

Water/Sediment Transport *(D_{24} and D_{42})*

- Diffusion from the water column to the sediment is characterized by a mass transfer coefficient u_8 or 10^{-4} *m/h*, which is the molecular diffusivity in water (2×10^{-6} m^2/h) divided by the path length *(0.02 m)*
- Ignored are the processes of bioturbation and shallow water current-induced turbulence which would increase $\boldsymbol{u_8}$
- The ***D*** value is $\boldsymbol{u_8 A_W Z_2}$.
- Deposition of suspended sediment is assumed to occur at a rate of $5000\ m^3/h$ over an area $A_W = 10^{10}\ m^2$.
- Thus the suspended sediment deposition velocity u_9 is $5000\ m^3/h/A_W = 5\times10^{-7}\ m/h$.

Water/Sediment Transport

- The water to sediment D value is

$$D_{24} = u_8 A_W Z_2 + u_9 A_W Z_5$$

Where **Z_5** is the Z value for the suspended sediment

- Sediment to water is treated similarly to **D_{24}**
- Re-suspension is assumed to occur at a rate which is 40 % that of deposition
- Therefore the re-suspension velocity u_{10} is 2×10^{-7} m/h and the **D** value for sediment to water transfer is

$$D_{42} = u_8 A_W Z_2 + u_{10} A_W Z_4$$

Soil/Water Transport (D_{32})

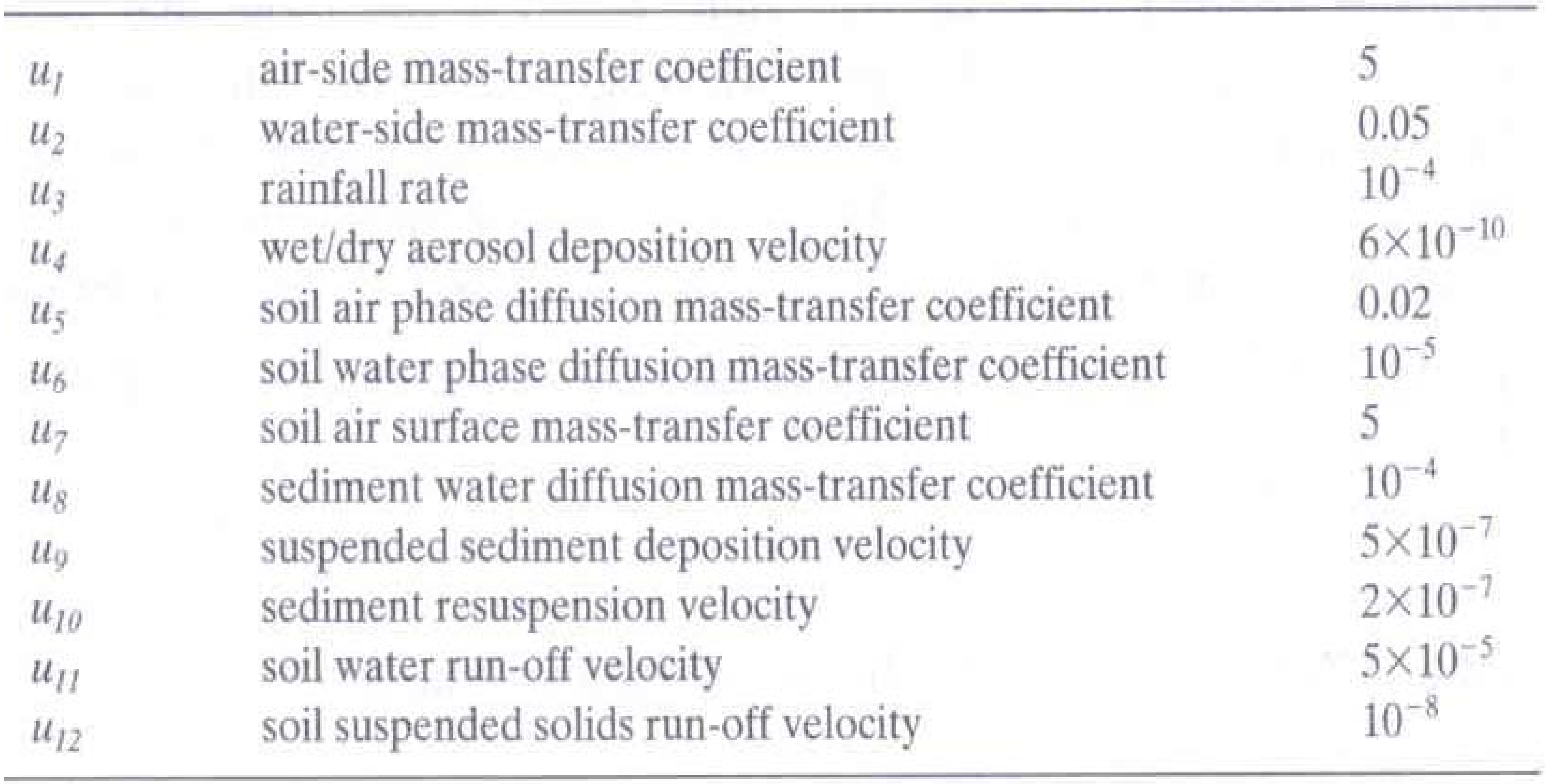
- Soil to water transfer occurs by surface run-off. The rate of water run-off is assumed to occur at 50 % the rate to rainfall
- The run-off water velocity $\boldsymbol{u_{11}}$ is then $0.5u_3 = 5\times10^{-5}\ m/h$
- The solids contained in the run-off water are assumed to be at a volumetric concentration of *200 ppm* in the water
- The run-off solids velocity $\boldsymbol{u_{12}}$ is $200\times10^{-6}\ u_{11}$.
- the D value is

$$\boxed{D_{32} = u_{11}A_S Z_2 + u_{12}A_S Z_3}$$

Where $\mathbf{A_S}$ is the solid surface area and $\mathbf{Z_2}$ is the Z value for the water and $\mathbf{Z_3}$ is the Z value for the soil solids.

- A summary of the intermediate transport parameters is shown in **Table 11.2-2**

Table 11.2-2. Intermedia diffusive and non-diffusive mass transfer coefficients (m/h)



u_1	air-side mass-transfer coefficient	5
u_2	water-side mass-transfer coefficient	0.05
u_3	rainfall rate	10^{-4}
u_4	wet/dry aerosol deposition velocity	6×10^{-10}
u_5	soil air phase diffusion mass-transfer coefficient	0.02
u_6	soil water phase diffusion mass-transfer coefficient	10^{-5}
u_7	soil air surface mass-transfer coefficient	5
u_8	sediment water diffusion mass-transfer coefficient	10^{-4}
u_9	suspended sediment deposition velocity	5×10^{-7}
u_{10}	sediment resuspension velocity	2×10^{-7}
u_{11}	soil water run-off velocity	5×10^{-5}
u_{12}	soil suspended solids run-off velocity	10^{-8}

Soil/Water Transport

- An additional non-diffusive transport mechanism which removes chemical from the sediment is burial
- The **D** value ($\mathbf{D_{A4}}$) is equal to

$$\boxed{D_{A4} = u_B A_W Z_4}$$

Where $\mathbf{u_B}$ is the sediment burial rate (2×10^{-7} m/h)

Advective Transport *(D_{Ai})*

- Chemical may directly enter into compartments by emissions and advective inputs from outside the model region
- The total rate of inputs for each compartment *i* is

$$\boxed{I_i = E_i + G_{Ai}C_{Bi}}$$

Where $\mathbf{E_i}$ *(moles/h) is the emission rate,* $\mathbf{G_{Ai}}$ *(m^3/h) is the advective flow rate, and* $\mathbf{C_{Bi}}$ *(moles/m^3) is the background concentration external to compartment i..*

- Chemicals may also exit the model domain from compartments by advective *(bulk flow)* processes having transfer values ($\mathbf{D_{Ai}}$)

$$\boxed{D_{Ai} = G_{Ai}Z_{Ci}}$$

Where $\mathbf{Z_{Ci}}$ *is the compartment i fugacity capacity* ***(Table 11.2-1)***

2.3 Reaction Loss Processes

- Reaction processes occurring in the environment include biodegradation, photolysis, hydrolysis, and oxidation
- A good approximation for reaction processes in the dilute limit commonly found in the environmental is to express as 1st order with rate constant $\boldsymbol{k_R}$ *(1/hr).*
- The rate of reaction loss for a chemical in a compartment $\boldsymbol{N_{Ri}}$ *(moles/h)* is

$$\boxed{N_{Ri} = k_{Ri} V_i C_i = k_{Ri} V_i Z_{Ci} f = D_{Ri} f}$$

Where $\mathbf{V_i}$ is the compartment volume, $\mathbf{C_i}$ is the molar concentration of the chemical

- The rate constants are compound-specific and have been tabulated for several compounds in the form of a reaction half-life, $t_{1/2}$, defined as the time required for the concentration to be reduced by one half of the initial by reaction

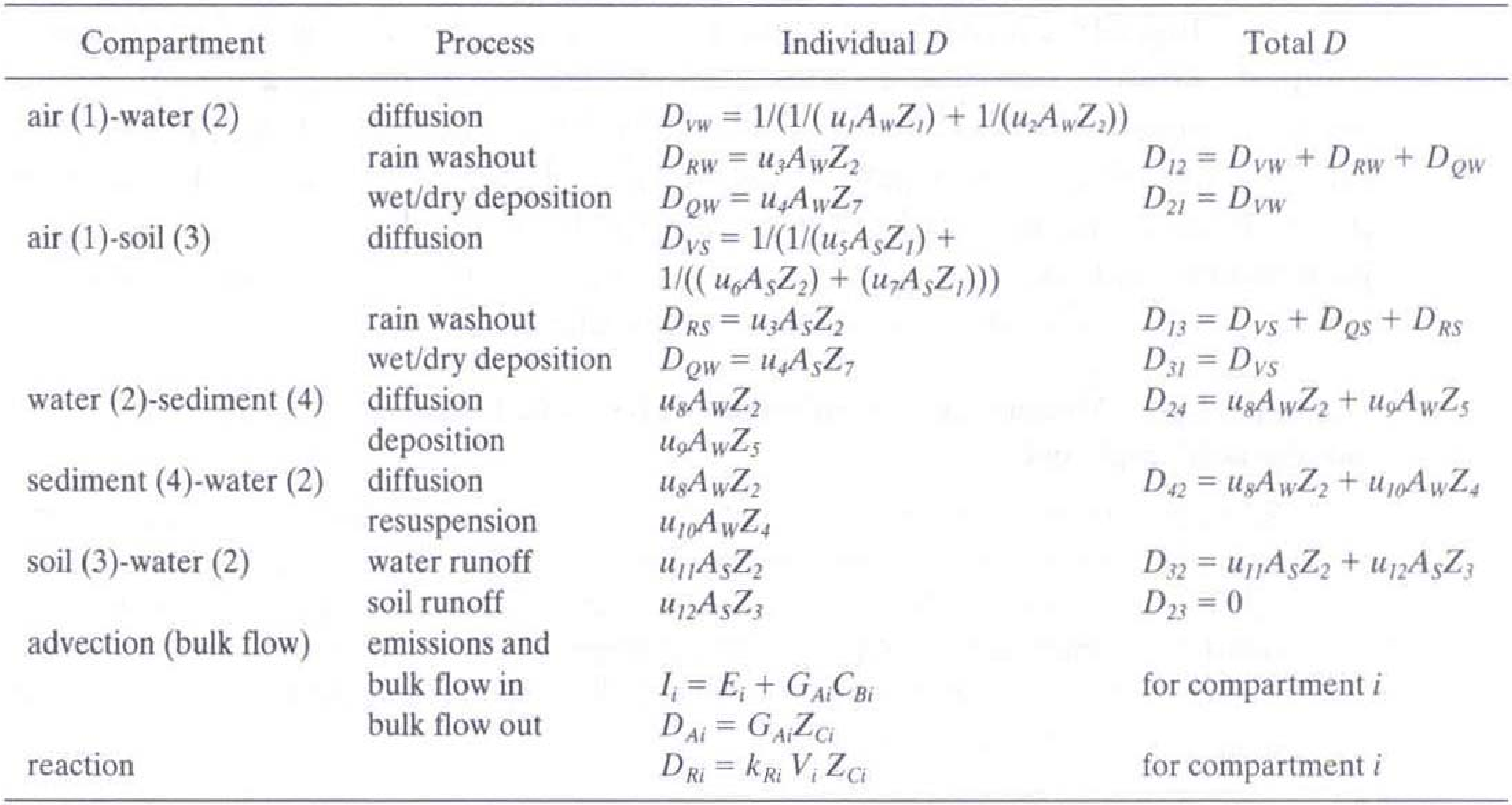
Reaction Loss Processes

- Tabulated half lives for compounds may represent the combined reaction mechanism, which can occur simultaneously in a given compartment
- The relation between $\boldsymbol{t_{1/2}}$ and $\boldsymbol{k_R}$ for a 1st order reaction is

$$\boxed{k_R = -\ln(0.5)/t_{1/2}}$$

- A summary of the D values for intermedia transport, advection, and reaction is shown in ***Table 11.2-3***

