Pollution Prevention and Risk Reduction for Chemical Processes

Module 3:
Evaluating the Environmental Performance of a Flowsheet

Background Reading:

D. R. Shonnard, Chapter 11 "Evaluating the Environmental Performance of a Flowsheet"

By the end of this section you should:

- **be aware of the major classes of environmental impact and human health concerns for releases from chemical processes**
- **be able to estimate air emission rates from units in chemical processes using EPA and/or commercial software**
- **be able to estimate environmental fate and concentrations of chemicals using a multimedia compartment model /software tool**
- **to construct metrics of environmental impact from estimated properties, emission rates, and environmental concentrations**
- **to apply these environmental metrics to evaluate and begin to optimize a chemical process flowsheet**

Outline:

I. Major Environmental and Human Health Impacts (11.1)
II. Air Emissions Estimation Methods and Software Tools (11.2)
III. Environmental Fates of Emissions and Wastes (11.3)
IV. Environmental Assessment of a Process Flowsheet (11.4)

I. Major Environmental and Human Health Impacts

After a chemical is emitted to the air or released to the water or soil, what impacts could that chemical have on the quality of the air and water resources in the environment? What human health impacts could that chemical have? What health impacts could it have on animals in the environment and what ecosystems are most vulnerable?

In order to answer these questions, we must begin to understand several important industrial and natural processes, including
a) emission / release rates,
b) environmental fate and transport processes, and
c) human and ecosystem health responses.

Emitted chemicals might become involved in complex environmental chemistry, leading to reaction products that may cause damage to human health and to sensitive environmental compartments. Damage to these environmental compartments lead directly to human health and ecosystem health impacts. Of main concern are criteria pollutants that are released to the air from combustion processes (O_3, CO, NO_2, SO_2, Particulate Matter, and Pb), organic compounds that can degrade water quality, and toxic pollutants released to all environmental media. Table 11.1 shows a list of major environment impacts by a number of industrial pollutants. The most important atmosphere impacts are

a) smog formation,
b) acid rain and deposition
c) stratospheric ozone depletion, and
d) global warming from infra-red active chemicals

while the most important health impacts are for long-term (chronic) exposure by inhalation of contaminated air and ingestion of contaminated water. These include

e) inhalation non-carcinogenic toxicity
f) ingestion non-carcinogenic toxicity
g) inhalation carcinogenic toxicity
h) ingestion carcinogenic toxicity
i) ecosystem toxicity (fish mortality)

Table 11.1 Major Atmospheric Impacts With Associated Pollutants and Reaction Products

Impacts	*Industrial Pollutants*	*Reaction Products*
<u>Atmospheric</u>		
Smog Formation	NO_x HC	O_3, CO_2, PAN, aerosols, OH•
Acid Deposition	SO_2 NO_x	H_2SO_4 HNO_3
Ozone Depletion	CFCs RX	Cl
Global Warming	CO_2 CH_4 NO_x O_3 CFCs	
<u>Human Health</u>		
Inhalation Non-carcinogenic	Organic pollutants released to all media	
Inhalation Carcinogenic	Inorganic pollutants in particulate matter	
Ingestion Non-carcinogenic	Organic pollutants released to all media	
Ingestion Carcinogenic	Inorganic pollutants released to all media	
<u>Ecosystem Health</u>		
Fish Toxicity	Organic pollutants released to all media	
Ingestion Carcinogenic	Inorganic pollutants released to all media	

NO_x - nitrogen oxides from combustion reactions
HC – hydrocarbons that volatilize into the air from mobile and stationary sources
CFCs - chlorofluorocarbons
RX - chlorinated hydrocarbons
PAN - Peroxy Acetyl Nitrate and other organic oxidants

II. Air Emissions Estimation Methods and Software Tools

Air emission is one of the three major pathways for pollutants to be released to the environment by industrial processes (release to air, water, and soil). Because of the more immediate threat to human health of air releases, much previous attention has been given to industrial unit operations that are major sources of air emissions. *Emission factors*, *correlations*, and *mathematical models* have been developed for many of these units. Table 11.2 is a summary of emission estimation methods for chemical process units and Table 11.3 is a list of software tools for estimating chemical process emissions (end of section).

II. A. Emission Factors

Emission factors are used to estimate release rates of chemicals (E, kg/unit time) from *unit operations* based on process unit, process throughput, and stream composition.

$$E = m_{VOC}\, EF_{av}\, M$$

where

- m_{VOC} **is the mass fraction of a volatile organic compound in the stream or process unit,**
- EF_{av} **(kg emitted/kg throughput) is the average emission factor ascribed to that stream or process unit, and**
- M **is the total mass flow rate through the unit (kg/unit time).**

Example problem 11-1 illustrates the use of emission factors to estimate uncontrolled releases to the air from distillation column condenser vents.

Example problem 11-1
Refinery distillation emissions estimation.

Your refinery is adding capacity and needs to estimate distillation emissions to assure compliance with local air quality regulations. The addition to the existing facility includes three new distillation columns. The flow rate through the condenser of each column is as follows; $2x10^4$ kg benzene/d through condenser #1, $5x10^4$ kg toluene/d through #2, and $3x10^4$ kg xylene/d through #3. Estimate the annual emission rates of each chemical in (kg/yr).

Solution
The mass fraction of each chemical in the condensers of each column is approximately one. A review of the emission factors listed in the Air CHIEF CD-ROM for distillation column condenser vents has a large variation, but an average value is of the order 0.1 g emitted / kg condenser throughput.

Benzene:
E(kg/yr) = (1.0)(0.1 g benzene/kg throughput)($2x10^4$ kg throughput/d)(365 d/yr)
= $7.3x10^5$ g benzene / yr = 730 kg benzene/yr.

Toluene:
E(kg/yr) = (1.0)(0.1 g toluene/kg throughput)($5x10^4$ kg throughput/d)(365 d/yr)
= $1.8x10^6$ g toluene / yr = 1,825 kg toluene/yr.

Xylenes:
E(kg/yr) = (1.0)(0.1 g xylene/kg throughput)($3x10^4$ kg throughput/d)(365 d/yr)
= $1.1x10^6$ g xylene / yr = 1,095 kg xylene/yr.

Emission rates from *<u>fugitive sources</u>* (large in number but small emitters individually) are estimated using

$E = m_{VOC} f_{av}$

Table 11.6 lists the average emission factors (f_{av} [kg VOC/hr/source]) for fugitive sources present in three major chemical process industrial catagories; - Synthetic Organic Chemical Manufacturing Industry (SOCMI), Petroleum Refineries, and Gas Plants. Liquid streams are classified into light and heavy service. A light liquid is defined as a stream in which the most volatile component (present ≥ 20% by weight)

has a vapor pressure at the stream temperature of ≥ 0.04 lb/in^2. The total emission for each chemical is obtained by summing the emission rate for each piece of equipment.

Example problem illustrates the use of fugitive source emission factors for a petroleum refinery.

Example problem 11-2
Refinery fugitive emissions estimation.

Your refinery is adding capacity and needs to estimate fugitive emissions to assure compliance with local air quality regulations. The addition to the existing facility includes 100 valves, 10 pumps, and 100 flanges. The stream composition is 0.2 wt fraction benzene, .5 wt fraction toluene, and .3 wt fraction mixed xylenes. Estimate the annual emission rate of each of these components in (kg/yr). Assume that the streams in the addition are in light liquid service.

Solution
The total emission rate for each chemical is the sum for all sources. Using the in Table 11.3 for these sources for light liquid service results in the following:
Benzene:
E(kg/yr) = (0.2)[(100 valves)(0.011 kg/valve/hr)+(10 pumps)(0.11 kg/pump/hr)+
(100 flanges)(0.00025 kg/flange/hr)](24 hr/d)(365 d/yr)
= 3,898 kg benzene / yr.

For toluene, the mass fraction is 0.5 in the formula above.
Toluene:
E(kg/yr) = 9,745 kg toluene / yr.

Similarly for mixed xylenes, with 0.3 as the mass fraction.
Xylenes:
E(kg/yr) = 5,847 kg xylenes / yr.

Emission rates of criteria pollutants from *<u>industrial combustion processes</u>* is also provided using emission factors, boiler type, fuel type, and sulfur composition.

$$E(kg/unit/yr) = \frac{(ED)(EF)}{(FV)(BE)}$$

- ***ED*** **is the energy demand of a process unit (energy demand/unit/yr),**
- ***EF*** **is the emission factor for the fuel type (kg/volume of fuel combusted),**
- ***FV*** **is the fuel value (energy/volume fuel combusted), and**
- ***BE*** **is the boiler efficiency (unitless; 0.75 to 0.90 are a typical range of values).**

Emission factors are shown in Tables 11.7 and 11.8. Typical heating values for solid, liquid, and gaseous fuels are provided in Table 11.9.

Example problem 11-3
Reboiler duty emissions of criteria pollutants and CO_2.

A distillation column is being used to separate toluene and ethyl acetate from a heavy oil (tetradecane). A commercial process simulator predicts that the reboiler duty is 6.16×10^6 Btu/hr. The reboiler steam is created by natural gas combustion with an efficiency of 0.7 in a low-NOx small industrial boiler. Estimate the annual emission rates of SO_2, NOx, and CO.

Solution
The emission factors for natural gas for a small industrial low-NOx boiler are obtained from Table 11.8. The fuel value of natural gas is 1,035 Btu/scf as shown in Table 11.9.

SO_2:

$$E(\text{kg/yr}) = \frac{(6.16\text{x}10^6\ \text{Btu/hr})(0.6\text{lbSO}_2/10^6\ \text{scf})}{(1{,}035\text{Btu/scf})(0.7)}(24\text{hr/d})(365\text{d/yr})(1\text{kg}/2.205\text{lb})$$

$$= 20.3\ \text{kg SO}_2\text{/yr.}$$

NOx:

$$E(\text{kg/yr}) = \frac{(6.16\text{x}10^6\ \text{Btu/hr})(81\text{lbNOx}/10^6\ \text{scf})}{(1{,}035\text{Btu/scf})(0.7)}(24\text{hr/d})(365\text{d/yr})(1\text{kg}/2.205\text{lb})$$

$$= 2{,}731\ \text{kg NOx/yr.}$$

CO:

$$E(\text{kg/yr}) = \frac{(6.16\text{x}10^6\ \text{Btu/hr})(61\text{lbCO}/10^6\ \text{scf})}{(1{,}035\text{Btu/scf})(0.7)}(24\text{hr/d})(365\text{d/yr})(1\text{kg}/2.205\text{lb})$$

$$= 2{,}060\ \text{kg CO/yr.}$$

Estimating emissions from *electricity consumption* in processes is given by;

$$E(kg/unit/yr) = \frac{(ED)(EF)}{(ME)(GE)}$$

where *ED* is the electricity demand of the unit per year, *ME* is the efficiency of the device (.75 to .95), and *GE* is the efficiency of electricity generation (.35). Emission factors (short tons emitted/kW hr) for electricity consumption can be calculated from the values in Table 11.10.