Table 11.2-3. ***D*** values in the Mackay level III model



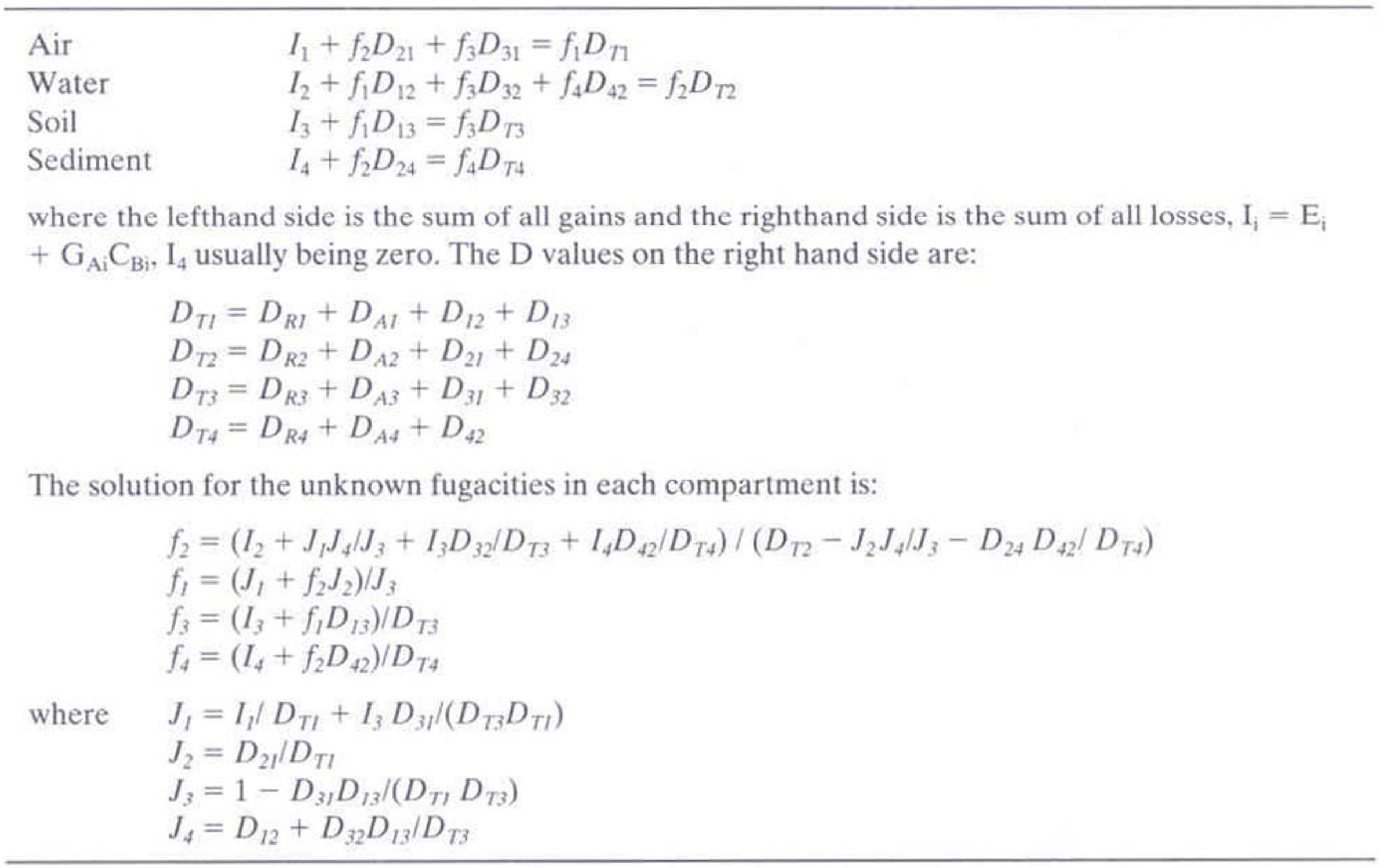
Compartment	Process	Individual D	Total D
air (1)-water (2)	diffusion	$D_{VW} = 1/(1/(u_1A_WZ_1) + 1/(u_2A_WZ_2))$	
	rain washout	$D_{RW} = u_3A_WZ_2$	$D_{12} = D_{VW} + D_{RW} + D_{QW}$
	wet/dry deposition	$D_{QW} = u_4A_WZ_7$	$D_{21} = D_{VW}$
air (1)-soil (3)	diffusion	$D_{VS} = 1/(1/(u_5A_SZ_1) +$ $1/((u_6A_SZ_2) + (u_7A_SZ_1)))$	
	rain washout	$D_{RS} = u_3A_SZ_2$	$D_{13} = D_{VS} + D_{QS} + D_{RS}$
	wet/dry deposition	$D_{QW} = u_4A_SZ_7$	$D_{31} = D_{VS}$
water (2)-sediment (4)	diffusion	$u_8A_WZ_2$	$D_{24} = u_8A_WZ_2 + u_9A_WZ_5$
	deposition	$u_9A_WZ_5$	
sediment (4)-water (2)	diffusion	$u_8A_WZ_2$	$D_{42} = u_8A_WZ_2 + u_{10}A_WZ_4$
	resuspension	$u_{10}A_WZ_4$	
soil (3)-water (2)	water runoff	$u_{11}A_SZ_2$	$D_{32} = u_{11}A_SZ_2 + u_{12}A_SZ_3$
	soil runoff	$u_{12}A_SZ_3$	$D_{23} = 0$
advection (bulk flow)	emissions and		
	bulk flow in	$I_i = E_i + G_{Ai}C_{Bi}$	for compartment i
	bulk flow out	$D_{Ai} = G_{Ai}Z_{Ci}$	
reaction		$D_{Ri} = k_{Ri}\,V_i\,Z_{Ci}$	for compartment i

11.2.4 Balance Equations

- As indicated in **Fig. 11.2-1,** there must be a balance between the rates of input from all emissions/bulk flow and intermedia transport and the rates of output from intermedia transport, advection, and reaction loss processes within each compartment at steady-state
- The written mole balance equations for each compartment is summarized in **Table 11.2-4**
- The fugacity calculations outlined here are obviously very complex. Routine hand calculations of environmental fugacities using this model are prohibitively time consuming. Fortunately, spreadsheet programs are available

  (ref) Mackay,D., **Multimedia Environmental Models. The Fugacity Approach**, 2nd ed, CRC Press, 2001, pp. 272
- Using these programs with a relatively small number of chemical-specific input partitioning and reaction parameters, environmental fate can be performed **(Example 11.2-1)**

Table 11.2-4. Mole balance equations for level III fugacity model



Air	$I_1 + f_2D_{21} + f_3D_{31} = f_1D_{T1}$
Water	$I_2 + f_1D_{12} + f_3D_{32} + f_4D_{42} = f_2D_{T2}$
Soil	$I_3 + f_1D_{13} = f_3D_{T3}$
Sediment	$I_4 + f_2D_{24} = f_4D_{T4}$

where the lefthand side is the sum of all gains and the righthand side is the sum of all losses, $I_i = E_i + G_{Ai}C_{Bi}$, I_4 usually being zero. The D values on the right hand side are:

$$D_{T1} = D_{R1} + D_{A1} + D_{12} + D_{13}$$
$$D_{T2} = D_{R2} + D_{A2} + D_{21} + D_{24}$$
$$D_{T3} = D_{R3} + D_{A3} + D_{31} + D_{32}$$
$$D_{T4} = D_{R4} + D_{A4} + D_{42}$$

The solution for the unknown fugacities in each compartment is:

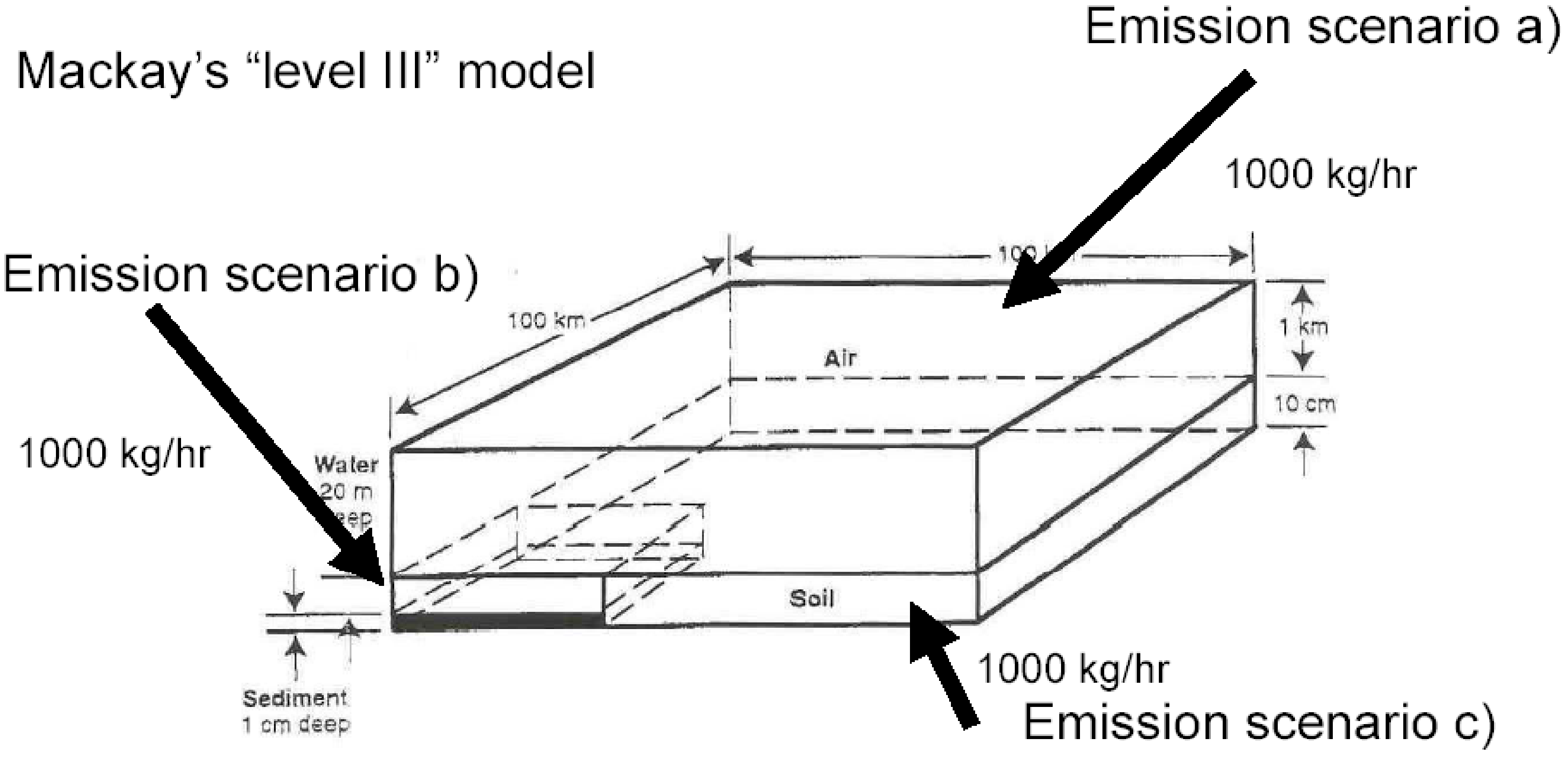
$$f_2 = (I_2 + J_1J_4/J_3 + I_3D_{32}/D_{T3} + I_4D_{42}/D_{T4}) \,/\, (D_{T2} - J_2J_4/J_3 - D_{24}\,D_{42}/\,D_{T4})$$
$$f_1 = (J_1 + f_2J_2)/J_3$$
$$f_3 = (I_3 + f_1D_{13})/D_{T3}$$
$$f_4 = (I_4 + f_2D_{42})/D_{T4}$$

where $J_1 = I_1/\,D_{T1} + I_3\,D_{31}/(D_{T3}D_{T1})$

$$J_2 = D_{21}/D_{T1}$$
$$J_3 = 1 - D_{31}D_{13}/(D_{T1}\,D_{T3})$$
$$J_4 = D_{12} + D_{32}D_{13}/D_{T3}$$

Multimedia prediction for benzene, ethanol, and pentachlorophenol

Mackay's "level III" model



Emission scenario a)

1000 kg/hr

Emission scenario b)

1000 kg/hr

1000 kg/hr

Emission scenario c)

MODEL DOMAIN (Not to scale)

Multimedia compartment model input data

Environmental Property	Unit	Spreadsheet Location	Benzene	Ethanol	PCP
Molecular Weight	g/mole	C6	78.11	46.07	266.34
Melting Point	ûC	C7	5.53	115	174
Dissociation Constant	log pK_a	C8			4.74
Solubility in Water	g/m^3	C11	1.78E+2	6.78E+5	14
Vapor Pressure	Pa	C12	1.27E+4	7.80E+3	4.15E-3
Octanol-Water Coefficient	log K_{ow}	C13	2.13	-0.31	5.05
Half-life in air	hr	C33	1.7E+1	5.5E+1	5.50E+2
Half-life in water	hr	C34	1.7E+2	5.5E+1	5.50E+2
Half-life in soil	hr	C35	5.5E+2	5.5E+1	1.7E+3
Half-life in sediment	hr	C36	1.7E+3	1.7E+2	5.50E+3

Multimedia compartment model: typical results

Chemical		*Percentage (%)*			
(emission scenario)	*Total mass (kg)*	*Air*	*Water*	*Soil*	*Sediment*
Benzene (a)	1.98×10^{4}	99.59	0.29	0.12	1.0×10^{-3}
Benzene (b)	1.41×10^{5}	4.48	95.17	5.5×10^{-3}	0.35
Benzene (c)	6.86×10^{4}	20.61	1.61	77.78	5.8×10^{-3}
Ethanol (a)	4.56×10^{4}	92.87	3.85	3.28	2.9×10^{-3}
Ethanol (b)	7.35×10^{4}	0.22	99.7	7.8×10^{-3}	0.08
Ethanol (c)	7.84×10^{4}	0.92	5.64	93.42	0.02
Pentachlorophenol (a)	2.07×10^{6}	0.26	2.56	97.07	0.11
Pentachlorophenol (b)	4.59×10^{5}	7.2×10^{-5}	96.19	0.03	3.78
Pentachlorophenol (c)	2.39×10^{6}	2.9×10^{-4}	0.54	99.44	0.02

(a) 1000 kg/hr emitted into the air compartment
(b) 1000 kg/hr emitted into the water compartment
(c) 1000 kg/hr emitted into the soil compartment

Multimedia compartment model typical results - interpretations

1. The percentages in each environmental compartment depend upon the ***emission scenario***
   - a) the highest air concentrations result from emission into the air
   - b) the highest water concentrations are from emission into water
   - c) the highest soil concentrations are from emission into soil
   - d) highest sediment concentrations are from emission into water

2. ***Chemical properties*** dictate percentages and amounts
   - a) high K_H results in high air concentrations and amounts
   - b) high K_{OW} results in high soil concentrations
   - c) high reactions half lives results in highest pollutant amounts

11.3 Tier 3 Metrics for Environmental Risk Evaluation of Process Design

We discuss here how to combine emissions estimation, environmental fate and transport information, and environmental impact data to obtain an assessment of the potential risks posed by releases from chemical process designs.

No single methodology has gained universal acceptance, several useful methodologies for indexing environmental and health impacts of chemicals have recently appeared in literature.

- **Major Indexing Methods**
  1) Abiotic Impact category – Global warming, ozone depletion, acidification, smog formation, etc.
  2) Biotic category – human health, plant, animal and other organism health, etc.

11.3 Tier 3 Metrics for Environmental Risk Evaluation of Process Design

In **Table 11.3-1**, 9 environmental and health-related indexes (metrics) for chemical process impacts are defined. These impacts affect local, regional, and global environmental issues.

1. Global warming and ozone depletion are problems with potentially global implications for a large proportion of the earth’s population.
2. Smog formation and acid deposition are regional problems that can affect areas in size ranging from large urban basins up to a significant fraction of continent.
3. Issues of toxicity and carcinogenicity are often of highest concern at the local scale in the vicinity of the point of release.

Table 11.3-1. Environmental impact index categories for process flowsheet evaluation

---

Health-Related Indexes

- Inhalation toxicity
- Ingestion toxicity
- Inhalation carcinogenicity
- Ingestion carcinogenicity

Abiotic Indexes

- Global warming
- Stratospheric ozone depletion
- Acid deposition
- Smog formation

Ecotoxicity Indexes

- Fish Aquatic Toxicity

9 environmental and health-related indexes for chemical process impacts

Relative Risk Index	**Equation**
Global Warming	$I^*_{GW,i} = GWP_i$
	$I^*_{GW,i} = N_C \dfrac{MW_{CO_2}}{MW_i}$
Ozone Depletion	$I^*_{OD,i} = ODP_i$
Smog Formation	$I^*_{SF,i} = \dfrac{MIR_i}{MIR_{ROG}}$
Acid Rain	$I^*_{AR,i} = \dfrac{ARP_i}{ARP_{SO_2}}$

GWP = global warming potential, N_C = number of carbons atoms, ***ODP*** = ozone depletion potential, ***MIR*** = maximum incremental reactivity, ***ARP*** = acid rain potential.