Carbon dioxide emission factors can be calculated for energy related combustion processes using fuel combustion stoichiometry (assume a liquid alkane hydrocarbon).

$$C_nH_{2n+2} + (1.5n+.5)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

The emission factor is 18 lb CO_2 emitted per U.S. gallon liquid fuel combusted. For natural gas combustion, the value is .12 lb CO_2 per standard cubic foot of gas combusted.

Example problem 11-4
Reboiler duty emissions of CO_2.

Estimate the annual emission rates of CO_2 for the same process as in Example problem 11-3 .

Solution
The CO_2 emission factor for natural gas combustion is 0.12 lb CO_2/scf.

CO_2:

$$E(kg/yr) = \frac{(6.16x10^6\ Btu/hr)(0.12lbCO_2/scf)}{(1{,}035Btu/scf)(0.7)}(24hr/d)(365d/yr)(1kg/2.205lb)$$
$$= 4.05x10^6\ kg\ CO_2/yr.$$

II. B. Emission Correlations

Correlations have been developed for estimating emissions from chemical process units. Storage tanks are prominent in this category. There are two major losses mechanisms from tanks; *working losses* (L_W) and *standing losses* (L_S). Working losses originate from the raising and lowering of the liquid level in the tank while standing losses are from fluctuations in tank temperature and pressure in response to local weather and diurnal changes. The total loss (lb/yr) is the sum of L_W and L_S for fixed-roof, floating-roof, and variable vapor space tanks. The correlation equations are complex and cumbersome to work with, but software is available to perform these calculations with user little defined input (Table 11.3, Tanks 4.0). Correlations are also available for losses of volatile organic compounds from wastewater treatment units (Table 11.3, Air CHIEF CD-ROM).

II. C. Mathematical Models of Process Units

Commercial process simulators are able to predict vent emissions for units that exhaust gaseous streams to the environment. Examples include gas-liquid absorption columns and adsorption columns.

Summary

This section has examined methods for estimating emissions to the air from specific unit operations in chemical processes, for fugitive sources, and for criteria emissions plus CO_2 from utility-related combustion processes. The methods used were emission factors, emission correlations, and mathematical models, including chemical process simulators for certain unit operations. These methods are listed in the order of increasing complexity and level of understanding of the underlying mechanisms.

Section 11.2: Questions for Discussion

1. **Emission estimation for fugitive sources requires a detailed knowledge of the exact numbers of valves, flanges, etc. At the conceptual design stage, this level of detail may not be known. Suggest ways to overcome this limitation for conceptual design.**
2. **How much SO_2 reduction was accomplished by using natural gas in example problem 11-3 instead of, for instance, no. 4 oil (see Table 11.8)?**
3. **Emission factors that have been developed over the years have a high degree of uncertainty associated with them. Emissions correlations (storage tanks) are believed to be much more accurate. Mathematical models, like process simulators, may represent the highest level of accuracy for emission estimation, if used properly and selectively in process design. Why would accurate process emissions be of fundamental importance in predicting the risks associated with process designs?**
4. **Referring to Table 11.1, discuss the main environmental and human health impacts that the emitted chemicals from example problems 11.1,- 11.4 might cause?**

Table 11.2 Summary of emission estimation methods used for different unit operations, fugitive sources, and utility consumption.

Emission Source	Emission Type	Emission Estimation Method	Description	Reference
Unit Operations	Atmospheric, high pressure, vacuum	Emission factor	Distillation, absorption, and stripping columns, reactors, sumps, decanters, cooling towers, dryers.	USEPA, 1998b;
Storage Tanks	Fixed, floating, and variable vapor space	Correla-tion	Equations, parameters, and methodology for different storage tanks. Emissions depend on dimensions, exterior, location, chemical stored, and etc.	USEPA, 1998a
Fugitive	SOCMI, PRI, Gas Plants	Emission factor	Based on hydrocarbon and hydrogen gas, light and heavy liquid, and general services. Emissions depend on annual production and number of parts that cause fugitive emission.	USEPA,1985 a,b; 1993; 1998a; Allen and Rosselot, 1997
Secondary	Aerated, non-aerated	Mass transfer theory	Emissions depend on diffusion, location, type of chemicals, oil film thickness, reactivity, and etc.	USEPA, 1998a; Allen and Rosselot, 1997
Fuel Oil Combustion	Fuel Oil No. 4, 5, and 6, and Distillate oil	Emission factor	Utility and industrial boilers, Emissions depend on sulfur contents. Cause emission of SOx, NOx, CO,CO_2, and TOC	USEPA, 1998a
Natural Gas Combustion	Industrial (small & large)	Emission factor	Emissions depend on combustor type- uncontrolled and controlled w/ low NOx burner or flue gas recirculation. Cause emission of SOx, NOx, CO, and CO_2	USEPA, 1998a
Electricity consumption	Produce from coal, petro-leum, natural gas fired, or average	Emission factor	Cause emission of SOx, NOx, CO, and CO_2	EF, 1992

SOCMI synthetic organic chemical manufacturing industry
PRI petroleum refinery industry
TOC total organic compound

Master

Table 11.3 List of software tools for estimating chemical process emissions from unit operations.

Emission Software	Description	Contact Information
Air CHIEF CD-ROM Version 6.0	Emission factors for criteria pollutants and hazardous air pollutants, and biogenic emissions. Wastewater treatment emissions model. Compilation of EPA emission documents.	US Government Printing Office, (202)-512-1800 Stock No. 055-000-00609-1 http://www.epa.gov/ttn/chief/airchief.html
Tanks 4.0	Storage tank emission estimation software based on correlation developed by the American Petroleum Institute (API). Includes fixed-roof, floating-roof, and vairable vapor space tanks	US EPA, Office of Air Quality Planning and Standards, Technology Transfer Network Web Site, http://www.epa.gov/ttn/chief/tanks.html
Emission Master®	Predicts emissions from process units for various steps, including; filling vessels, purging and sweeping, heating, depressurization, vacuum, gas evolution during reaction, solids drying, storage tanks, and other user-defined activities**.**	Mitchell Scientific, Inc. Westerfield, NJ 07091-2605
Commercial Process Simulators	Predicts flow rates and compositions of gaseous streams vented to the environment. Absorbers, adsorption columns, etc.	Hyprotech, Simulation Sciences, Aspen, etc.
EFRAT ; the Environmental Fate and Risk Assessment Tool	Integrates emission estimation factors and correlations from various US EPA sources. Also calculates the environmental fate and transport of emitted pollutants. Generates 9 relative risk indexes. Links to commercial process simulators.	Michigan Technological University, Center for Clean Industrial and Treatment Technologies, (http://cpas.mtu.edu/cencitt)

Table 11.6: Average Emission Factors for Estimating Fugitive Emissions

Source	Service	Emission Factor, f_{av} (kg/hour/source)		
		SOCMI[a]	Refinery[b]	Gas Plant[a]
Valves	Hydrocarbon gas	0.00597	0.027	-
	Light liquid	0.00403	0.011	-
	Heavy liquid	0.00023	0.0002	-
	Hydrogen gas	-	0.0083	-
	All	-	-	0.02
Pump Seals	Light liquid	0.0199	0.11	-
	Heavy liquid	0.00862	0.021	-
	Liquid	-	-	0.063
Compressor Seals	Hydrocarbon gas	0.228	0.63	-
	Hydrogen gas	-	0.05	-
	All	-	-	0.204
Pressure-relief Valves	Hydrocarbon gas	0.104	0.16	-
	Liquid	0.007[c]	0.007[c]	-
	All	-	-	0.188
Flanges and other connections	All	0.00183	0.00025	0.0011
Open-ended lines	All	0.0017	0.002	0.022
Oil/water separators (uncovered)	All	-	14,600[d]	-
Sampling connections	All	0.015	-	-

[a] USEPA (1993) except as noted, SOCMI - Synthetic Organic Chemical Manufacturing Industry
[b] USEPA(1998) except as noted.
[c] USEPA(1985b)
[d] based on limited data (330,000 bbl/day capacity) (USEPA, 1998)

Table 11.7: Criteria Pollutant Emission Factors (*EF*)for Uncontrolled Releases From Residual and Distillate Oil Combustion (EPA, 1998).

Firing Configuration (SCC)[a]	SO_2[b] kg/10^3 L	SO_3 kg/10^3 L	NO_X[c] kg/10^3 L	CO[d,e] kg/10^3 L	Filterable PMg kg/10^3 L	TOC[f] kg/10^3 L
Utility boilers						
No. 6 oil fired, normal firing	19S	0.69S	8	0.6	g	0.125
No. 6 oil fired, tangential firing	19S	0.69S	5	0.6	g	0.125
No. 5 oil fired, normal firing	19S	0.69S	8	0.6	g	0.125
No. 5 oil fired, tangential firing	19S	0.69S	5	0.6	g	0.125
No. 4 oil fired, normal firing	18S	0.69S	8	0.6	g	0.125
No. 4 oil fired, tangential firing	18S	0.69S	5	0.6	g	0.125
Industrial boilers						
No. 6 oil fired (1-02-004-01/02/03)	19S	0.24S	6.6	0.6	g	0.154
No. 5 oil fired (1-02-004-04)	19S	0.24S	6.6	0.6	g	0.154
Distillate oil fired (1-02-005-01/02/03)	17S	0.24S	2.4	0.6	g	0.03
No. 4 oil fired (1-02-005-04)	18S	0.24S	2.4	0.6	g	0.03
Commercial/institutional/residential combustors						
No. 6 oil fired	19S	0.24S	6.6	0.6	g	0.193
No. 5 oil fired	19S	0.24S	6.6	0.6	g	0.193
Distillate oil fired	17S	0.24S	2.4	0.6	g	0.067
No. 4 oil fired	18S	0.24S	2.4	0.6	g	0.067
Residential furnace (No SCC)	17S	0.24S	2.2	0.6	0.3	0.299

[a] SCC = Source Classification Code.

[b] S indicates that the weight % of sulfur in the oil should be multiplied by the value given.

[c] Expressed as NO_2. Test results indicate that at least 95% by weight of NOx is NO for all boiler types except residential furnaces, where about 75% is NO. For utility vertical fired boilers use 12.6 kg/10^3 L at full load and normal (>15%) excess air. Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are related to fuel nitrogen content, estimated by the following empirical relationship: kg NO_2 /10^3 L = 2.465 + 12.526(N), where N is the weight percent of nitrogen in the oil.