9 environmental and health-related indexes for chemical process impacts

Relative Risk Index	Equation
Human Toxicity Ingestion Route	$I^{*}_{ING} = \frac{C_{W,i}\ LD_{50,Toluene}}{C_{W,Toluene}\ LD_{50,i}}$
Human Toxicity Inhalation Route	$I^{*}_{INH} = \frac{C_{A,i}\ LC_{50,Toluene}}{C_{A,Toluene}\ LC_{50,i}}$
Human Carcinogenicity Ingestion Route	$I^{*}_{CING} = \frac{C_{W,i}\ HV_{i}}{C_{W,Benzene}\ HV_{Benzene}}$
Human Carcinogenicity Inhalation Route	$I^{*}_{CINH} = \frac{C_{A,i}\ HV_{i}}{C_{A,Benzene}\ HV_{Benzene}}$
Fish Toxicity	$I^{*}_{FT} = \frac{C_{W,i}\ LC_{50\,f,PCP}}{C_{W,PCP}\ LC_{50\,f,i}}$

LD_{50} = lethal dose 50% mortality, **LC_{50}** = lethal concentration 50% mortality, and **HV** = hazard value for carcinogenic health effects.

The index is normally expressed as a product of inherent impact potential (IIP) and exposure potential (EP), following risk assessment guides (NRC, SETAC). The general form of **dimensionless environmental risk index** is defined as

$$\boxed{(Dimensionless\ Risk\ Index)_i = \frac{[(EP)(IIP)]_i}{[(EP)(IIP)]_B} \qquad (11.1)}$$

where *B is the benchmark compound* and i the chemical of interest.

To estimate the index ***I*** for a particular impact category due to all of the chemicals released from a process, one must sum the contributions for each chemical weighed by their emission rate

$$\boxed{I = \sum_i \left(Dimensionless\ Risk\ Index\right)_i \times m_i} \tag{11.2}$$

where m_i is the mass emission rate of chemical i from the entire process (kg/hr)

The following is a brief summary of environmental and health indexes which have been used to compare impacts of chemicals, processes, or products.

Quantitative risk calculation

Carcinogenic Risk Example (inhalation route)

Exposure Dose

Dose - Response Relationship, Slope Factor $(mg/(kg\bullet d))^{-1}$

$$\text{Risk}_i = \left[\frac{(C_a \times CR \times EF \times ED)}{(BW \times AT)} \times SF \right]_i$$

CR - contact rate (m^3 air inhaled / day)
EF - exposure frequency (days exposed / yr)
ED - exposure duration (yr)
BW - body weight (kg)
AT - averaging time (number of days in a lifetime)

Result: # excess cancers per 10^6 cases in the population; 10^{-4} to 10^{-6} acceptable

Disadvantage: Only a single compartment is modeled / Computationally inefficient
Highly uncertain prediction of risk

Relative risk calculation (what is the relative toxic potency?)

Carcinogenic Risk Example (inhalation route)

$$\text{Relative Risk} = \frac{\left[\dfrac{(C_a \times CR \times EF \times ED)}{(BW \times AT)} \times SF\right]_i}{\left[\dfrac{(C_a \times CR \times EF \times ED)}{(BW \times AT)} \times SF\right]_{Benchmark}}$$

$$= \frac{\left[C_a \times SF\right]_i}{\left[C_a \times SF\right]_{Benchmark}}$$

Result: Risk of a chemical relative to a well-studied benchmark compound

Advantage: If C is calculated for all compartments using a multimedia compartment model, computationally efficient

11.3.1 Global Warming

A common index for global warming is the global warming potential (GWP), which is the cumulative infrared energy capture from the release of 1 kg of a green house gas relative to that from 1 kg of CO_2

$$\boxed{GWP_i = \frac{\int_0^n a_i C_i \, dt}{\int_0^n a_{CO2} C_{CO2} \, dt}} \qquad (11.3)$$

$\boldsymbol{a_i}$ is the predicted radiative forcing of gas $\boldsymbol{i}$ (Wm^{-2}) (which is a function of the chemical's infrared absorbance properties and $\boldsymbol{C_i}$), $\boldsymbol{C_i}$ is its predicted concentration in the atmosphere (ppm), and $\boldsymbol{n}$ is the number of years over which the integration is performed, for example, 100 years.

The concentration is a function of time (**t**), primarily due to loss within the troposphere by chemical reaction with hydroxyl radicals: For CO_2, ***n*** =120 years.

In appendix D, Table D-1 is a list of global warming potentials for green house gases.

The global warming potential for each chemical is influenced mostly by the chemical's troposphere RTD and the strength of its infrared radiation absorbance (band intensities). All of these gases are extremely volatile, do not dissolve in water and do not absorb to soil and sediments, and they will persist in the atmosphere after being released from sources.

The global warming index for the entire chemical process is the sum of the emissions weighted GWPs for each chemical,

$$\boxed{I_{GW} = \sum_i (GWP_i \times m_i)} \qquad (11.4)$$

where m is the mass emission rate of chemical *i* from the entire process (kg/hr)

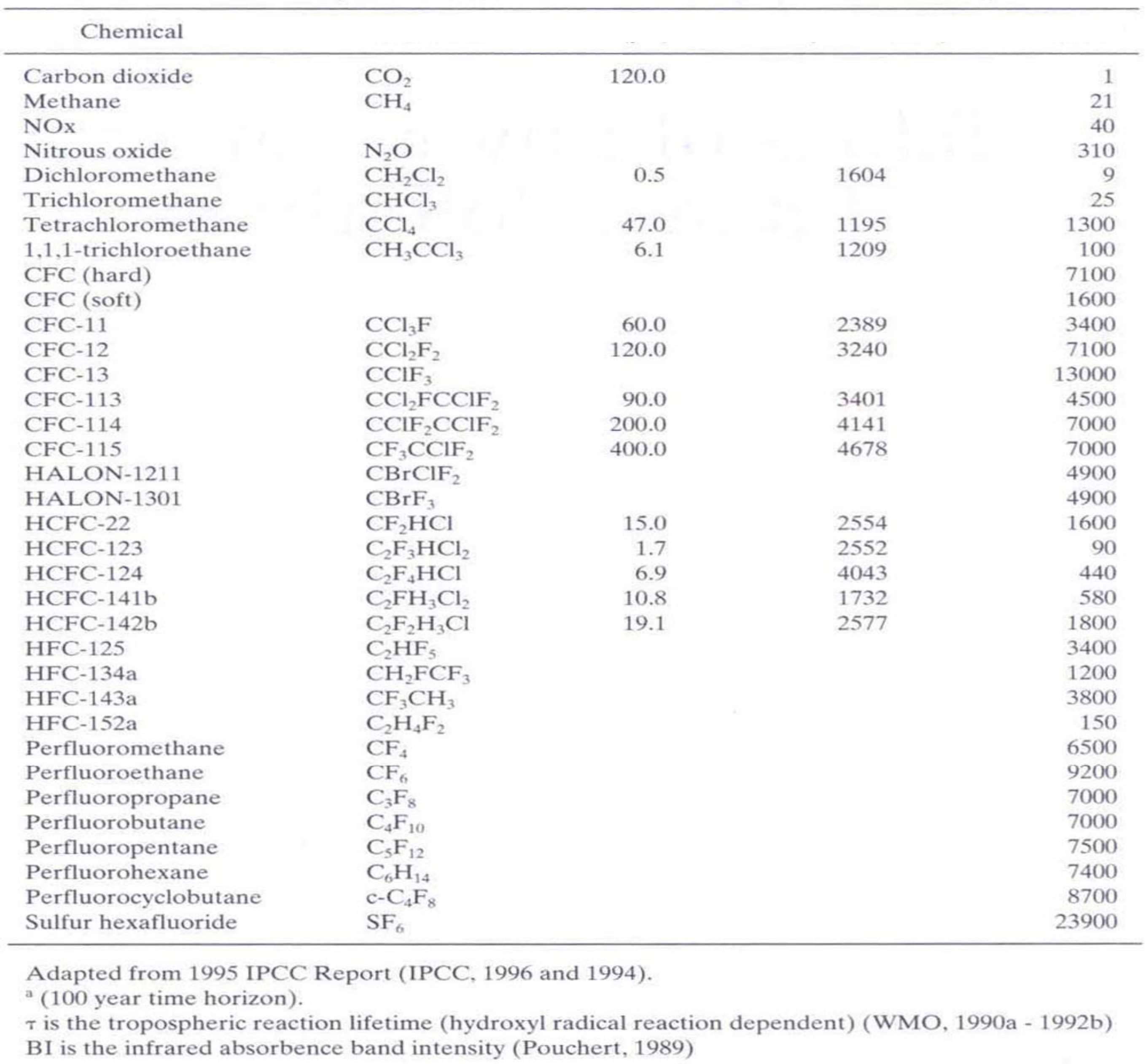
The global warming index accounts for direct effects of the chemical, but most chemicals are so short-lived in the atmosphere (due to the action of hydroxyl radicals in the troposphere) that they disappear (become converted to CO_2) long before any significant effect can be felt.

However, organic chemicals of fossil fuel origin will have an indirect global warming effect because of the CO_2 released upon oxidation within the atmosphere and within other compartments of the environment. To account for this indirect effect for organic compounds with atmospheric RTD less that ½ year, an indirect GWP is defined as

$$\boxed{GWP_i\,(Indirect) = N_C\,\frac{MW_{CO2}}{MW_i}} \qquad (11.5)$$

where N_c is the number of carbon atoms in the chemical and the Molecular weight MW convert from a molar basis

Table D-1. Global warming potentials for greenhouse gases (CO_2 is the benchmark)



Chemical				
Carbon dioxide	CO_2	120.0		1
Methane	CH_4			21
NOx				40
Nitrous oxide	N_2O			310
Dichloromethane	CH_2Cl_2	0.5	1604	9
Trichloromethane	$CHCl_3$			25
Tetrachloromethane	CCl_4	47.0	1195	1300
1,1,1-trichloroethane	CH_3CCl_3	6.1	1209	100
CFC (hard)				7100
CFC (soft)				1600
CFC-11	CCl_3F	60.0	2389	3400
CFC-12	CCl_2F_2	120.0	3240	7100
CFC-13	$CClF_3$			13000
CFC-113	CCl_2FCClF_2	90.0	3401	4500
CFC-114	$CClF_2CClF_2$	200.0	4141	7000
CFC-115	CF_3CClF_2	400.0	4678	7000
HALON-1211	$CBrClF_2$			4900
HALON-1301	$CBrF_3$			4900
HCFC-22	CF_2HCl	15.0	2554	1600
HCFC-123	$C_2F_3HCl_2$	1.7	2552	90
HCFC-124	C_2F_4HCl	6.9	4043	440
HCFC-141b	$C_2FH_3Cl_2$	10.8	1732	580
HCFC-142b	$C_2F_2H_3Cl$	19.1	2577	1800
HFC-125	C_2HF_5			3400
HFC-134a	CH_2FCF_3			1200
HFC-143a	CF_3CH_3			3800
HFC-152a	$C_2H_4F_2$			150
Perfluoromethane	CF_4			6500
Perfluoroethane	CF_6			9200
Perfluoropropane	C_3F_8			7000
Perfluorobutane	C_4F_{10}			7000
Perfluoropentane	C_5F_{12}			7500
Perfluorohexane	C_6H_{14}			7400
Perfluorocyclobutane	c-C_4F_8			8700
Sulfur hexafluoride	SF_6			23900

Adapted from 1995 IPCC Report (IPCC, 1996 and 1994).

[a] (100 year time horizon).

τ is the tropospheric reaction lifetime (hydroxyl radical reaction dependent) (WMO, 1990a - 1992b)

BI is the infrared absorbence band intensity (Pouchert, 1989)

Example 11.3-1

Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

1,1,1-Trichloroethane (TCA) is used as an industrial solvent for metal cleaning, as a reaction intermediate, and for other important uses (US EPA, 1979-1991). A major processing route for TCA is by hydrochlorination of vinyl chloride in the presence of an FeCl3 catalyst to produce 1,1-dichloroethane, followed by chlorination of this intermediate.

Sources for air emissions include distillation condenser vents, storage tanks, handling and transfer operations, fugitive sources, and secondary emissions from wastewater treatment. We wish to estimate the global warming impact of the air emissions from this process, including direct impacts to the environment (from 1,1,1-TCA) and indirect impacts from energy usage (CO_2 and NO_x release) in the analysis.

Example 11.3-1

Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

Data below show the major chemicals that impact global warming when emitted from the process.

Determine the global warming index for the process and the percentage contribution for each chemical.

Data: Air Emissions (15,500 kg 1,1,1-TCA/hr)

Chemical	m_i (kg/hr)	GWP_i
TCA	10	100
CO_2	7,760	1
N_2O	0.14	310

TCA emissions were estimated using data for trichloroethylene (US EPA, 1079-1991). CO_2 and N_2O emission rates were estimated from a life cycle assessment of ethylene production (Allen and Rosselot, 1997; Boustead, 1993)

Example 11.3-1

Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

Solution: Using Eq. 11.3-4, the process global warming index is.

$$
\begin{aligned}
\boldsymbol{I_{GW}} &= (10\text{kg/hr})(100)+(7760\text{kg/hr})(1)+(0.14\text{kg/hr})(310) \\
&= 1{,}000+7{,}760+43.4 \\
&= 8{,}803.4 \text{ kg/hr}
\end{aligned}
$$

The percent of the process I_{GW} for each chemical is:
1,1,1-TCA (11.4%), CO_2 (88.1%), N_2O (0.5%)

Example 11.3-1

Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

Discussion: This case study demonstrates that the majority of the global warming impact from the production of 1,1,1-TCA is from the energy requirement of the process and not from the emission of the chemical with the highest global warming potential.

This analysis assumes that a fossil fuel was used to satisfy the energy requirements of the process. If renewable resources were used (biomass-based fuels), the impact of CO_2 on global warming would be significantly reduced. Finally, the majority of the global warming impact of 1,1,1-TCA could very well be felt during the use stage of its life cycle, not the production stage. A complete life cycle assessment of 1,1,1-TCA is necessary to demonstrate this.