[d] CO emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.

[e] Emission factors for CO_2 from oil combustion should be calculated using kg CO_2/10^3 L oil = 31.0 C (distillate) or 34.6 C (residual).

[f] Filterable PM is that particulate collected on or prior to the filter of an EPA Method 5 (or equivalent) sampling train. PM-10 values include the sum of that particulate collected on the PM-10 filter of an EPA Method 201 or 201A sampling train and condensable emissions as measured by EPA Method 202.

[g] Particulate emission factors for residual oil combustion are, on average, a function of fuel oil grade and sulfur content:

No. 6 oil: 1.12(S) + 0.37 kg/10^3 L, where S is the weight % of sulfur in oil.
No. 5 oil: 1.2 kg/10^3 L
No. 4 oil: 0.84 kg/10^3 L
No. 2 oil: 0.24 kg/10^3 L

Table 11.8: Emission Factors for Sulfur Dioxide (SO_2), Nitrogen Oxides (NOx), and Carbon Monoxide (CO) from Natural Gas Combustion[a] (USEPA, 1998).

Combustor Type	SO_2[b]		NOx[c]		CO	
	kg/10^6 m^3	lb/10^6 ft^3	kg/10^6 m^3	lb/10^6 ft^3	kg/10^6 m^3	lb/10^6 ft^3
Utility/large Industrial Boilers						
Uncontrolled	9.6	0.6	8800	550[d]	640	40
Controlled - Low NOx burners	9.6	0.6	1300	81[d]	ND	ND
Controlled - Flue gas recirculation	9.6	0.6	850	53s	ND	ND
Small Industrial Boilers						
Uncontrolled	9.6	0.6	2240	140	560	35
Controlled - Low NOx burners	9.6	0.6	1300	81[d]	980	61
Controlled - Flue gas recirculation	9.6	0.6	480	30	590	37
Commercial Boilers						
Uncontrolled	9.6	0.6	1600	100	330	21
Controlled - Low NOx burners	9.6	0.6	270	17	425	27
Controlled - Flue gas	9.6	0.6	580	36	ND	ND
Residential Furnaces						
Uncontrolled	9.6	0.6	1500	94	640	40

[a] Units are kg of pollutant/10^6 cubic meters natural gas fired and lb. of pollutant/10^6 cubic feet natural gas fired. Based on an average natural gas fired higher heating value of 8270 kcal/m^3 (1000 Btu/scf). The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. ND = no data. NA = not applicable.

[b] Based on average sulfur content of natural gas, 4600 g/10^6 Nm^3.

[c] Expressed as NO_2. For tangentially fired units, use 4400 kg/10^6 m^3 (275 lb/10^6 ft^3. Note that NOx emissions from controlled boilers will be reduced at low load conditions.

[d] Emission factors apply to packaged boilers only.

Table 11.9 Typical Heating Values for Solid, Liquid, and Gaseous Fuels (Perry and Green, 1984)

Fuel Oil, Btu/U.S. gal	
No. 1	137,000
No. 2	139,600
No. 4	145,100
No. 5	148,800
No. 6	152,400
Propane, Btu/U.S. gal	91,500
Natural gas, Btu/Standard ft^3	1,035
Coal, Btu/lb	
Bituminous	11,500-14,000
Subbituminous	8,300-11,500
Lignite	6,300-8,300

Table 11.10 Emissions from Fossil-Fueled Steam-Electric Generating Units (EF, 1992).

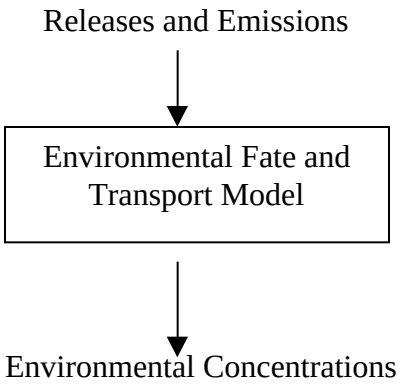
Emission ('000 short tons[a])	Coal Fired	Petroleum Fired	Gas Fired	Total[b]
Carbon Dioxide	1,499,131	87,698	156,748	1,747,418
Sulfur Dioxide	14,126	637	1	14,766
Nitrogen Oxides	6,879	208	599	7,690
Power generated (billion kW hr)	1,551	111	264	2,796

a 1 short ton equal to 2,000 pounds or 0.8929 metric tons

b Also include light oil, methane, coal/oil mixture, propane gas, blast furnace gas, wood, and refuse.

III. Environmental Fates of Emissions and Wastes

An environmental fate and transport model is used to transform industrial emissions and releases into environmental concentrations.



The ecosystem and human health risks are a direct result of exposure to these environmental concentrations. Further, the concentrations predicted by the model are determined by

- **the properties of the chemicals,**
- **the characteristics of the physical environment, and**
- **the environmental processes incorporated into the model.**

The most common modeling approaches used by environmental scientists and engineers, specific examples, and their advantages and disadvantages are

- **single-compartment models**
  - **Gaussian Dispersion Model (atmosphere)**
  - **Advection-Dispersion Equation (groundwater)**
  - **Streeter-Phelps Equation (river)**
  - **advantages: relatively rigerous and comprehensive, relatively few parameters needed, modest computer resources needed**
  - **disadvantages: only one compartment concentration provided, multiple models needed to provide multimedia predictions.**
- **multimedia-compartment models**
  - **Mackay Fugacity Models (air, water, soil, sediment)**

advantages: includes many environmental processes, relatively small number of parameters needed, provides multimedia concentrations.
disadvantages: mathematical rigor is compromised by simplifications and assumptions, lack of experimental data needed to verify models, accuracy of predictions are believed to be only order of magnitude.

Mackay "Level III" Multimedia Compartment Model (Figure 11.3-1)

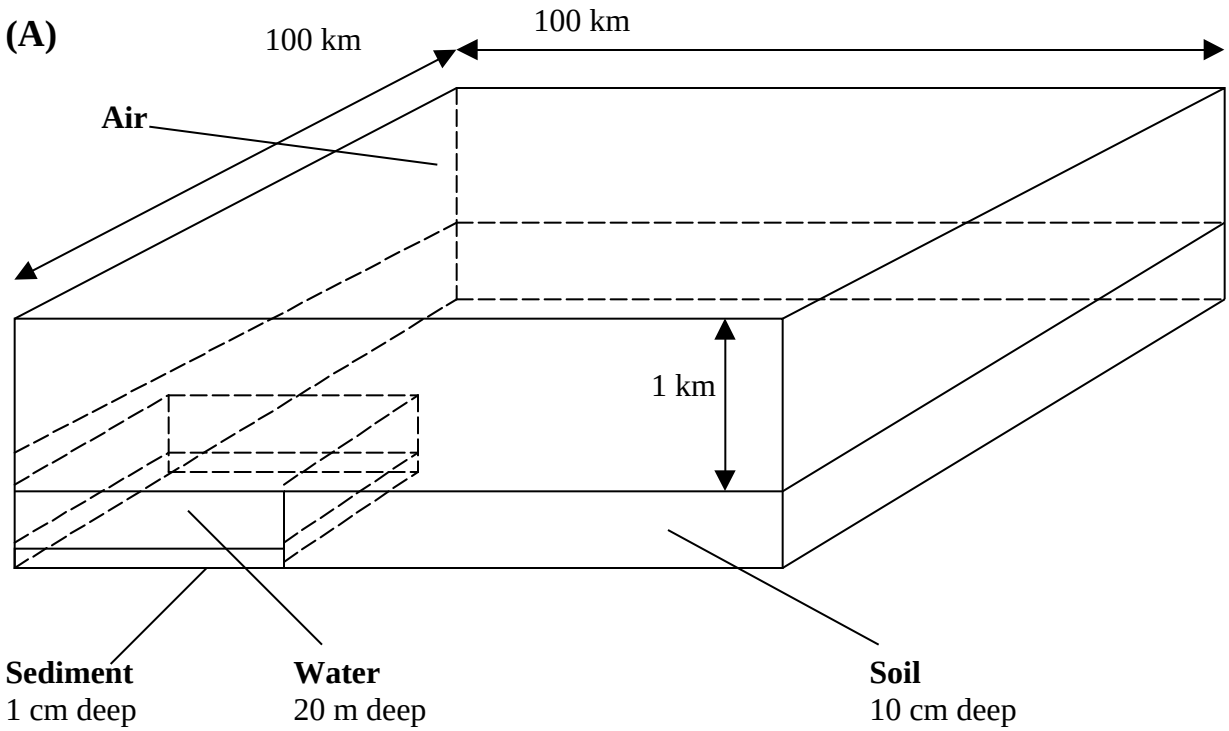
Compartment Properties

	Air	Water	Soil	Sediment
Compartment area m^2	$1x10^{10}$	$1x10^{9}$	$9x10^{9}$	$1x10^{9}$
Compartment depth, m	$1x10^{3}$	$2x10^{-2}$	$1x10^{-2}$	$1x10^{-3}$
Compartment volume, m^3	$1x10^{13}$	$2x10^{7}$	$9x10^{7}$	$1x10^{6}$
Volume fraction air	1	0	0.2	0
Volume fraction water	0	1	0.3	0.8
Volume fraction solid	$2x10^{-11}$	$5x10^{-6}$	0.5	0.2
Volume fraction fish biomass	0	$1x10^{-6}$	0	0
Phase Densities, kg/m^3	1.2	1000	2400	2400
Fraction organic carbon on solids	0	0.2	0.02	0.04

Inputs to Compartments
- **Direct emission; (E_i) (moles/hr)**
- **Advective by flow (G_{Ai}); ($G_{Ai}C_{Bi}$) (moles/hr)**

Intermedia Transfer
- **Diffusion and advection processes; (D_{ij}) (moles/(Pa•hr))**

Loss Processes
- **Advection out of compartments; (D_{Ai}) (moles/(Pa•hr))**
- **Reaction processes; (D_{Ri}) (moles/(Pa•hr))**



(B)

Figure 11.3-1 Schematic diagram of fugacity level III model domain (A) and the intermedia transport mechanisms (B).