11.3.2 Ozone Depletion

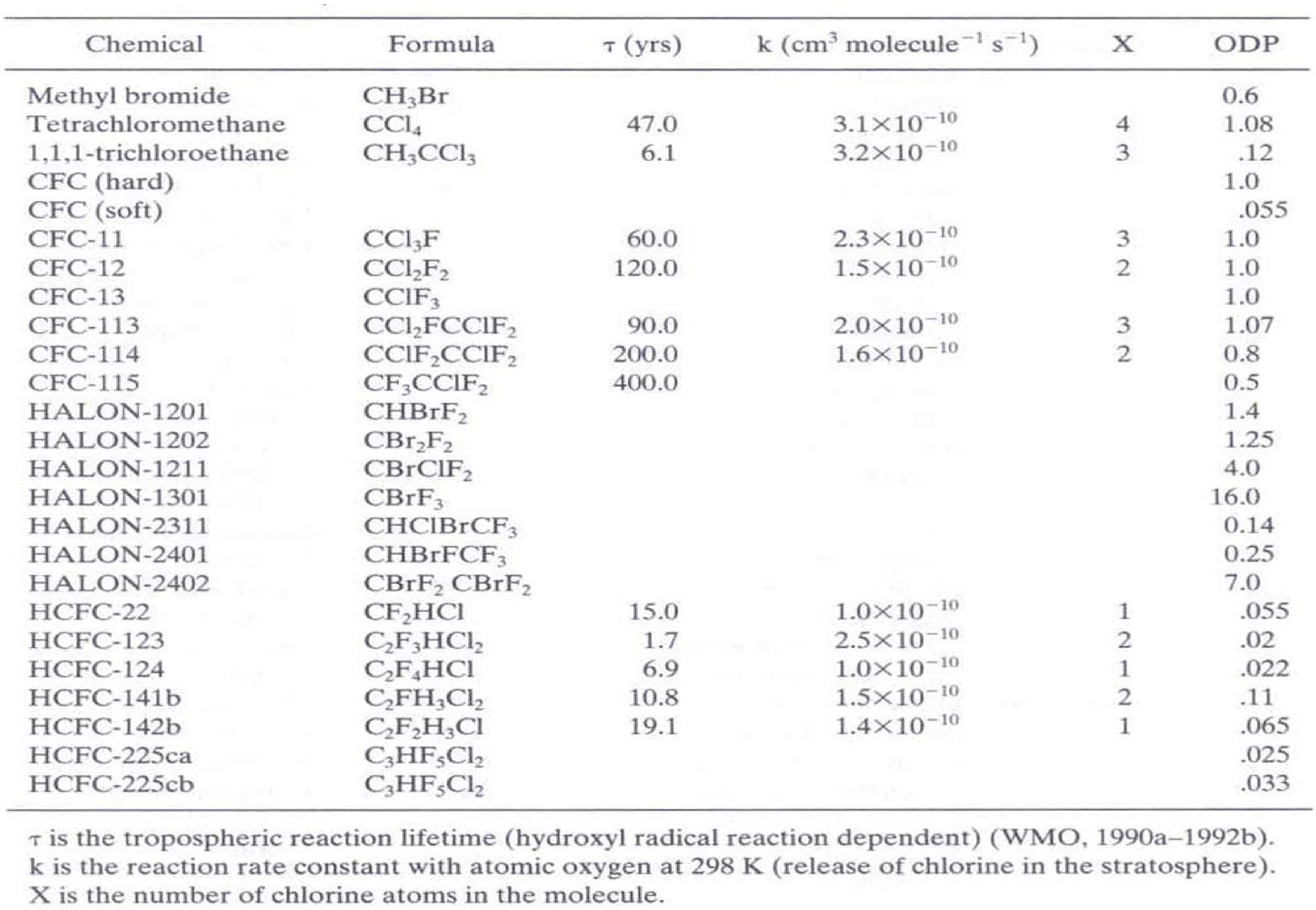
The ozone depletion potential(ODP) of a chemical is the predicted time- and height-integrated change **δ[O_3]** in stratospheric ozone caused by the release of a specific quantity of the chemical relative to that caused by the same quantity of a benchmark compound, trichlorofluoromethane (CFC-11, CCl_3F)

$$ODP_i = \frac{\delta[O_3]_i}{\delta[O_3]_{CFC-11}} \qquad (11.6)$$

Model Calculation Sources : WMO, ODPs for a number of environmentally hazard chemicals **(Appendix D, Table D-2)**. The ozone depletion index for a plant is ther sum of emitted chemical rates. The equivalent emission of CFC-11 for entire process is then;

$$I_{OD} = \sum_i (ODP_i \times m_i) \qquad (11.7)$$

Table D-2. Ozone-depletion potentials for several industrially important compounds



Chemical	Formula	τ (yrs)	k (cm^3 $molecule^{-1}$ s^{-1})	X	ODP
Methyl bromide	CH_3Br				0.6
Tetrachloromethane	CCl_4	47.0	3.1×10^{-10}	4	1.08
1,1,1-trichloroethane	CH_3CCl_3	6.1	3.2×10^{-10}	3	.12
CFC (hard)					1.0
CFC (soft)					.055
CFC-11	CCl_3F	60.0	2.3×10^{-10}	3	1.0
CFC-12	CCl_2F_2	120.0	1.5×10^{-10}	2	1.0
CFC-13	$CClF_3$				1.0
CFC-113	CCl_2FCClF_2	90.0	2.0×10^{-10}	3	1.07
CFC-114	$CClF_2CClF_2$	200.0	1.6×10^{-10}	2	0.8
CFC-115	CF_3CClF_2	400.0			0.5
HALON-1201	$CHBrF_2$				1.4
HALON-1202	CBr_2F_2				1.25
HALON-1211	$CBrClF_2$				4.0
HALON-1301	$CBrF_3$				16.0
HALON-2311	$CHClBrCF_3$				0.14
HALON-2401	$CHBrFCF_3$				0.25
HALON-2402	$CBrF_2$ $CBrF_2$				7.0
HCFC-22	CF_2HCl	15.0	1.0×10^{-10}	1	.055
HCFC-123	$C_2F_3HCl_2$	1.7	2.5×10^{-10}	2	.02
HCFC-124	C_2F_4HCl	6.9	1.0×10^{-10}	1	.022
HCFC-141b	$C_2FH_3Cl_2$	10.8	1.5×10^{-10}	2	.11
HCFC-142b	$C_2F_2H_3Cl$	19.1	1.4×10^{-10}	1	.065
HCFC-225ca	$C_3HF_5Cl_2$				.025
HCFC-225cb	$C_3HF_5Cl_2$				.033

τ is the tropospheric reaction lifetime (hydroxyl radical reaction dependent) (WMO, 1990a–1992b).
k is the reaction rate constant with atomic oxygen at 298 K (release of chlorine in the stratosphere).
X is the number of chlorine atoms in the molecule.

3.3 Acid Rain

The potential for acidification for any compound is related to the number of moles of H^+ created per number of moles of the compound emitted. The balanced chemical equation can provide this relation

$$X + \bullet\bullet\bullet\bullet \quad \rightarrow \quad \alpha H^+ + \bullet\bullet\bullet\bullet \qquad (11.8)$$

where X is the emitted chemical that initiates acidification and α (moles of H^+/mole X) is a molar stoichiometric coefficient

Acidification is normally expressed on a mass basis and therefore H^+ created per mass of emitted substance (η_i, moles H^+/kg *i*) is

$$\eta_i = \frac{\alpha_i}{MW_i} \qquad (11.9)$$

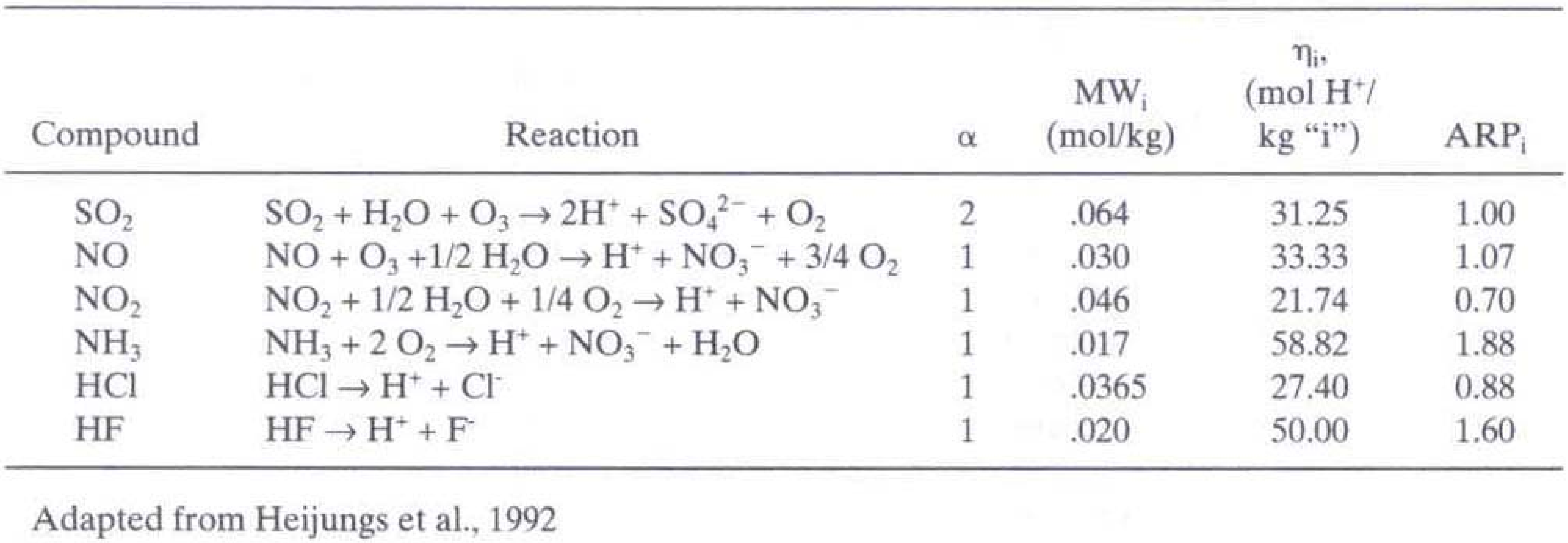
If we introduce a benchmark compound (SO_2) and express the acid rain potential (ARP) of any emitted acid-forming chemical relative to it,

$$ARP_i = \frac{\eta_i}{\eta_{SO2}} \qquad (11.10)$$

The number of acidifying compounds emitted by industrial sources is limited to a rather small number of combustion byproducts and other precursor or acidic species emitted directly onto the environment. Appendix D, Table D-3 lists the SRP for pollutants. The total acidification potential of an entire process is defined similarly $\boldsymbol{I_{GW}}$ and $\boldsymbol{I_{OD}}$.

$$I_{AR} = \sum_i (ARP_i \times m_i) \qquad (11.11)$$

Table D-3. Acid rain potential for a number of acidifying chemicals



Compound	Reaction	α	MW_i (mol/kg)	η_i, (mol H^+/ kg “i”)	ARP_i
SO_2	$SO_2 + H_2O + O_3 \rightarrow 2H^+ + SO_4^{2-} + O_2$	2	.064	31.25	1.00
NO	$NO + O_3 + 1/2\ H_2O \rightarrow H^+ + NO_3^- + 3/4\ O_2$	1	.030	33.33	1.07
NO_2	$NO_2 + 1/2\ H_2O + 1/4\ O_2 \rightarrow H^+ + NO_3^-$	1	.046	21.74	0.70
NH_3	$NH_3 + 2\ O_2 \rightarrow H^+ + NO_3^- + H_2O$	1	.017	58.82	1.88
HCl	$HCl \rightarrow H^+ + Cl^-$	1	.0365	27.40	0.88
HF	$HF \rightarrow H^+ + F^-$	1	.020	50.00	1.60

Adapted from Heijungs et al., 1992

3.4 Smog Formation

The most important process for ozone formation in the lower atmosphere is photo-dissociation of NO_2

$$NO_2 + h\nu \rightarrow O(^3P) + NO$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

where **M** is nitrogen or molecular oxygen.

This cycle results in O_3 concentration being in a photo-stationary state dictated by NO_2 photolysis rate and rate of $[NO_2]/[NO]$. The role of VOCs in smog formation is to form radicals which convert NO to NO_2 without causing O_3 destruction, thereby increasing the ratio $[NO_2]/[NO]$, and increasing O_3.

$$VOC + \bullet OH \rightarrow \bullet RO_2 + other \cdot oxidation \cdot product$$

$$\bullet RO_2 + NO \rightarrow NO_2 + radicals$$

$$radicals \rightarrow \bullet OH + other \cdot oxidation \cdot products$$

The tendency of individual VOCs to influence O_3 levels depends on its hydroxyl radical (•OH) rate constant and elements of its reaction mechanism, including radical initiation, radical termination, and reaction which remove NO_x.

In general, predicted VOC incremental reactivities are greatest when NO_x levels are high relative to reactive organic gases (ROG) and lowest when NO_x is relatively low.

Although several reactivity scale are possible, the most relevant for comparing VOC is the maximum incremental reactivity (MIR), which occurs under high NOx conditions when the highest ozone formation occurs. The **smog formation potential (SFP)** is based on the maximum reactivity scale.

$$SFP_i = \frac{MIR_i}{MIR_{ROG}} \qquad (11.12)$$

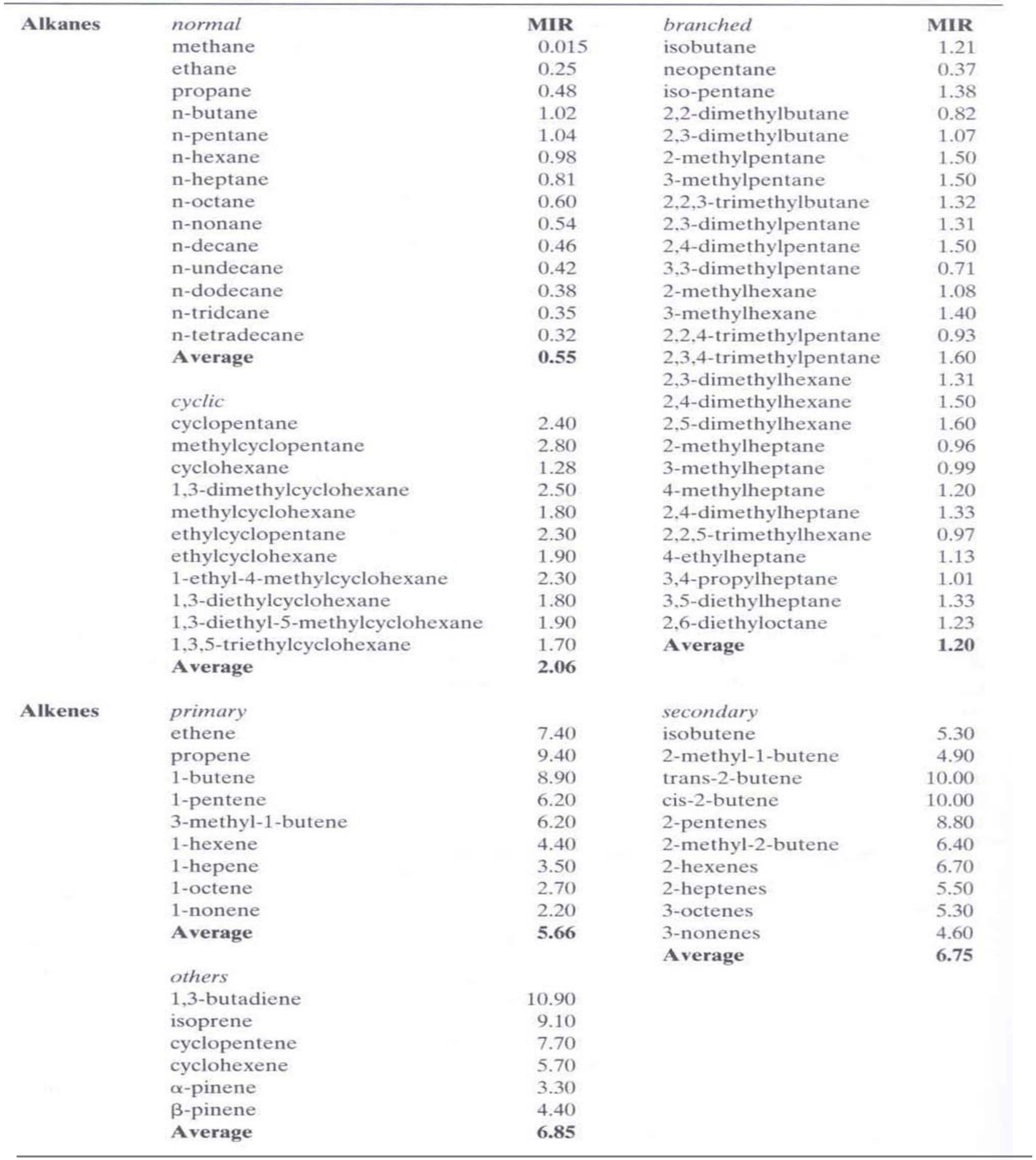
where MIR_{ROG} is the average value for background reactive organic gases, the benchmark compound for the index. This normalized and dimensionless index is similar to the one proposed by the Netherlands Agency for the Environment (Heijungs, 1992)