III. A. Fugacity Based Model (symbol definitions in Nomenclature)
Fugacity **- thermodynamic property of a chemical and is defined as the** ***"escaping tendency"*** **of the chemical from a given environmental phase (air, water, soil organic matter, etc.).**

Fugacity of a Chemical in Air Phase – equal to the chemical's partial pressure

$f = y\,\varphi\,P_T \approx P$

The concentration is related to fugacity via the Ideal Gas Law

$C_1 = n/V = P/(RT) = f/(RT) = f\,Z_1$

Fugacity of a Chemical in Water Phase

$f = x\,\gamma\,P^s$

The concentration is related to fugacity

$C_2 = x/\upsilon_w = f/(\upsilon_w\,\gamma\,P^s) = f/H = f\,Z_2$

Fugacity of a Chemical in Solid Phase

The concentration of a chemical sorbed to a solid phase can be related to the concentration of the chemical in water phase, via the Distribution Coefficient (K_d)

$C_s = K_d\,C_2$

The sorbed concentration is related to fugacity

$\rho_i\,C_s = [1/H]\,K_{oc}\,\varphi_3\,\rho_3\,f/1000 = Z_3\,f$

A summary of fugacity equations is given in Table 11.21.

Table 11.21 Fugacity Capacities (Z) Values for the Various Phases and Compartments in the Environment

Environmental Phases		Phase Densities (kg/m^3)
Air Phase	$Z = 1/(R\ T)$	1.2
Water Phase	$Z_2 = 1/H$	1,000
Soil Phase	$Z_3 = [1/H]\ K_{oc}\ \varphi_3\ \rho_i\ /1000$	2,400
Sediment Phase	$Z_4 = [1/H]\ K_{oc}\ \varphi_4\ \rho_4\ /1000$	2,400
Suspended Sediment Phase	$Z_5 = [1/H]\ K_{oc}\ \varphi_5\ \rho_5\ /1000$	2,400
Fish Phase	$Z_6 = [1/H]\ 0.048\ \rho_6\ K_{ow}$	1,000
Aerosol Phase	$Z_7 = [1/(R\ T)]\ 6x10^6/P^S_L$	

where
- R = gas constant (8.314 Pa• m^3/[mole•K])
- T = absolute temperature (K)
- H = Henry's constant (Pa•m^3/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/m^3)
- φ_i = mass fraction organic carbon in phase *i* (g/g)

Environmental Compartments

Air Compartment (1)	$Z_{C1} = Z_1 + 2x10^{-11}\ Z_7$	(approximately 30 μg/m^3 aerosols)
Water Compartment (2)	$Z_{C2} = Z_2 + 5x10^{-6}\ Z_5 + 10^{-6}\ Z_6$	(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).

Intermedia Transport

The diffusive rate of transfer *N* (moles/h) from a compartment i to compartment j is defined by;

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

Non-diffusive transport between compartments (rain wash-out and wet - dry deposition of atmospheric particles)

$N = GC = GZf = Df$ (moles/h)

<u>Advective Transport</u>

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

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

Chemical may also exit the model domain from compartments by advective (bulk flow) processes having transfer values (D_{Ai})

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

<u>Reaction Loss Processes</u>

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 environment is to express them as first order with rate constant k_R (hr^{-1}). The rate of reaction loss for a chemical in a compartment N_{Ri} (moles/hr) is

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

A summary of the D values for intermedia transport, advection, and reaction are summarized in Table 11.23.

<u>Balance Equations</u>

We write mole balance equations for each compartment as summarized in Table 11.24

Table 11.23. *D* Values in the Mackay Level III model (Adapted from Mackay and Paterson, 1991)

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 wash out	$D_{RW} = u_3A_WZ_2$	$D_{12} = D_{VW} + D_{RW} + D_{QW}$
	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 wash out	$D_{RS} = u_3A_SZ_2$	$D_{13} = D_{VS} + D_{QS} + D_{RS}$
	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	$u_8A_WZ_2$	$D_{24} = u_8A_WZ_2.+ u_9A_WZ_5$
	resuspension	$u_{10}A_WZ_4$	$D_{42} = u_8A_WZ_2.+ u_{10}A_WZ_4$
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"

Table 11.24. Mole Balance Equations for the Mackay 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 left hand side is the sum of all gains and the right hand side is the sum of all losses, Ii = Ei + GaiCCi, I4 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

$$J_1 = I_1/\, D_{T1} + I_3\, D_{31}/(D_{T3}D_{T1})$$
$$J_2 = D_{21}/D_{T1}$$
$$J_3 = 1 - D_{31}D_{13}/(D_{T1}\, D_{T3})$$
$$J_4 = D_{12} + D_{32}D_{13}/D_{T3}$$

The fugacity calculations outlined in the previous pages are obviously very complex. Routine hand calculations of environmental fugacities using this model are prohibitively time consuming. Fortunately, spreadsheet programs are available for carrying out these calculations (Mackay et al, 1992, Volume 4). Using these programs and equipped with a relatively small number of chemical-specific input partitioning and reaction parameters, environmental fate calculations can be quickly performed as shown in the following example problem.

Example problem 11-5
Multimedia Concentrations of Benzene, Ethanol, and Pentachlorophenol

Benzene, ethanol, and pentachlorophenol (PCP) are examples of organic pollutants with very different environmental properties, as shown in the Table below. Benzene and ethanol are volatile (high vapor pressures) and have comparatively short reaction half lives. Pentachlorophenol has long reaction half lives in the compartments, low volatility and water solubility, and strong sorptive properties (high K_{ow}). Benzene is the most reactive in air and ethanol is the most reactive in water, soil, and sediment.

i. Use the Mackay "level III" spreadsheet to determine the amounts of each chemical and their percentages in the four environmental compartments at steady-state for three distinct emissions scenarios

a) 1000 kg/hr emitted into the air only
b) 1000 kg/hr emitted into the water only, and
c) 1000 kg/hr emitted into the soil only.

ii. Discuss the compartmental distribution and the total amount of each chemical in the model domain in light of the environmental property data presented below.

Solution
After entering the environmental properties for each chemical in the tabulated spreadsheet locations, one can have the spreadsheet recalculate the resulting environmental fugacities, molar concentrations, and finally mass amounts in each compartment. For emission into air, locations F276 - F279 contain the amounts in the four compartments; air, water, soil, and sediment. Locations G276 - G279 contain the corresponding percentages in these compartments. Similar results are contained in rows 286 - 289 for emission into water and in rows 296 - 299 for emission into soil. The following table (Table 11.E-2) highlights these results for all three emission scenarios and for each of the three chemicals

<u>Discussion of Results</u>: There are several key items to summarize from Table 11.E-2, all of which will help us interpret how the model performs. First, the majority of the chemical can be found in the compartment into which the chemical was emitted. The percentages in each compartment relay this information. The only exception is for PCP when emitted into the air. The chemical has such a low vapor pressure (4.15E-3 Pa) that rain washout and wet/dry deposition effectively remove it from the atmosphere, leading to accumulation in the soil. Secondly, the total amounts of the chemical in each compartment of the environment increases with increasing reaction half life, as shown by the relatively large amounts of PCP compared to benzene and ethanol. Note also that PCP has relatively large values of reaction half life in each compartment compared to the other two chemicals.

Example problem 11-5 (continued)

Conclusions: One obvious conclusion from this simple comparison is that the environmental engineer or scientist has control over where the chemical is found in the environment at steady-state by deciding into which compartment to release unavoidable emissions. Also, one has control over the degree of accumulation for a chemical in each compartment, by carefully considering of the relevant environmental properties. These properties include reaction half life, vapor pressure, water solubility, and octanol-water partition coefficient. Uncertainties associated with the Mackay level "III" model suggest that only order of magnitude estimates of environmental concentrations are feasible. By adopting it in this text, it is believed that the model can provide environmental fate information of sufficient accuracy for making relative comparisons between chemicals and chemical processes.

(Example Prob. 11-5) Environmental Property Data for Mackay "Level III" Model

Environmental Property	**Unit**	**Spreadsheet Location**	**Benzene**	**Ethanol**	**PCP**
MolecularWeight	g/mole	C6	78.11	46.07	266.34
Melting Point	˚C	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

(Example Prob. 11-5) Environment Compartment mass amounts and percentages for Benzene, Ethanol, and PCP (pentachlorophenol)

Chemical	Amounts (kg)				Total	Percentages (%)			
(emission scenario)	air	water	soil	sediment	(kg)	air	water	soil	sediment
Benzene (a)	1.97E+4	5.67E+1	2.44E+1	2.03E-1	1.98E+4	99.59	0.29	0.12	1.0E-3
Benzene (b)	6.31E+3	1.34E+5	7.81E+0	4.79E+2	1.41E+5	4.48	95.17	5.5E-3	0.35
Benzene (c)	1.79E+4	1.40E+3	6.75E+4	5.01E+0	8.68E+4	20.61	1.61	77.78	5.8E-3
Ethanol (a)	4.24E+4	1.75E+3	1.49E+3	1.33E+0	4.56E+4	92.87	3.85	3.28	2.9E-3
Ethanol (b)	1.64E+2	7.32E+4	5.71E+0	5.56E+1	7.35E+4	0.22	99.70	7.8E-3	0.08
Ethanol (c)	7.27E+2	4.43E+3	7.33E+4	3.36E+0	7.84E+4	0.92	5.64	93.42	0.02
PCP (a)	5.28E+3	5.29E+4	2.01E+6	2.08E+3	2.07E+6	0.26	2.56	97.07	0.11
PCP (b)	3.33E-1	4.41E+5	1.27E+2	1.73E+4	4.59E+5	7.3E-5	96.19	0.03	3.78
PCP (c)	6.94E+0	1.32E+4	2.38E+6	5.18E+2	2.39E+6	2.9E-4	0.54	99.44	.02

Summary

This section has examined methods for estimating environmental concentrations given emission estimates for chemical processes. Although many single compartment environmental fate and transport models exist, for screening level assessments of concentrations, a "level III" multimedia compartment model of Mackay was chosen because of it's balance of mathematical rigor, modest input parameter requirements, and computational efficiency. The model was used to predict the relative concentration differences between the environmental fate of three chemically different organic compounds; benzene, ethanol, and pentachlorphenol. The model concentrations were shown to be sensitive to chemical-specific properties such as reaction half-lives and octanol-water partition coefficient as well as the route of release into the environment (air, water, or soil).

Section 11.3: Questions for Discussion

1. **The Mackay model is complex. How would you go about constructing a formal study to learn more about the model and how it works? Suggest a few approaches to take.**

IV. Environmental Assessment of a Process Flowsheet

In this section, we will learn how to combine the environmental fate and transport information with impact data to obtain an assessment of the potential risks posed by releases from chemical process designs.

The general form of the dimensionless risk index is defined as;

$$\text{Index} = \frac{[(EP)(IIP)]_i}{[(EP)(IIP)]_B}$$

where (EP) is an exposure parameter, (IIP) is an inherent impact parameter, "B" stands for a benchmark compound and "i" the chemical of interest.