Appendix D, Table D-4 contains a listing of calculated MIR values for many common VOCs found in fuels, paints, and solvents. Most of chemicals in Appendix D, Table D-4 are volatile and will maintain a presence in the atmosphere after release into the air, with the exception of the higher molecular weight organics. The total smog formation potential is the sum of MIRs and emission rates for each smog-forming chemical in process. The process equivalent emission of ROG is

$$I_{SF} = \sum_i (SFP_i \times m_i) \qquad (11.13)$$

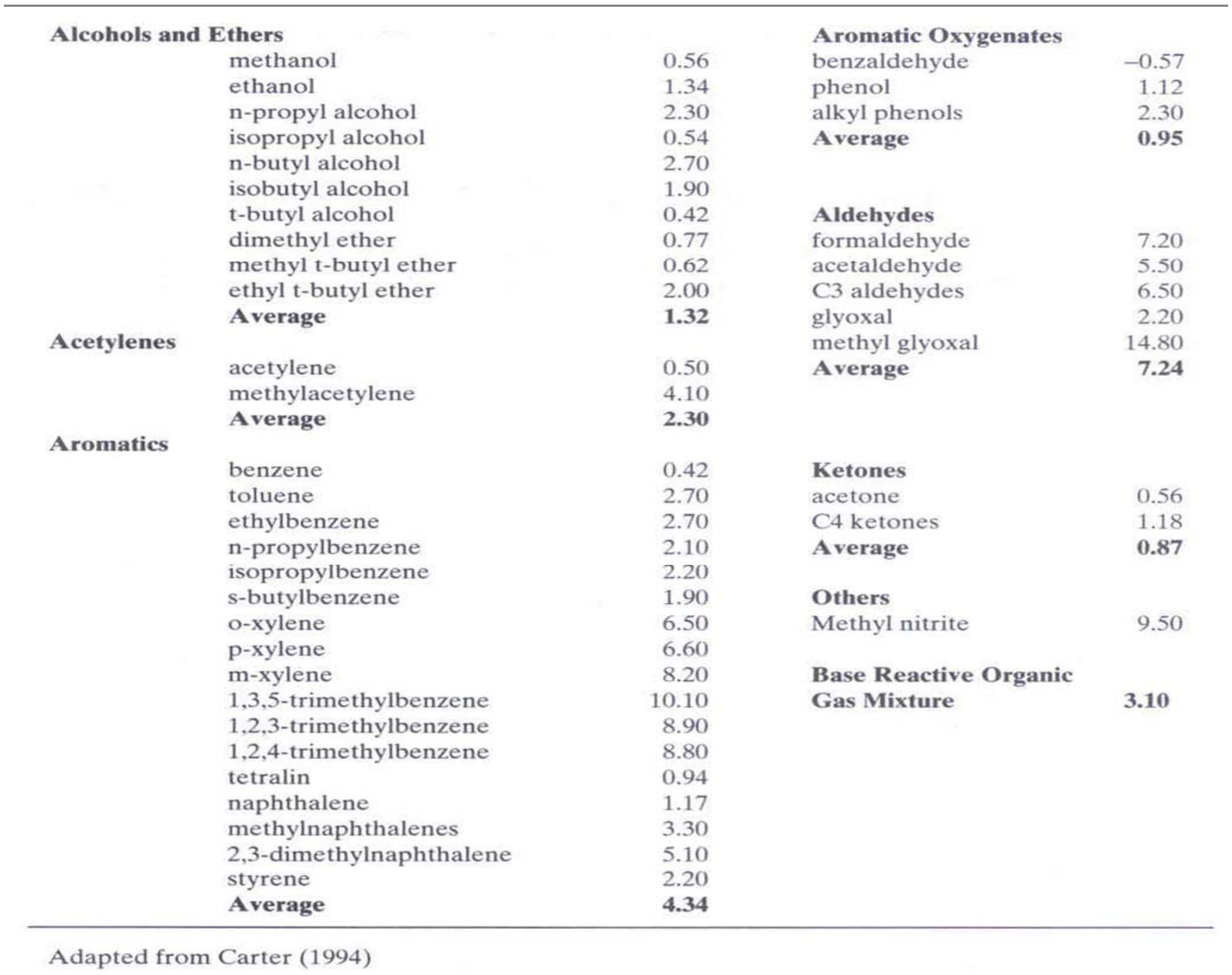
Table D-4a.

Smog formation potential for a number of acidifying chemicals



Alkanes	*normal*	**MIR**	*branched*	**MIR**
	methane	0.015	isobutane	1.21
	ethane	0.25	neopentane	0.37
	propane	0.48	iso-pentane	1.38
	n-butane	1.02	2,2-dimethylbutane	0.82
	n-pentane	1.04	2,3-dimethylbutane	1.07
	n-hexane	0.98	2-methylpentane	1.50
	n-heptane	0.81	3-methylpentane	1.50
	n-octane	0.60	2,2,3-trimethylbutane	1.32
	n-nonane	0.54	2,3-dimethylpentane	1.31
	n-decane	0.46	2,4-dimethylpentane	1.50
	n-undecane	0.42	3,3-dimethylpentane	0.71
	n-dodecane	0.38	2-methylhexane	1.08
	n-tridcane	0.35	3-methylhexane	1.40
	n-tetradecane	0.32	2,2,4-trimethylpentane	0.93
	Average	**0.55**	2,3,4-trimethylpentane	1.60
			2,3-dimethylhexane	1.31
	cyclic		2,4-dimethylhexane	1.50
	cyclopentane	2.40	2,5-dimethylhexane	1.60
	methylcyclopentane	2.80	2-methylheptane	0.96
	cyclohexane	1.28	3-methylheptane	0.99
	1,3-dimethylcyclohexane	2.50	4-methylheptane	1.20
	methylcyclohexane	1.80	2,4-dimethylheptane	1.33
	ethylcyclopentane	2.30	2,2,5-trimethylhexane	0.97
	ethylcyclohexane	1.90	4-ethylheptane	1.13
	1-ethyl-4-methylcyclohexane	2.30	3,4-propylheptane	1.01
	1,3-diethylcyclohexane	1.80	3,5-diethylheptane	1.33
	1,3-diethyl-5-methylcyclohexane	1.90	2,6-diethyloctane	1.23
	1,3,5-triethylcyclohexane	1.70	**Average**	**1.20**
	Average	**2.06**		
Alkenes	*primary*		*secondary*	
	ethene	7.40	isobutene	5.30
	propene	9.40	2-methyl-1-butene	4.90
	1-butene	8.90	trans-2-butene	10.00
	1-pentene	6.20	cis-2-butene	10.00
	3-methyl-1-butene	6.20	2-pentenes	8.80
	1-hexene	4.40	2-methyl-2-butene	6.40
	1-hepene	3.50	2-hexenes	6.70
	1-octene	2.70	2-heptenes	5.50
	1-nonene	2.20	3-octenes	5.30
	Average	**5.66**	3-nonenes	4.60
			Average	**6.75**
	others			
	1,3-butadiene	10.90		
	isoprene	9.10		
	cyclopentene	7.70		
	cyclohexene	5.70		
	α-pinene	3.30		
	β-pinene	4.40		
	Average	**6.85**		

Table D-4a. Smog formation potential for a number of acidifying chemicals



Alcohols and Ethers		
	methanol	0.56
	ethanol	1.34
	n-propyl alcohol	2.30
	isopropyl alcohol	0.54
	n-butyl alcohol	2.70
	isobutyl alcohol	1.90
	t-butyl alcohol	0.42
	dimethyl ether	0.77
	methyl t-butyl ether	0.62
	ethyl t-butyl ether	2.00
	Average	**1.32**
Acetylenes		
	acetylene	0.50
	methylacetylene	4.10
	Average	**2.30**
Aromatics		
	benzene	0.42
	toluene	2.70
	ethylbenzene	2.70
	n-propylbenzene	2.10
	isopropylbenzene	2.20
	s-butylbenzene	1.90
	o-xylene	6.50
	p-xylene	6.60
	m-xylene	8.20
	1,3,5-trimethylbenzene	10.10
	1,2,3-trimethylbenzene	8.90
	1,2,4-trimethylbenzene	8.80
	tetralin	0.94
	naphthalene	1.17
	methylnaphthalenes	3.30
	2,3-dimethylnaphthalene	5.10
	styrene	2.20
	Average	**4.34**

Aromatic Oxygenates	
benzaldehyde	–0.57
phenol	1.12
alkyl phenols	2.30
Average	**0.95**
Aldehydes	
formaldehyde	7.20
acetaldehyde	5.50
C3 aldehydes	6.50
glyoxal	2.20
methyl glyoxal	14.80
Average	**7.24**
Ketones	
acetone	0.56
C4 ketones	1.18
Average	**0.87**
Others	
Methyl nitrite	9.50
Base Reactive Organic Gas Mixture	**3.10**

Adapted from Carter (1994)

Example 11.3-2 Solvent recovery from a gaseous waste stream: Effect of process operation on indexes for global warming, smog formation, and acidification

A gaseous waste stream is generated within a plastic film processing operation from a drying step. The stream (12,000 scfm) is currently being vented to the atmosphere and it contains 0.5% (vol.) of total VOCs having equal mass percentages of toluene and ethyl acetate with the balance being nitrogen. Figure 11.3-1 is a process flow diagram of an absorption technology configuration to recovery and recycle the VOCs back to the film process (Sangwichien, 1998).

Since the waste stream may already meet environmental regulations for smog formation and human toxicity, the key issue is how much of the VOCs to recover and how much savings on solvent costs can be realized.

Example 11.3-2

In this problem, we do not deal with the economic issues, but rather show that when considering environmental impacts, there are trade-offs for several impacts depending on the percent recovery of the VOCs.

The gaseous waste stream enters the absorption column where the VOCs (toluene and ethyl acetate) transfer from the gas phase to the absorption oil (tetradecane: $C_{14}H_{30}$). The effectiveness of this transfer depends largely on the oil flow rate, as the percentage recovery of VOCs increases with increasing oil flow rate. The VOCs are separated from the absorption column after cooling. The VOCs are recovered as a mixed product from the condenser of the distillation column and stored in a tank for re-use in the plastic film process.

Example 11.3-2

The main emission sources are the absorption column, the vent on the distillation column, the vent on the storage tank (not shown), utility related pollutions, and fugitive sources.

Solution: Table 11.3.-2 shows the effect of absorber oil flow rate on the emissions from the solvent recovery process.

A commercial process simulator (HYSYS) was used to generated mass and energy balances and to calculate the VOC emission rates from the absorber unit.

Within the Environmental Fate and Risk Assessment Tool (EFRAT, refer to Appendix F for a list of software resources.) EPA emission factors and correlations were used to calculate VOC emission rates from the distillation column, storage tank, and fugitive sources.

Example 11.3-2

CO_2, CO, TOC, NO_x, and SO_x emission rates were also calculated within EFRAT based on the energy requirements of the process and an assumed fuel type (fuel oil no. 4).

Figure 11.3-2 shows the recovery of toluene and ethyl acetate as a function of absorption oil flow rate in the process. As the absorber oil flow rate is increased, the emissions of toluene and ethyl acetate from the absorber unit decrease, reflecting an increased percent recovery from the gaseous waste stream. Most of the toluene (99.5%) is recovered at a flow rate of only 50 kgmole/hr. To recover a significant percentage of ethyl acetate requires a much larger oil flow rate. Toluene is recovered more quickly with oil flow rate compared to ethyl acetate because the oil is more selective towards toluene. Emissions of utility related pollutants (CO_2, CO, TOC, NO_x, and SO_x) increase in proportion to the oil flow rate. The emissions of the absorption oil (n-C_{14}) remains relatively constant with oil flow rate.

Example 11.3-2

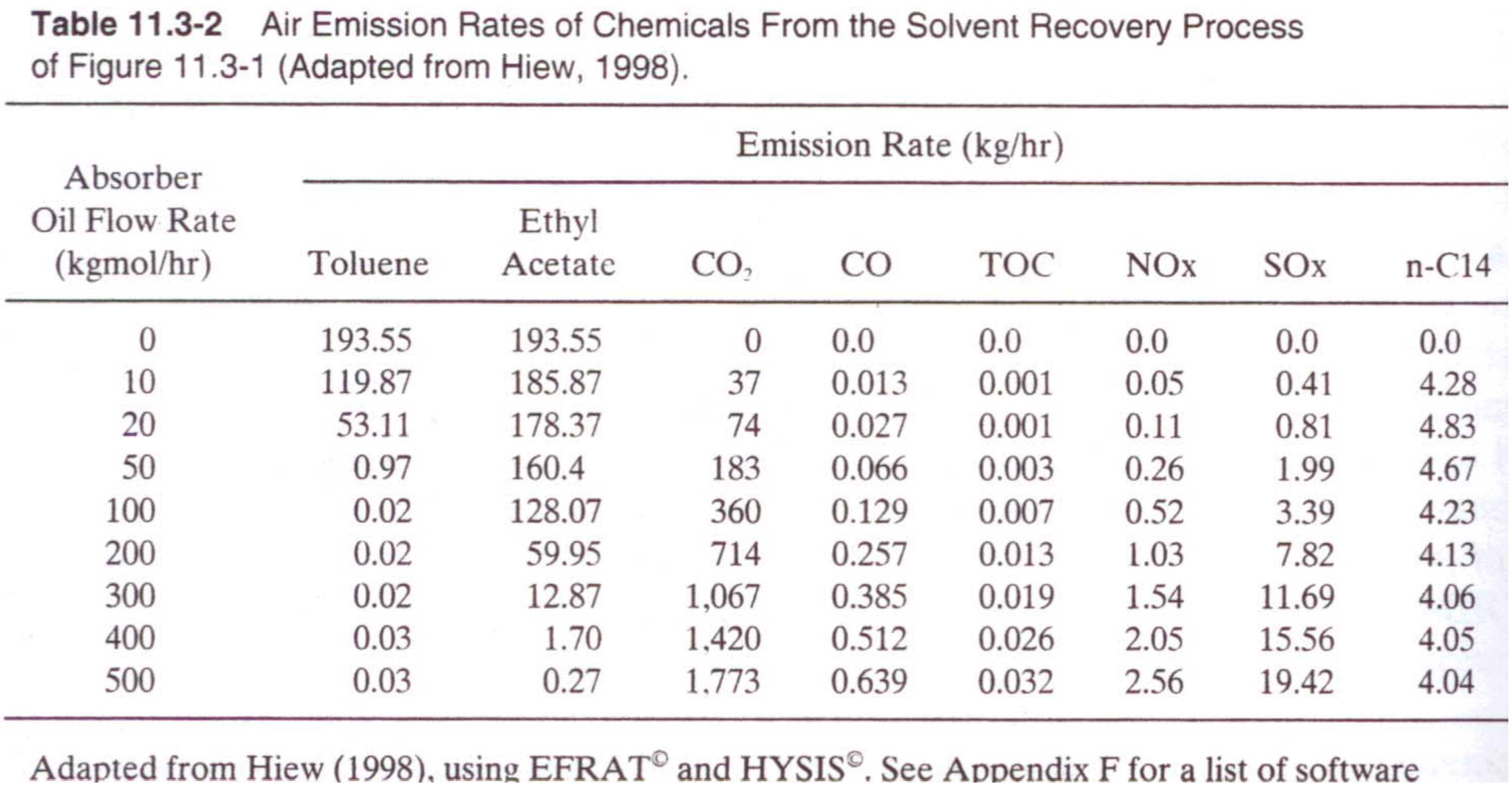


Table 11.3-2 Air Emission Rates of Chemicals From the Solvent Recovery Process of Figure 11.3-1 (Adapted from Hiew, 1998).