Table 11.4-1 lists nine human health and environmental impact indexes following this index definition.

Table 11.4-1 Human Health and Environmental Impact Indexes

Dimensionless Risk Index	Eqn. #	Equation	Parameter / Software Source(s)
Ingestion Route Toxicity Potential	1	$INGTP_i = \frac{C_{i,a}/RfD_i}{C_{Toluene,a}/RfD_{Toluene}}$	$C_{i,a}$ & $C_{Toluene,a}$ – Mackay Model, 1992-4; **RfD** $_i$ & **RfD**$_{Toluene}$ – EPA 1994, 1997
Inhalation Route Toxicity Potential	2	$INHTP_i = \frac{C_{i,a}/RfC_i}{C_{Toluene,a}/RfC_{Toluene}}$	$C_{i,a}$ & $C_{Toluene,a}$ – Mackay Model, 1992-4; **RfC** $_i$ & **RfC**$_{Toluene}$ – EPA 1994, 1997
Ingestion Route Carcinogenicity Potential	3	$INGCP_i = \frac{C_{i,w} \times (SF_i)_{ING}}{C_{Benzene,w} \times (SF_{Benzene})_{ING}}$	$C_{i,w}$ & $C_{Benzene,w}$ – Mackay Model, 1992-4; ***SF*-** EPA 1994, 1997
Inhalation Route Carcinogenicity Potential	4	$INHCP_i = \frac{C_{i,a} \times (SF_i)_{INH}}{C_{Benzene,a} \times (SF_{Benzene})_{INH}}$	$C_{i,w}$ & $C_{Benzene,w}$ – Mackay Model, 1992-4; ***SF*-** EPA 1994, 1997
Fish Toxicity Potential	5	$FTP_i = \frac{C_{i,w} \times LC_{50f,PCP}}{C_{PCP,w} \times LC_{50f,i}}$	$C_{i,w}$ & $C_{PCP,w}$ – Mackay Model, 1992-4; LC_{50f} - Verschueren, 1996; Davis, 1994

C_i is the concentration if species "i".
RfD is the reference dose; LD50 may be substituted for RfD.
RfC is the reference concentration, LC50 may be substituted for RfC, and Hazard Value (HV, Davis 1994) may be substituted for SF (slope factor).

Dimensionless Risk Index	Eqn. #	Equation	Parameter / Software Source(s)
Global Warming	6	GWP_i	***GWP*-** Fisher, 1990a; WMO, 1992a; IPCC, 1991, 1996
	6a	$GWP_i = N_C \times \frac{MW_{CO_2}}{MW_i}$	N_C –
Ozone Depletion	7	ODP_i	***ODP*-** Fisher, 1990b; WMO, 1990a; WMO 1992b
Smog Formation	8	$SFP_i = \frac{MIR_i}{MIR_{ROG}}$	***MIR*-** Carter, 1994; Heijungs, 1992
Acid Rain	9	ARP_i	***ARP*-** Heijungs, 1992; Goedkoop, 1995

GWP is global warming potential.
ODP is the ozone depletion potential.
MIR is the maximum incremental reactivity for forming ozone in the lower atmosphere.
ARP is the acid rain potential.

IV. A. Human Toxicity

In it's most simplistic form, chemical toxicity to humans and ecosystems is a function *dose* and *response*. The dose is dependent upon a complex series of steps involving the manner of release, environmental fate and transport of chemicals, and uptake mechanisms. 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*. From an engineering point of view, a quantitative risk assessment may not be necessary in order to assess the health impacts of chemical process designs. We will develop and use *toxicity potentials* for non-carcinogenic and carcinogenic health effects for ingestion and inhalation routes of exposure.

Non-Carcinogenic Toxicity: Non-carcinogenic toxicity in humans is thought to be 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 it's *reference dose* (RfD (mg/kg/d) or *reference concentration* (RfC (mg/m^3)) for ingestion and inhalation exposure, respectively (U.S. EPA, 1997a; U.S. EPA, 1994). Because RfDs and RfCs are not available for all chemicals, we will use lethal doses (LD_{50}) and concentrations (LC_{50}) as additional toxicological parameters for health assessments. Lists of LD_{50} and LC_{50} are tabulated in additional sources (NTP, 1997).

The toxicity potential for ingestion route exposure is defined as equation 1 in Table 11.4-1.

$$INGTP_i = \frac{[(C_{i,w})(2\ L/d)/(70\ kg)]/(RfD_i)}{[(C_{Toluene,w})(2\ L/d)/(70\ kg)]/(RfD_{Toluene})} = \frac{C_{i,w}/RfD_i}{C_{Toluene,w}/RfD_{Toluene}}$$

$C_{i,w}$ and $C_{Toluene,w}$ are the steady-state concentrations of the chemical and the benchmark compound (Toluene) in the water compartment after release of 1000 kg/hr of each into the water compartment, as predicted by the multimedia compartment model. The factor of 2 L/d and 70 kg are the standard ingestion rate and body weight used for risk assessment.

The toxicity potential for inhalation exposure is defined as equation 2 in Table 11.4-1, where $C_{I,a}$ and $C_{Toluene,a}$ are the concentrations of chemical "i" and of the benchmark compound (Toluene) in the air compartment

of the environment after release of 1000 kg/hr of each into the air compartment, as predicted by the multimedia compartment model.

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

$$I_{ING} = \sum_i INGTP_i \cdot m_i$$

Similarly for inhalation route toxicity;

$$I_{INH} = \sum_i INHTP_i \cdot m_i$$

where m_i is the mass emission rate of chemical "i" from the entire process (kg/hr). This step will provide the equivalent process emissions of toxic chemicals in the form of the benchmark compound, Toluene.

<u>Carcinogenic Toxicity:</u> The ingestion route carcinogenic potential for a chemical is equation 3 in Table 11.4-1, where SF $(mg/kg/d)^{-1}$, 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 in humans. The higher the value of SF, the higher is the carcinogenic potency of a chemical. Lists of SF values for many chemicals can be found in the following references (U.S. EPA, 1997; U.S. EPA, 1994). Because SFs are not yet available for all chemicals of interest, weight of evidence (WOE) classifications have been tabulated for many industrial chemicals by consideration of evidence by a panel of experts. The definitions of each weight of evidence classification is shown in Table 11.28. 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 equation 4 in Table 11.4-1.

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

$$I_{CING} = \sum_i INGCP_i \cdot m_i$$

and for inhalation,

$$I_{CINH} = \sum_i INHCP_i \cdot m_i$$

<u>Fish Toxicity:</u> The fish toxicity index, is one important indicator for ecotoxicity. It is defined as equation 5 in Table 11.4-1. PCP was chosen to be the benchmark compound since it is a well-studied toxic chemical for fish. *LC_{50}* (mg/L) is the concentration of a substance in water that causes death to 50 percent of the fish population if continuously exposed to a fixed concentration of a chemical for a short period of time (48-96 hr).

The fish toxicity index for the entire process is again a summation for each chemical.

$$I_{FT} = \sum_i FTP_i \cdot m_i$$

<u>Global Warming</u>: A common index for global warming is the global warming potential (GWP), which is the time integrated climate forcing from the release of 1 kg of a greenhouse gas relative to that from 1 kg of carbon dioxide (IPCC, 1991):

$$GWP_i = \frac{\int_0^n a_i C_i \, dt}{\int_0^{120\ yr} a_{CO_2} C_{CO_2} \, dt}$$

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

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

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

<u>Ozone Depletion</u>: The ozone depletion potential (ODP) of a chemical is the predicted time- and height-integrated change (δ) 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) (Fisher et al., 1990b).

$$ODP_i = \frac{\delta[O_3]_i}{\delta[O_3]_{CFC\text{-}11}}$$

Model calculations for ODP have been carried out using one- and two-dimensional photochemical models.

The process equivalent emission of CFC-11 is then;

$$I_{OD} = \sum_i (ODP_i \cdot m_i)$$

<u>Acid Rain</u>; 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 relationship;

$$X + \cdots \rightarrow \alpha H^+ + \cdots$$

where X is the emitted chemical substance which initiates acidification and α (moles H^+/mole X) is a molar stoichiometric coefficient. Acidification is normally expressed on a mass basis and therefore the H^+ created per mass of substance emitted (η_i, moles H^+/kg "i") is;

$$\eta_i = \frac{\alpha_i}{MW_i}$$

where MW_i is the molecular weight of the emitted substance (moles "i"/kg "i"). As before, we can introduce a benchmark compound (SO_2) and express the acid rain potential (ARP_i) of any emitted acid forming chemical relative to it (Heijungs, 1992).

$$ARP_i = \frac{\eta_i}{\eta_{SO_2}}$$

The process equivalent emission of SO_2 is;

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

<u>Smog Formation</u>; A scientifically-based smog formation assessment tool will aid in identifying pollution prevention opportunities for reducing smog formation. The only important process for ozone formation in the lower atmosphere is photodissociation of NO_2,

$$NO_2 + hv \text{ ------> } O(^3P) + NO$$
$$O(^3P) + O_2 + M \text{ ------> } O_3 + M$$
$$O_3 + NO \text{ ------> } NO_2 + O_2$$

where M is nitrogen or molecular oxygen. This cycle results in O_3 concentration being in a photostationary state dictated by the NO_2 photolysis rate and ratio of $[NO_2]/[NO]$. The role of VOCs is to form radicals which can convert NO to NO_2 without causing O_3 destruction, thereby increasing the ratio $[NO_2]/[NO]$, and increasing O_3.

$$VOC + \cdot OH \text{ ------> } RO_2 + \text{products}$$
$$RO_2 + NO \text{ ------> } NO_2 + \text{radicals}$$
$$\text{radicals} \text{ ------> } \cdot OH + \text{products}$$

The tendency of individual VOCs to influence O_3 levels depends upon its hydroxyl radical ($^{\bullet}OH$) rate constant and elements of its reaction mechanism, including radical initiation, radical termination, and reactions which remove NOx. Incremental reactivity (IR) has been proposed as a method for evaluating smog formation potential for individual organic compounds. It is defined as the change in moles of ozone formed as a result of emission into an air shed of one mole (on a carbon atom basis) of the VOC (Carter and Atkinson, 1989).

The smog formation potential (SFP) is based on the maximum incremental reactivity scale of Carter (Carter, 1994) .

$$SFP_i = \frac{MIR_i}{MIR_{ROG}}$$

where MIR_{ROG} is the average value for background "reactive organic gases", the benchmark compound for this index.

The process equivalent emission of the base ROG mixture is;

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

Table 11.24 Global Warming Potentials for Greenhouse Gases (CO_2 is the benchmark)

Chemical	Formula	τ (yrs)	BI (atm^{-1} cm^{-2})	GWP[a]
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 absorbance band intensity (Pouchert, 1989; U.S.EPA, 1997b)

Table 11.25 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	$3.1x10^{-10}$	4	1.08
1,1,1-trichloroethane	CH_3CCl_3	6.1	$3.2x10^{-10}$	3	.12
CFC (hard)					1.0
CFC (soft)					.055
CFC-11	CCl_3F	60.0	$2.3x10^{-10}$	3	1.0
CFC-12	CCl_2F_2	120.0	$1.5x10^{-10}$	2	1.0
CFC-13	$CClF_3$				1.0
CFC-113	CCl_2FCClF_2	90.0	$2.0x10^{-10}$	3	1.07
CFC-114	$CClF_2CClF_2$	200.0	$1.6x10^{-10}$	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	$1.0x10^{-10}$	1	.055
HCFC-123	$C_2F_3HCl_2$	1.7	$2.5x10^{-10}$	2	0.02
HCFC-124	C_2F_4HCl	6.9	$1.0x10^{-10}$	1	.022
HCFC-141b	$C_2FH_3Cl_2$	10.8	$1.5x10^{-10}$	2	0.11
HCFC-142b	$C_2F_2H_3Cl$	19.1	$1.4x10^{-10}$	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.

Table 11.26. Acid Rain Potential for a Number of Acidifying Chemicals

Compound	Reaction ARP_I	α	MW_I (mol/kg)	η_i, (mol H^+/ kg "i")	
SO_2	$SO_2 + H_2O + O_3 \rightarrow 2H^+ + SO_4^{2-} + O_2$	2	.064	31.25	1.00
NO	$SO + O_3 + 1/2\ H_2O \rightarrow H^+ + NO_3^- + 3/4\ O_2$	1	.030	33.33	1.07
NO2	$NO_2 + 1/2\ H_2O + 1/4\ O_2 \rightarrow H^+ + NO_3^-$	1	.046	21.74	0.70
NH3	$NH_3 + 2\ O_2 \rightarrow H^+ + NO_3^- + H_2O$	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)

Table 11.27 Maximum Incremental Reactivities (MIR) for Smog (O_3) Formation

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-dimethylpentane	0.82
	n-pentane	1.04	2,3-dimethylpentane	1.07
	n-hexane	0.98	2-methylpentane	1.50
	n-heptane	0.81	3-methylpentane	1.50
	n-hexane	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-metnylhexane	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	1.66
	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-trumethylhexane	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-diethylhfeptane	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	trnas-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-octaene	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			
	13-butadiene	10.90		
	isoprene	9.10	**Alcohols and Ethers**	
	cyclopentene	7.70	methanol	0.56
	cyuclohexene	5.70	ethanol	1.34
	a-pinene	3.30	n-propyl alcohol	2.30
	b-pinene	4.40	isopropyl alcohol	0.54
	Average	**6.85**	n-butyl alcohol	2.70
			isobutyl alcohol	1.90
			t-butyl alcohol	0.42
Acetylenes			dimethyl ether	0.77
	acetylene	0.50	methyl t-butyl ether	0.62
	methylacetylene	4.10	ethyl t-butyl ether	2.00
	Average	**2.30**	**Average**	**1.32**
Aromatics				
	benzene	0.42	**Aromatic Oxygenates**	
	toluene	2.70	benzaldehyde	-0.57
	ethylbenzene	2.70	phenol	1.12
	n-propylbenzene	2.10	alkyl phenols	2.30
	isopropylbenzene	2.20	**Average**	**0.95**
	s-butylbenzene	1.90		
	o-xylene	6.50		
	p-xylene	6.60	**Aldehydes**	
	m-xylene	8.20	formaldehyde	7.20
	1,3,5-trimethylbenzene	10.10	acetaldehyde	5.50
	1,2,3-trimethylbenzene	8.90	C3 aldehydes	6.50
	1,2,4-trimethylbenzene	8.80	glyoxal	2.20
	tetralin	0.94	methyl glyoxal	14.80
	naphthalene	1.17	**Average**	**7.24**
	methylnaphthalenes	3.30		
	2,3-dimethylnaphthalene	5.10		
	styrene	2.20		
	Average	**4.34**	**Ketones**	
			acetone	0.56
			C4 ketones	1.18
Others			**Average**	**0.87**
	Methyl nitrite	9.50		
Base ROG Mixture				**3.10**

Adapted from Carter (1994)

Table 11.28 Weight of Evidence (WOE) Classifications (US EPA, 1997; Davis, 1994)

Group	Definition
A	Human Carcinogen. This classification is used only when is sufficient evidence from epidemiologic studies to support a causal association between exposure to the agent and cancer.
B	Probable Human Carcinogen. This group is divided into two subgroup, 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.
C	Possible Human Carcinogen. This classification is used when there is limited evidence of carcinogenicity in animals in the absence of human data.
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.
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.

Example Problem 11.4-3 *Solvent Recovery from a Gaseous Waste Stream: Effect of Process Operation on Indexes for Inhalation and Ingestion Toxicity, Global Warming, Smog Formation, and Acidification.*

A gaseous waste stream is generated within a plastics 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. Figure 11.E-1 is a process flow diagram of an absorption technology configuration to recovery and recycle the VOCs back to the film process. 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. In this problem, we will not deal with the economic issues, but rather will show that when considering environmental impacts, there are "trade offs" for several impacts depending upon the percent recovery of the VOCs.

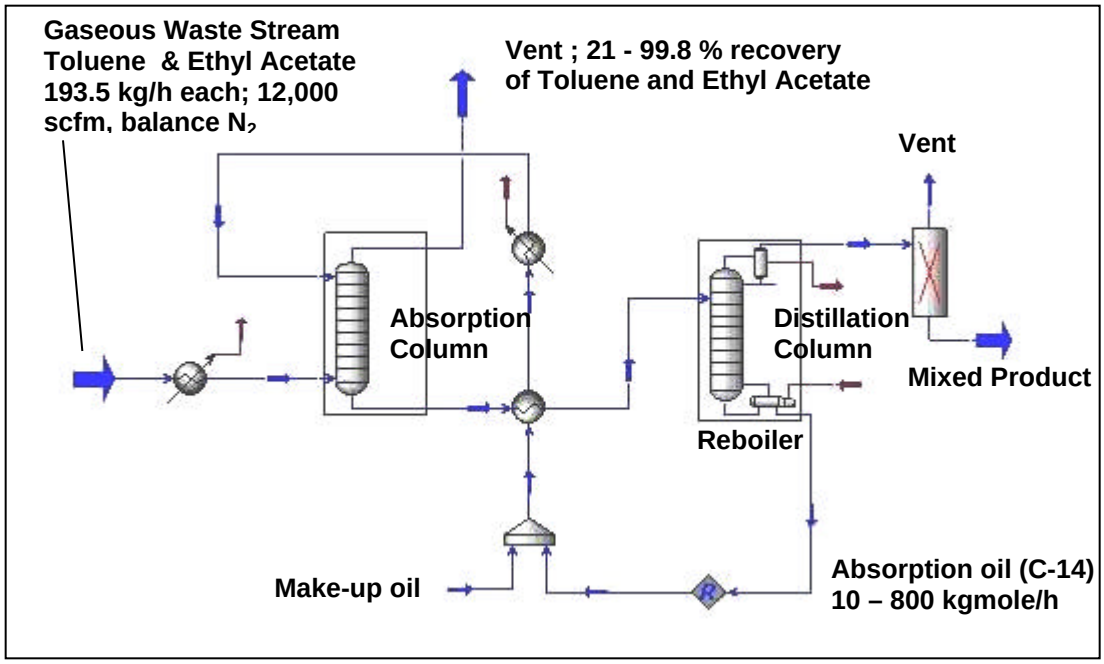


Figure 11.E-1 Schematic diagram of a solvent recovery and recycle process using absorption into heavy oil (n-tetradecane) followed by distillation.

The gaseous waste stream enters the absorption column where the VOCs (toluene and ethyl acetate) transfer from the gas phase to the liquid phase (absorption oil, n-tetradecane (n-C14)). The effectiveness of this transfer depends upon the oil flow rate, as the percent recovery of VOCs is expected to increase with increasing oil flow rate. The VOCs are separated from the absorption oil in the distillation column and the oil is then recycled back to the absorption column. 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. The main emission sources are the absorption column, the vent on the distillation column, the vent on the storage tank (not show), and fugitive sources.

Solution

Emissions: Table 11.E-3 shows the effect of absorber oil flow rate on the emissions from the solvent recovery process. A process simulator (HYSYS) was used to generate mass and energy balances and to calculate the VOC emission rates from the absorber unit. EPA emission factors were used to calculate the CO_2, CO, TOC, NOx, and SOx emission rates based on the energy requirements of the process and an assumed fuel type (fuel oil no. 4). 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 kgmoles/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. Figure 11.E.2 shows the recovery of toluene and ethyl acetate as a function of absorption oil flow rate in the process. Emissions of the utility related pollutants (CO_2, CO, TOC, NOx, and SOx) increase in proportion to the oil flow rate. The emissions of the absorption oil (n-C14) remains relatively constant with oil flow rate.

Table 11.E-3 Air emission rates of chemicals from the solvent recovery process of Figure 11.E-1

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	52	0.013	0.001	0.05	0.41	4.28
20	53.11	178.37	103	0.027	0.001	0.11	0.81	4.83
50	0.97	160.4	253	0.066	0.003	0.26	1.99	4.67
100	0.02	128.07	499	0.129	0.007	0.52	3.39	4.23
200	0.02	59.95	991	0.257	0.013	1.03	7.82	4.13
300	0.02	12.87	1,482	0.385	0.019	1.54	11.69	4.06
400	0.03	1.70	1,973	0.512	0.026	2.05	15.56	4.05
500	0.03	0.27	2,463	0.639	0.032	2.56	19.42	4.04

Adapted from Hiew (1998)

Atmospheric Indexes: Relative risk indexes for global warming (I_{GW}), smog formation (I_{SF}), and acidification (I_{AR}) have been calculated for the solvent recovery process at each flow rate using the emission rates in Table 11.E-3 and the impact potential values for each chemical (Tables 11.24, 11.26, and 11.27). For the smog formation potential (MIR) of ethyl acetate, the average MIR of the ethers (1.32) and

ketones (0.87) listed in Table 11.27 were used as an approximation (1.10). As an example calculation, the smog formation index of the process will be determined at an absorption oil flow rate of 50 kgmole/hr. The equation for smog formation index is

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

		$SFP_i \cdot m_i$
Toluene:	(0.87)(0.97 kg/hr)	0.84
Ethyl Acetate:	(0.32)(160.4 kg/hr)	51.33
Tetradecane:	(0.1)(4.67 kg/hr)	0.47
Total:		**52.64**

Shown in Figures 11.E.3 - 11.E.5 are the relative risk indexes for the solvent recovery process of Figure 11.E.1. We observe in Figure 11.E.3 that the global warming index is minimized by operating the process at approximately 50 kgmole/hr. An explanation for this behavior follows. At an oil flow rate of 0 kgmole/hr, all of the VOCs are emitted directly to the air, resulting in an elevated global warming impact after the organics are oxidized to CO_2. Nearly a 40% reduction in the global warming index is realized by operating the process at an absorption oil flow rate of 50 kgmole/hr. Apparently, the benefit of reducing the emissions of toluene and ethyl acetate are only slightly offset by the emission of greenhouse gases from process utilities. However, above 50 kgmole/hr, the process utilities increase at a substantial rate compared to the rate of additional recovery of the VOCs, driving the index higher. Therefore, the optimum flow rate is approximately 50 kgmole/hr for global warming.