Absorber Oil Flow Rate (kgmol/hr)	Emission Rate (kg/hr)							
	Toluene	Ethyl Acetate	CO_2	CO	TOC	NOx	SOx	n-C14
0	193.55	193.55	0	0.0	0.0	0.0	0.0	0.0
10	119.87	185.87	37	0.013	0.001	0.05	0.41	4.28
20	53.11	178.37	74	0.027	0.001	0.11	0.81	4.83
50	0.97	160.4	183	0.066	0.003	0.26	1.99	4.67
100	0.02	128.07	360	0.129	0.007	0.52	3.39	4.23
200	0.02	59.95	714	0.257	0.013	1.03	7.82	4.13
300	0.02	12.87	1,067	0.385	0.019	1.54	11.69	4.06
400	0.03	1.70	1,420	0.512	0.026	2.05	15.56	4.05
500	0.03	0.27	1,773	0.639	0.032	2.56	19.42	4.04

Adapted from Hiew (1998), using EFRAT© and HYSIS©. See Appendix F for a list of software

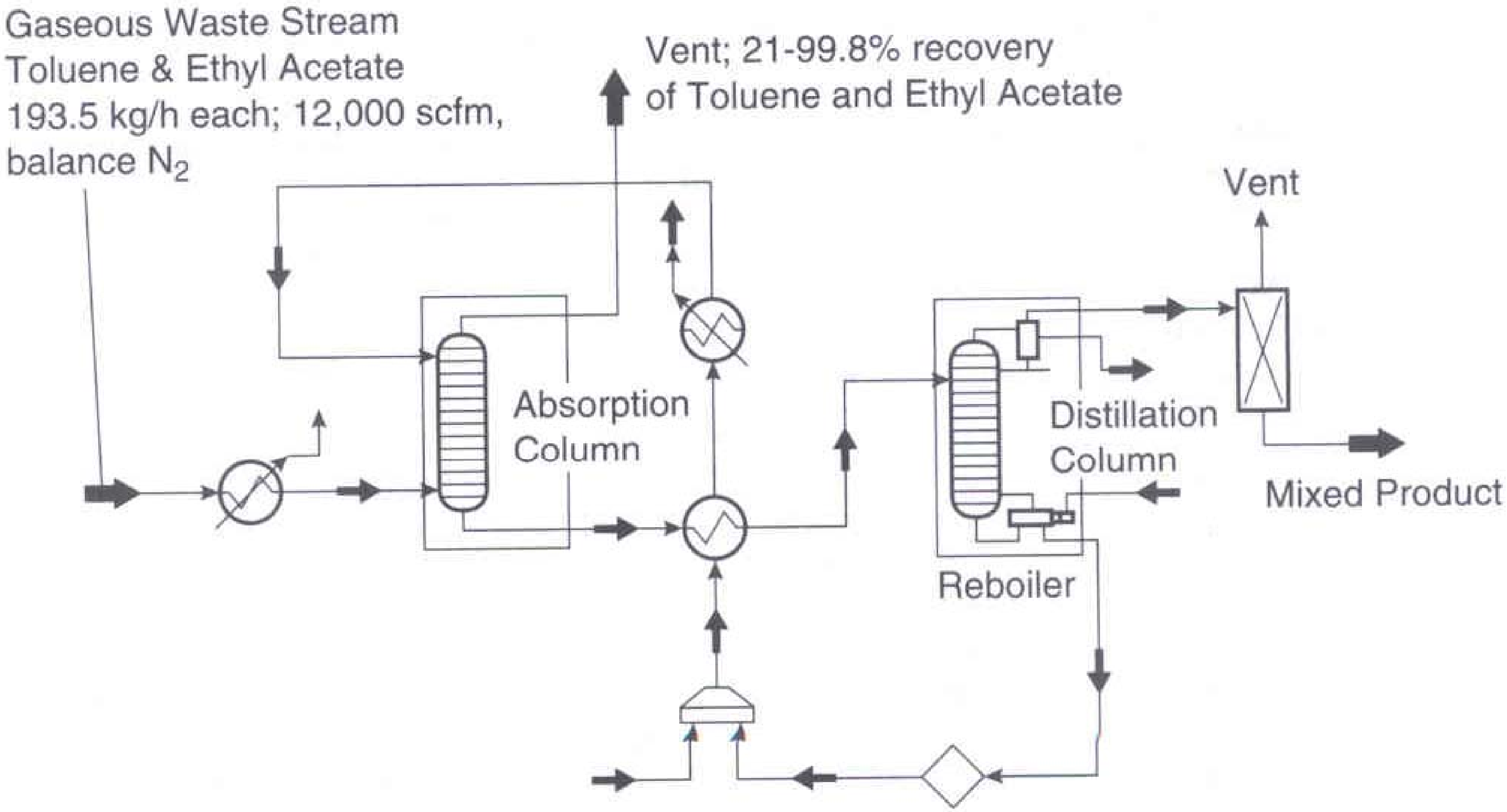
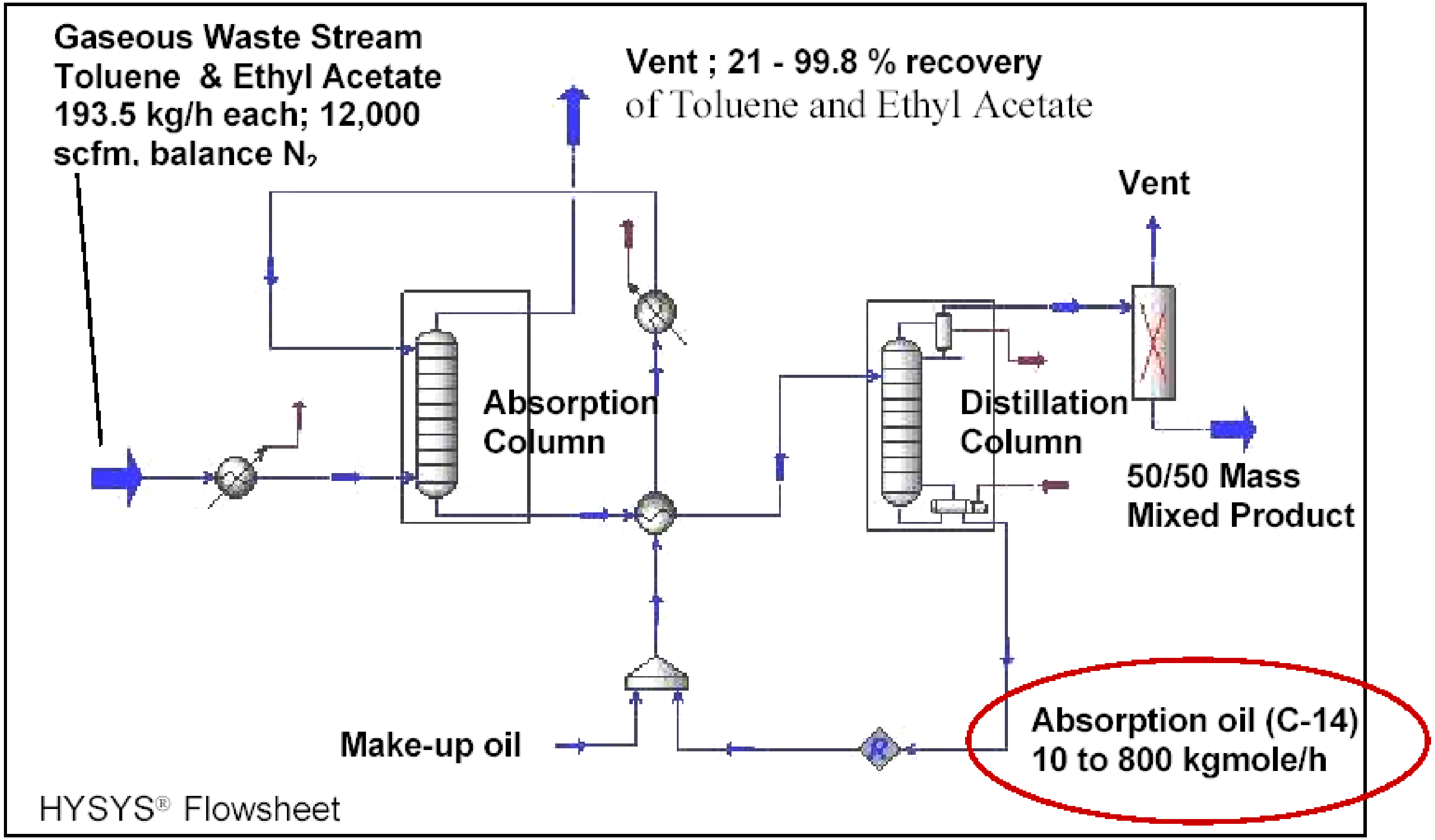


Fig. 11.3-1 Schematic diagram of a solvent recovery and recycle process using absorption into heavy oil (n-tetradecane) followed by distillation

Absorption - distillation process: analysis of VOC recovery/recycle



Gaseous Waste Stream
Toluene & Ethyl Acetate
193.5 kg/h each; 12,000 scfm, balance N_2

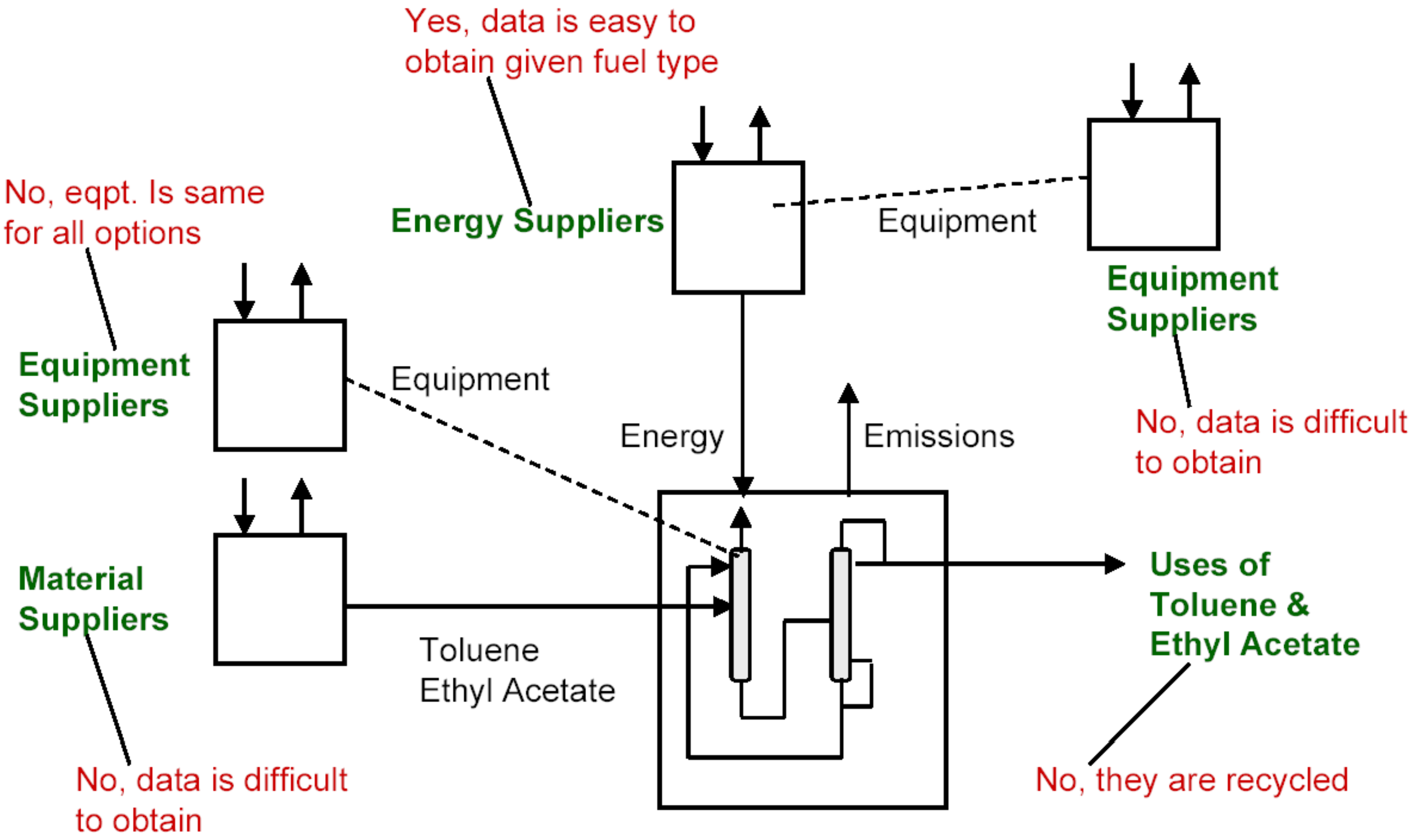
Vent ; 21 - 99.8 % recovery of Toluene and Ethyl Acetate

50/50 Mass Mixed Product

Absorption oil (C-14)
10 to 800 kgmole/h

HYSYS® Flowsheet

Absorption - distillation process: (boundaries on analysis?)



Yes, data is easy to obtain given fuel type

Energy Suppliers

No, eqpt. Is same for all options

Equipment Suppliers

Equipment Suppliers

No, data is difficult to obtain

Material Suppliers

No, data is difficult to obtain

Uses of Toluene & Ethyl Acetate

No, they are recycled

Example 11.3-2

Relative risk indexes for global warming, smog formation, and acidification have been calculated for solvent recovery process at each flow rate. These values were generated by applying Equations 11-4, 11-13, and 11-11, respectively.

$$I_{GW} = \sum_i (GWP_i \times m_i)$$

$$I_{SF} = \sum_i (SFP_i \times m_i)$$

$$I_{AR} = \sum_i (ARP_i \times m_i)$$

Using the emission rates in Table 11.3-2 and the impact potential values for each chemical (Appendix D, Table D-1, D-3, and D-4). For the smog formation potential (SFP=MIR) of ethyl acetate, the average MIR of the ethers (1.13) and ketones (0.87) listed in Appendix D, Table D-4 were used as an approximation. As an example calculation, the smog formation index of the process will be determined at an absorption oil flow rate of 50 kgmole/hr.

Example 11.3-2

$$I_{SF} = \sum_{i} (SFP_i \times m_i)$$

Toluene:	(0.87)(0.97 kg/hr)	0.84 kg/hr
Ethyl acetate:	(0.32)(160.4 kg/hr)	51.33 kg/hr
Tetradecane:	(0.1)(4,67 kg/hr)	0.47 kg/hr
Total:		**52.64 kg/hr**

Shown in Figures 11.3-3 through 11.3-5 are the relative impact indexes for the solvent recovery process.

Unit-specific emission summary

UNIT OPERATION "METHOD"	Mass Flow (kg/hr)	Emission rate (kg/hr)							
		Toluene	Ethyl Acetate	C-14	SOx	NOx	CO_2	CO	TOC
Absorption Column "HYSIS"	19,840	0.002	128	4.23					
Distillation Column "emission factor"	259.1	0.019	0.007						
Fugitive Sources "emission factor"	259.1	0.062	0.062						
Storage Tank "correlation"	259.1	0.0014	0.0014						
Reboiler Energy (10^6 Btu/hr)	6.16				3.93	0.52	499	0.129	0.007
Total Emissions (kg/hr)		0.088	128.07	4.23	3.93	0.52	499	0.129	0.007

Where are the centers for energy consumption and emissions?