As shown in Figure 11.E.4, the acid rain index for the process increases in nearly direct proportion to the absorption oil flow rate. This behavior occurs because the only acidifying species emitted from the process are from the process utility requirements, which increase in proportion to the absorption oil flow rate. The optimum flow rate for acidification would be at 0 kgmole/hr for the absorption flow rate.

The smog formation index (Figure 11.5) shows a very large decrease in the index with absorption oil flow rate up to 50 kgmole/hr (recovery of toluene) and a gradual decrease from 50 to 500 kgmole/hr (recovery of ethyl acetate). The optimum flow rate for minimizing the smog formation index is therefore 500 kgmole/hr.

Human Health Indexes: The calculations were conducted using a standard emission of 1000 kg/hr of each compound into the air compartment when evaluating both ingestion and inhalation toxicities. This approach was adopted rather than using the actual emission rates of each compound, because only the ratios of concentrations are needed in the index calculation, and the concentration ratios are not a function of emission rate using the Mackay model.

Chemical	Molecular Weight	Melting point	Fugacity	Vapor pressure	Solubility	Log K_{OW}
		(°C)	ratio	@25°C (Pa)	(g/m^3)	
Toluene	92.13	-95.0	1.0	3800	550	2.70
Ethyl Acetate	88.11	-82.0	1.0	12000	80800	0.70
Hexane	86.17	-95.3	1.0	20000	10	4.00

Chemical	Half life (hr)				Concentration (g/m^3)	
	Air	Water	Soil	Sediment	Air	Water
Toluene	17	550	1700	5500	1.97E-07	4.00E-07
Ethyl Acetate	55	55	170	550	4.36E-07	5.00E-06
Hexane	17	550	1700	5500	1.97E-07	1.50E-09

The toxicological properties (RfDs, RfCs) are incomplete for the three chemicals in this design. We are forces to use LD_{50} and LC_{50} data when gaps occur. The table below summarizes the toxicology data and calculated ingestion and inhalation toxicity potentials using the air and water concentrations in the table above and the toxicity equations listed above.

	Inhalation RfC	Oral RfD	LC_{50}	LD_{50}	Toxicity Potentials	
	(mg/cu.m)	(mg/kg/day)	(ppm)	(mg/kg)	INHTP	INGTP
Toluene	0.4	0.2	4000	5000	1.0E+00	1.0E+00
Ethyl Acetate	-	0.9	3200		2.8E+00	2.8E+00
Hexane	0.2	-	-	28700	2.0E+00	6.5E-04

Figures 11.E.6 and 11.E.7 show the change in process inhalation and ingestion toxicity index with absorption oil flow rate using the tabulated emission rate data and concentrations calculated by the Mackay model.

Discussion: These indexes demonstrate the complexities in evaluating chemical process using multiple indexes of environmental performance. It is difficult to identify a single absorption oil flow rate that simultaneously minimizes all five indexes. However, we can see that significant reductions in the global warming (42%), smog formation (82%), inhalation toxicity (39%), and ingestion toxicity (39%) indexes are realized at an oil flow rate of 50 kgmole/hr, with only a modest increase in the acid rain index. This observation suggests that a decision to operate

the process at 50 kgmole/hr might be a good compromise. In reality, the decision to operate the process at any given flow rate will only be made after economic and safety considerations have been taken into account.

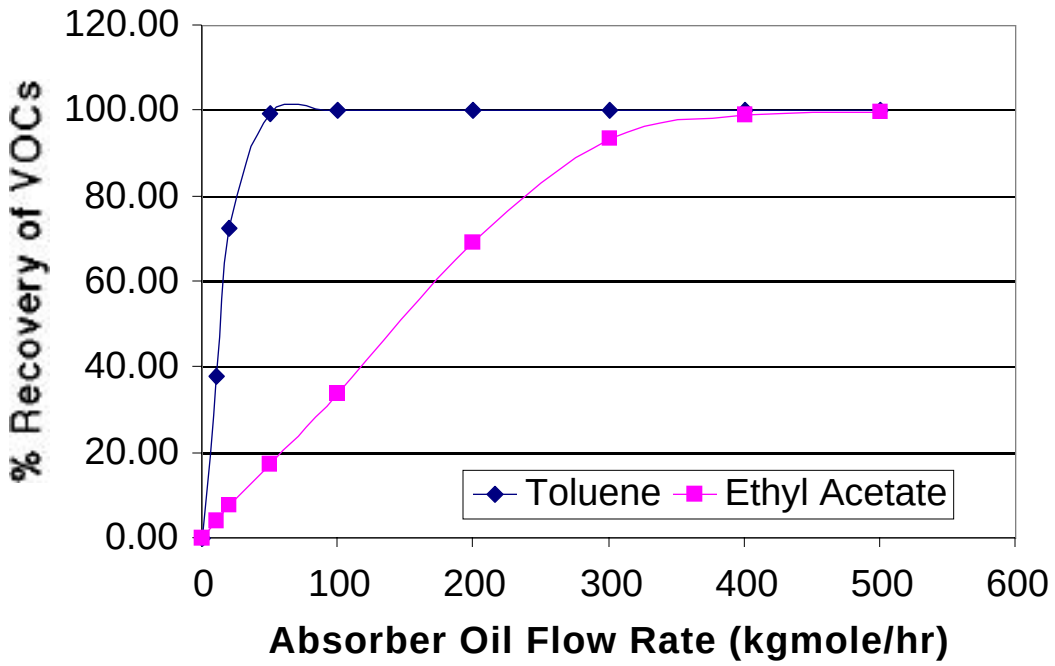


Figure 11.E.2 VOC recovery efficiency for the solvent recovery process of Figure 11.E.1.

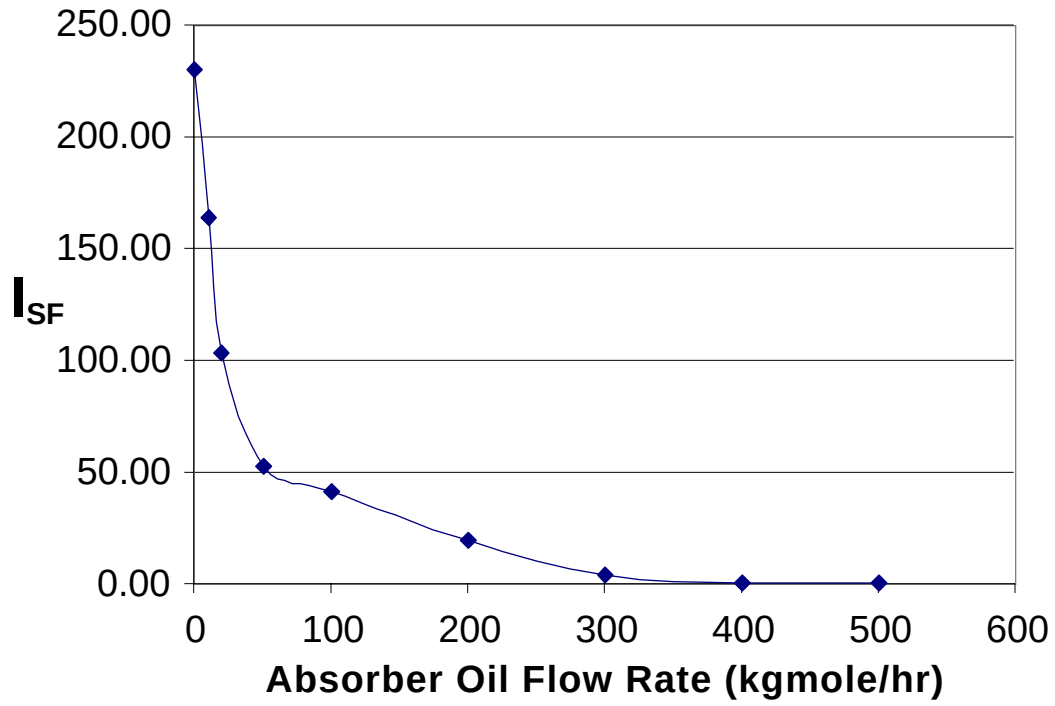


Figure 11.E.3 The global warming index (kg/hr) for the solvent recovery process of Figure 11.E.1.

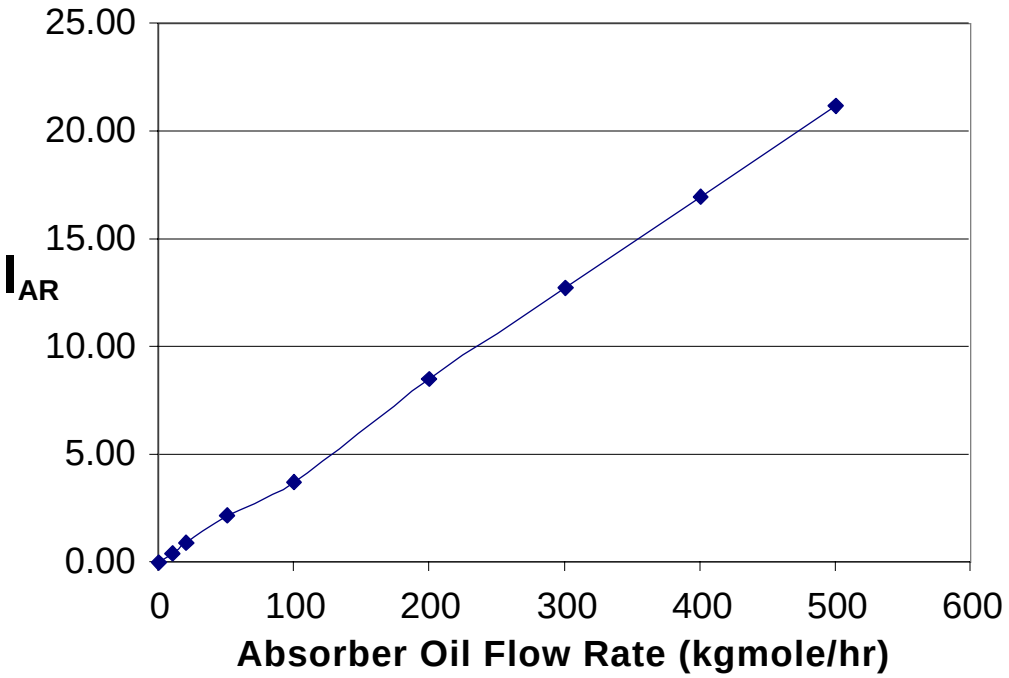


Figure 11.E.4 The acid rain index (kg/hr) for the solvent recovery process of Figure 11.E.1.

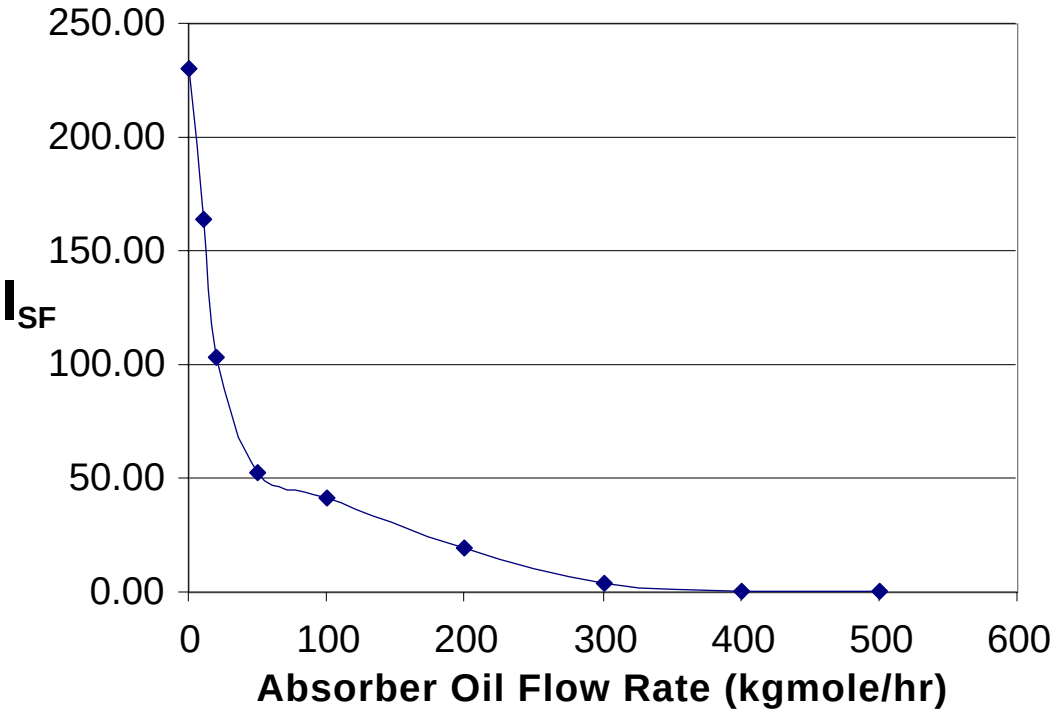


Figure 11.E.5 The smog formation index (kg/hr) for the solvent recovery process of Figure 11.E.1

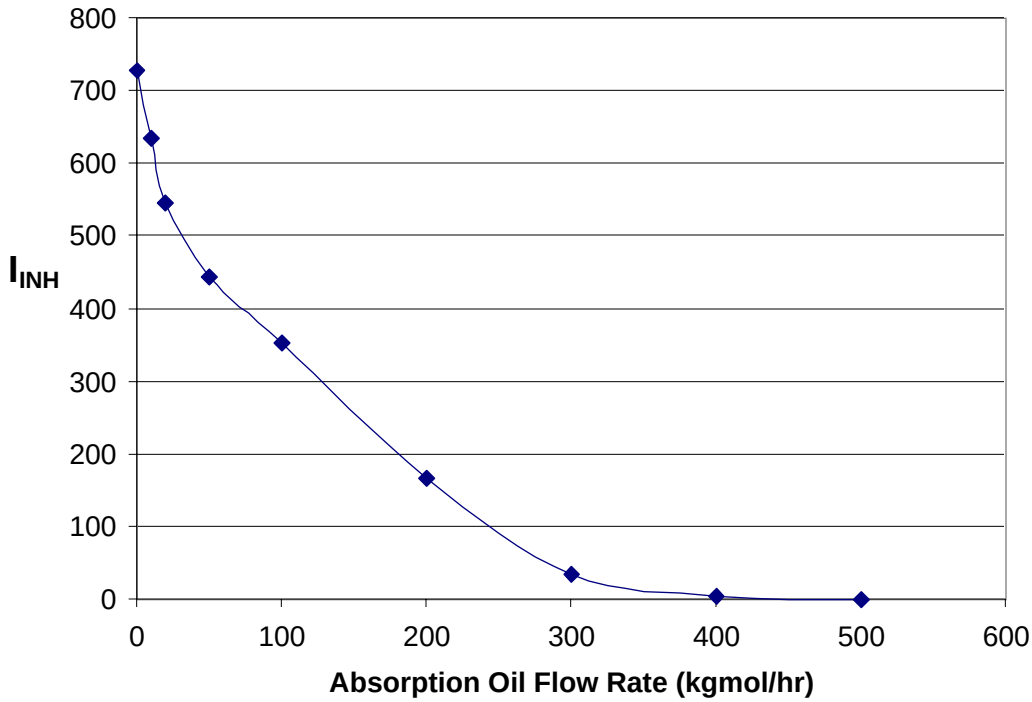


Figure 11.E.6 Inhalation toxicity index (kg/hr) for the Solvent Recovery and Recycle Process

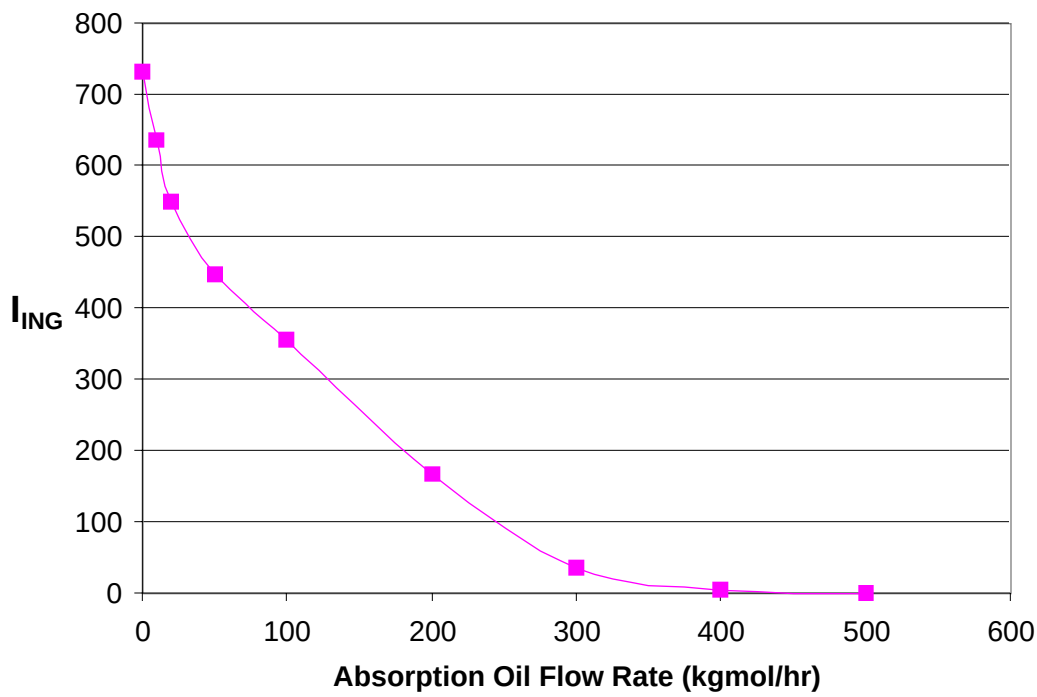


Figure 11.E.7 Inhalation toxicity index (kg/hr) for the Solvent Recovery and Recycle Process

Nomenclature

C	phase concentration (mole/m^3) = fZ
C_2	concentration of chemical in water (moles/L water)
C_3	concentration of chemical on soil solids (moles/m^3 solids)
C_s	concentration sorbed to solids (moles/kg soil solids or sediment solids)
D_{ij}	intermedia transport parameter for diffusion from compartment i to j (mole/(Pa•hr))
E_i	emission rate into compartment "i" (moles/h)
f	fugacity (Pa)
f_i	fugacity in compartment "i"
G	volumetric flow rate of transported material (rainwater, suspended sediment, etc.) (m^3/h)
G_{Ai}	the advective flow rate into compartment "i" (m^3/h)
H	Henry's constant for the chemical (Pa• m^3/mole)
K_d	equilibrium distribution coefficient (L solution /kg solids) = K_{oc_3}
K_{oc}	organic carbon-based distribution coefficient (L/kg) = = 0.41 K_{ow}
K_{ow}	octanol-water partition coefficient (dimensionless)
k_{Ri}	first order reaction rate constant for a chemical in compartment "i" (hr^{-1})
n	moles of the chemical
P	partial pressure of the chemical in air (Pa)
P^s	saturation vapor pressure of pure liquid chemical the system temperature (Pa)
P_T	total pressure (Pa)
R	ideal gas constant (8.31 Pa• m^3/[mole•K]),
T	absolute temperature (K)
V	volume containing the chemical (m^3)
υ_w	molar volume of water (1.8x10^{-5} m^3/mole)
x	mole fraction of chemical in water
Z	fugacity capacity (Pa•m^3/mole)
Z_1	air phase fugacity capacity for each chemical = $1/RT$ = 4.04x10^{-4} moles/(m^3•Pa) at 25˚C
Z_2	water phase fugacity capacity for each chemical
Z_{Ci}	compartment "i" fugacity capacity (Pa•m^3/mole)
y	mole fraction of the chemical in the air phase

Greek

φ	fugacity coefficient (dimensionless) = 1 for air phase
φ_3	mass fraction of organic carbon in the soil phase (g organic carbon/g soil solids)
γ	activity coefficient of chemical in water
ρ_3	solid phase density (kg solid/ m^3 solid)

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