100 kgmole/hr Oil Flow Rate;

Oil Temperature = 82˚F; ΔT=180˚F

Risk index summary

	Relative Risk Index (I*)								
Compound	I^*_{GW}	I^*_{OD}	I^*_{SF}	I^*_{AR}	I^*_{ING}	I^*_{INGC}	I^*_{INH}	I^*_{INHC}	I^*_{FT}
Toluene	3.34	0	0.9	0.0	1	0	1.0	0	0.02
Ethyl Acetate	2	0	0.3	0.0	9.7	0	3.3	0	0.04
SOx	0	0	0.0	1.0	0	0	0.0	0	0.00
NOx	40	0	0.0	0.7	0	0	0.0	0	0.00
CO2	1	0	0.0	0.0	0	0	0.0	0	0.00
CO	0	0	0.0	0.0	0	0	141.2	0	0.00
C-14	3.1	0	0.0	0.0	0	0	0.0	0	0.00
TOC	3.1	0	1.0	0.0	0	0	0.0	0	0.00

Which chemicals have the highest impact indexes?

Process environmental summary

100 kgmole/hr Oil Flow Rate;

Oil Temperature = 82˚F; ΔT=180˚F

$$\text{Process Index } (I) = \sum_{i=1}^{N} (I_i^*) \times (m_i)$$

All units in kg/yr

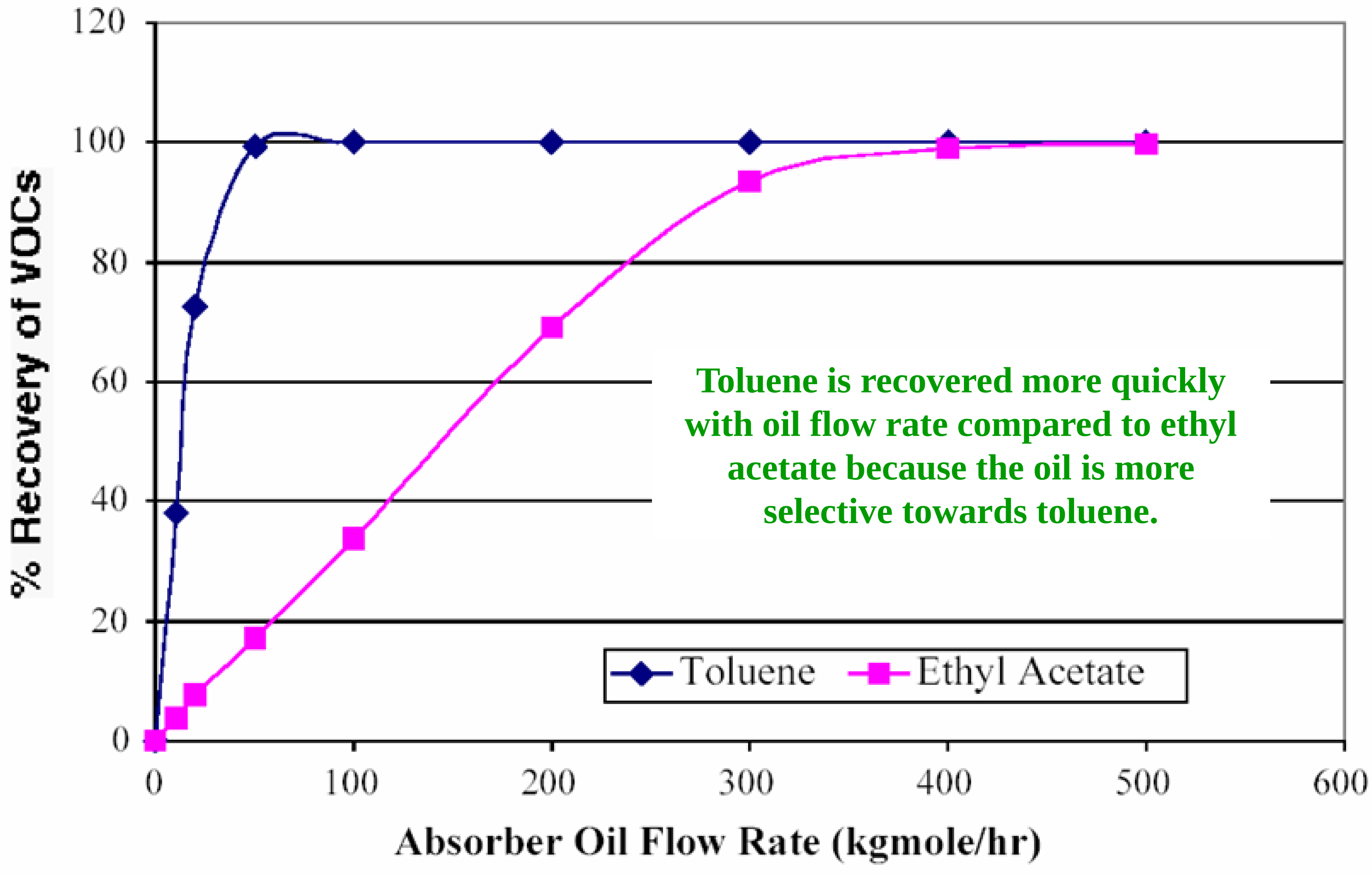
Emission from	I_{FT}	I_{ING}	I_{INH}	I_{GW}	I_{SF}	I_{AR}
utility	0.00E+00	0.00E+00	1.44E+05	5.21E+06	1.70E+02	1.27E+04
absorber	4.67E+04	1.08E+07	3.73E+06	2.36E+06	3.74E+05	0.00E+00
tank	3.36E+00	6.43E+02	2.55E+02	2.95E+02	1.09E+02	0.00E+00
distillation column	5.06E+00	6.43E+02	3.60E+02	6.82E+02	3.12E+02	0.00E+00
fugitive	3.12E+01	5.30E+03	2.35E+03	2.90E+03	1.12E+03	0.00E+00

Emission of	I_{FT}	I_{ING}	I_{INH}	I_{GW}	I_{SF}	I_{AR}
Ethyl Acetate	4.68E+04	1.09E+07	3.73E+06	2.24E+06	3.72E+05	0.00E+00
Toluene	1.92E+01	1.22E+03	1.22E+03	4.07E+03	2.11E+03	0.00E+00
Tetradecane	0.00E+00	0.00E+00	0.00E+00	1.15E+05	1.14E+03	0.00E+00
Carbon dioxide	0.00E+00	0.00E+00	0.00E+00	4.87E+06	0.00E+00	0.00E+00
Carbon monoxide	0.00E+00	0.00E+00	1.44E+05	0.00E+00	0.00E+00	0.00E+00
Nitrogen dioxide	0.00E+00	0.00E+00	0.00E+00	3.40E+05	0.00E+00	6.39E+03
Sulfur dioxide	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.36E+03
TOC	0.00E+00	0.00E+00	0.00E+00	6.51E+02	1.35E+02	0.00E+00

- going beyond the release of mass to the release of impact -

Figure 11.3-2:

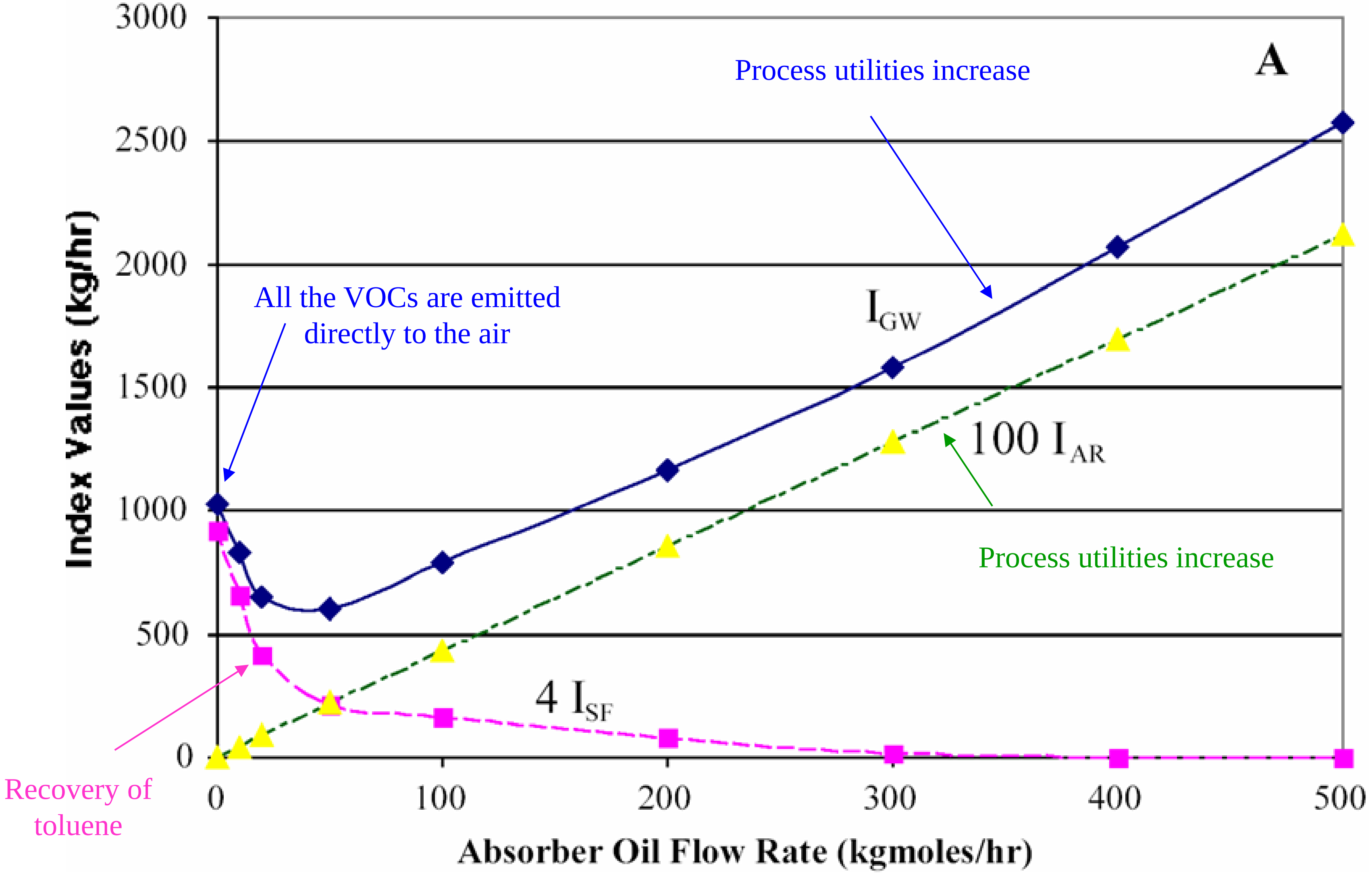
VOC recovery efficiency for the solvent recovery process



Toluene is recovered more quickly with oil flow rate compared to ethyl acetate because the oil is more selective towards toluene.

Figure 11.3-2:

Environmental indexes for the solvent recovery process



Interpretation of environmental assessment results

Risk reductions at 50 kgmole/hr flow rate

→ Global Warming Index - 41% reduction
→ Smog Formation Index - 86 % reduction
→ Acid Rain Index - small increase
→ Inhalation Route Toxicity Index - 78 % reduction
→ Ingestion Route Toxicity Index - 18 % reduction
→ Ecotoxicity (Fish) Index - 19 % reduction

Absorber oil choice is not an optimum

→ Oil selectively absorbs toluene, but ethyl acetate has a higher value

Multiple indexes complicate the decision

11.3.5 Toxicity

The chemical toxicity to humans and ecosystems is a function of dose and response. The dose is dependent on a complex series of steps involving the manner of release, environmental fate and transport of chemicals, and uptake mechanisms. The final two steps dictate the extent of exposure.

Key questions which affect the administered dose include:

- Where are the emissions released to-the air, water, soil ?
- Are the chemicals altered by environmental reactions, or are they persistent ?
- How are the chemicals taken up by the body ?
- Through breathing contaminated air ?
- Through drinking contaminated water ?
- By direct contact with and transfer through the skin ?

11.3.5 Toxicity

The effective dose is dependent on processes occurring in the body including absorption, distribution, storage, transformation, and elimination. The response by the target organ in the body is a very complex function of chemical structure and modes of action and is the purview of the field of toxicology.

Clearly, the complexity of toxicology precludes and exact determination of all adverse effects to human and ecosystem health from the release of a chemical. From engineering point of view, an exact assessment may not be necessary. Both inhalation and ingestion are the dominant routes of exposure for human contact with toxic chemicals in the environment.

Non-Carcinogenic Toxicity

Non-carcinogenic toxicity in humans is controlled by a threshold exposure, such that doses below a threshold value do not manifest a toxic response whereas doses above this level do. A key parameter for each chemical is therefore its ***RfD****(mg/kg/d)* or ***RfC*** *(mg/m^3)* for ingestion and inhalation exposure, respectively. Exposures to concentrations in the water or air which result in doses or concentrations above these reference levels is believed to cause adverse effect.

Lists of RfD and RfC data are available in electronic or paper copy form (US EPA, 1997; US EPA 1994). Because RfDs and RfCs are not available for all chemicals, we use lethal doses (LD_{50}) and concentration (LC_{50}) as additional toxicological parameters for health assessments. Lists of LD_{50} and LC_{50} are tabulated in additional sources (NTP, 1997). TLVs, PELs, and RELs are additional toxicity properties that, like RfD and RfC, are based on low-dose studies.

For the purpose of an approximate assessment of risk, concentrations in the air or water can be calculated using the multimedia compartment model shown in section 11.2. The toxicity potential for ingestion route exposure is defined as

$$INGTP_i = \frac{\left[(C_{i,w})(2L/d)/(70kg)\right]/(RfD_i)}{\left[(C_{Toluene,w})(2L/d)/(70kg)\right]/(RfD_{Toluene})} \quad (11\text{-}14)$$

where $C_{i,w}$ and $C_{toluene,w}$ are the steady-state concentrations of chemical *i* and the benchmark compound (toluene) in the water compartment after release of 1000 kg/hr of each into the water compartment as predicted by multimedia compartment model of section 11.2. The factor 2L/d and 70 kg are standard ingestion rate and body weight for risk assessment (Pratt, 1993). The product of the concentration and the ingestion rate divided by the weight provides the exposure dose. This exposure dose is divided by the reference dose to determine whether this dose poses a toxicological risk.

The ratio of these risks for the chemical and the benchmark compound results in the ingestion toxicology potential. The toxicity potential for inhalation exposure is defined similarly by

$$INHTP_i = \frac{C_{i,a} / RfC_i}{C_{Toluene,a} / RfC_{Toluene}} \qquad (11\text{-}15)$$

where $C_{i,a}$ and $C_{toluene,a}$ are the concentrations of chemical i and of the benchmark compound in the air compartment after release of 1000 kg/hr of each into the air compartment. The doses are not shown in the equation because the inhalation rate (20 m^3/d) and body weight cancel out. The ratio of the risks for inhalation exposure is the potential for inhalation toxicity relative to the benchmark compound.

In order to determine a non-carcinogenic toxicity index for the entire process, we must multiply each chemical’s toxicity potential with its emission rate from the process and sum these for all chemicals released

$$I_{ING} = \sum_i (INGTP_i \times m_i) \qquad (11\text{-}16)$$

Similarly for inhalation route toxicity is

$$I_{INH} = \sum_i (INHTP_i \times m_i) \qquad (11\text{-}17)$$

Carcinogenic Toxicity

We develop two indexes for cancer-related risk, based on predicted concentrations of chemicals in the air and water from a release of 1000 kg/hr. The concentrations are converted to doses using standard factors and then risk for the chemical and benchmark compound, benzene, is calculated. The carcinogenic potential for a chemical is determined by taking the ratio of the chemical’s risk to that for the benchmark compound. The ingestion route carcinogenic potential for a chemical is

$$INGCP_i = \frac{(C_{i,w})/(SF_i)}{(C_{Benzene,w})(SF_{Benzene})} \qquad (11\text{-}18)$$

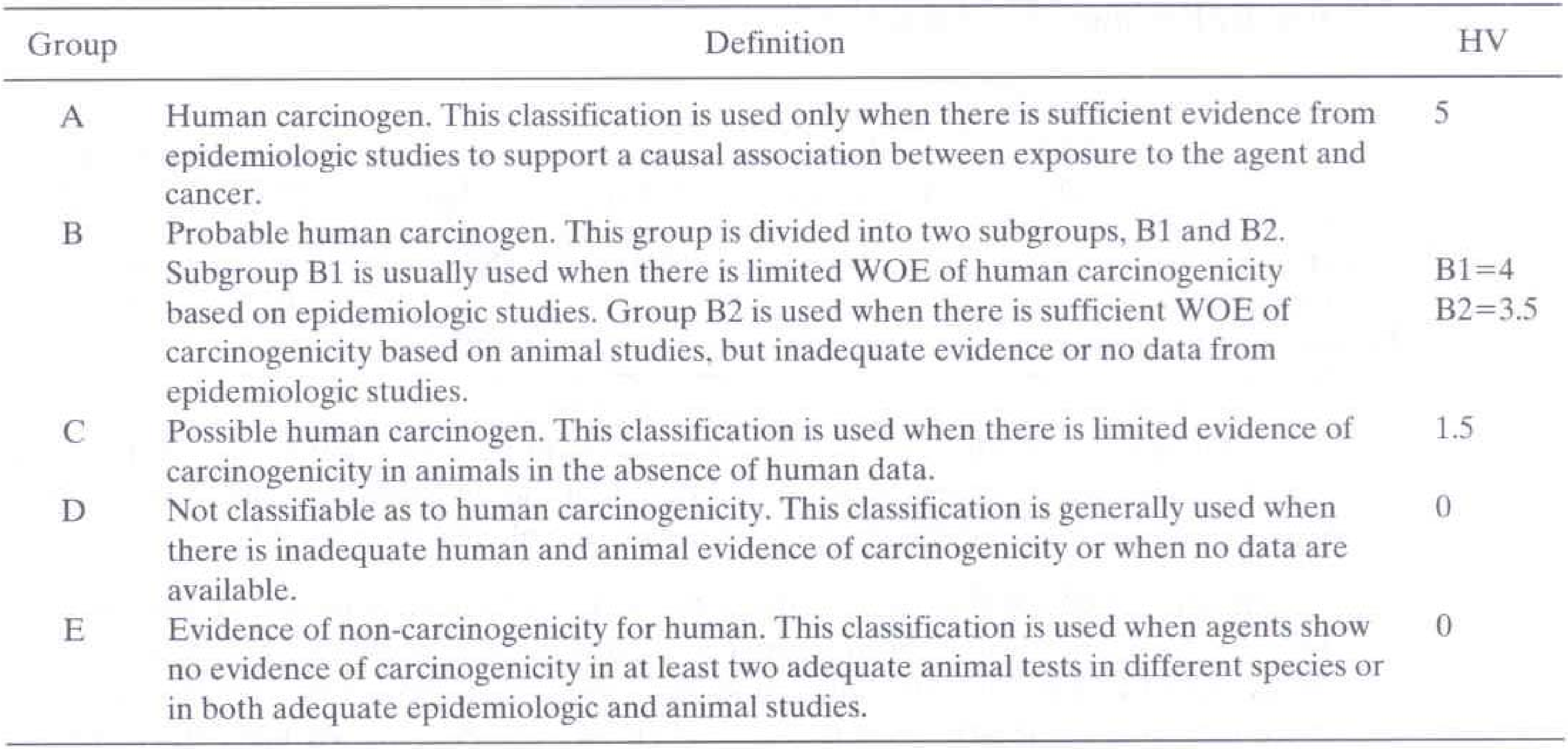
where SF $(\mathrm{mg/kg/d})^{-1}$, the cancer potency slope factor, is the slope of the excess cancer versus administered dose data.

The dose-response data is normally taken using animal experiments and extrapolated to low doses. The higher the value of SF, the higher is the carcinogenic potency of a chemical. List of SF values for many chemicals can be found in the following references (US EPA, 1997; US EPA 1994). Because SFs are not yet available for all chemicals, weight of evidence (WOE) classifications is used. The definitions of each WOE is shown in Table 11.3-3 along with a numerical hazard value (HV). The value of HV can be used in Equations 11-18 and 11-19 in the absence of SF data. Data for WOE can be found in the following sources (NIHS, 1997; OSHA, 1997; IRIS, 1997).

A similar definition for the inhalation carcinogenic potential for a chemical is

$$INHCP_i = \frac{(C_{i,a})/(SF_i)}{(C_{Benzene,a})(SF_{Benzene})} \qquad (11\text{-}19)$$

Table 11.3-3. Weight of evidence(WOE) classifications



Group	Definition	HV
A	Human carcinogen. This classification is used only when there is sufficient evidence from epidemiologic studies to support a causal association between exposure to the agent and cancer.	5
B	Probable human carcinogen. This group is divided into two subgroups, B1 and B2. Subgroup B1 is usually used when there is limited WOE of human carcinogenicity based on epidemiologic studies. Group B2 is used when there is sufficient WOE of carcinogenicity based on animal studies, but inadequate evidence or no data from epidemiologic studies.	B1=4 B2=3.5
C	Possible human carcinogen. This classification is used when there is limited evidence of carcinogenicity in animals in the absence of human data.	1.5
D	Not classifiable as to human carcinogenicity. This classification is generally used when there is inadequate human and animal evidence of carcinogenicity or when no data are available.	0
E	Evidence of non-carcinogenicity for human. This classification is used when agents show no evidence of carcinogenicity in at least two adequate animal tests in different species or in both adequate epidemiologic and animal studies.	0

The carcinogenic toxicity index for the entire process is again a summation for each carcinogen. For ingestion, it is

$$I_{CING} = \sum_i (INGCP_i) \times m_i \qquad (11\text{-}20)$$

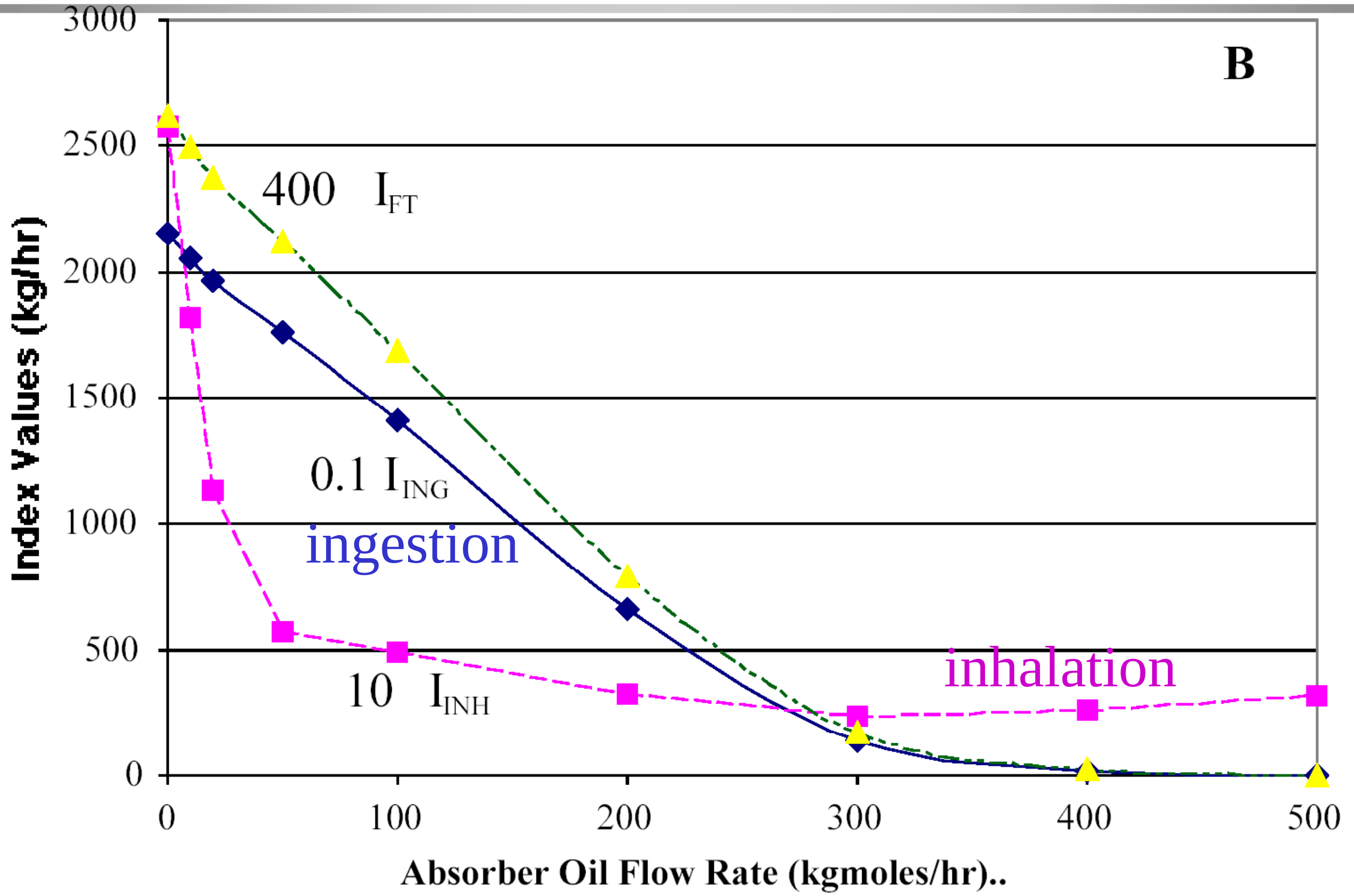
and for inhalation

$$I_{CINH} = \sum_i (INHCP_i) \times m_i \qquad (11\text{-}21)$$

Example 11.3-3

Toxicity evaluation of the solvent recovery process in Fig. 11.3-1

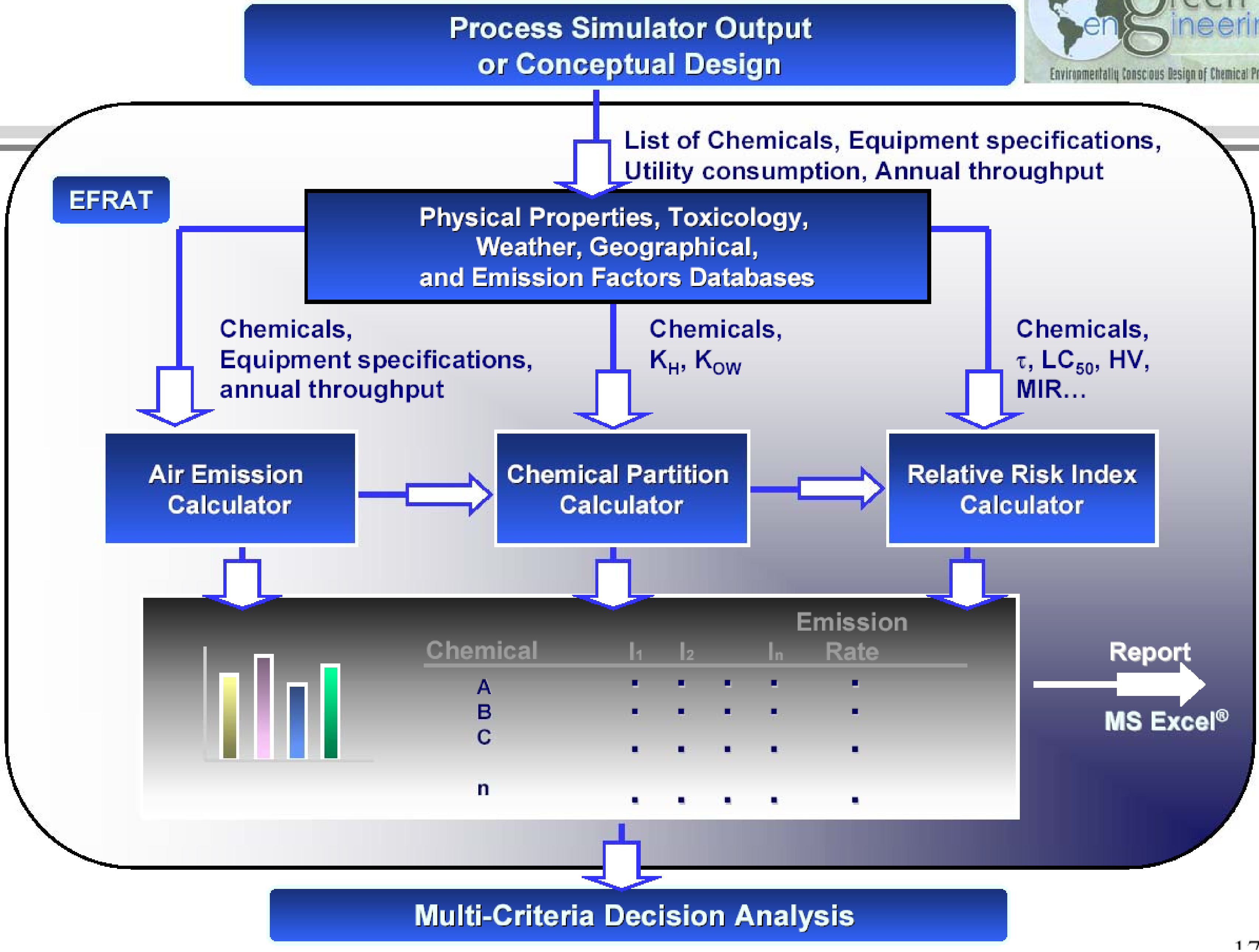
Environmental Index Profiles



A similar response over the parameter space for I_{FT}, I_{ING}, and I_{INH}

Summary

Here a systematic methodology for evaluating environmental and health-based impacts for chemical process designs. The methodology includes pollutant release of emission estimation, environmental fate and transport of pollutants, and relative risk assessment using the benchmarking concept



Process Simulator Output or Conceptual Design

List of Chemicals, Equipment specifications, Utility consumption, Annual throughput

EFRAT

Physical Properties, Toxicology, Weather, Geographical, and Emission Factors Databases

Chemicals, Equipment specifications, annual throughput

Chemicals, K_H, K_{OW}

Chemicals, τ, LC_{50}, HV, MIR…

Air Emission Calculator

Chemical Partition Calculator

Relative Risk Index Calculator

Report

MS Excel®

Multi-Criteria Decision Analysis

Software tools for environmental impact assessment of process designs

Environmental Fate and Risk Assessment Tool (EFRAT)

- links with HYSYS for automated assessments

WAste Reduction Algorithm (WAR)

- reported to be linked with ChemCAD
- US EPA National Risk Management Research Laboratory
  Cincinnati, OH

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