Detailed Environmental Assessment of Chemical Process Flowsheets - Chapter 11

David R. Shonnard
Department of Chemical Engineering
Michigan Technological University

Outline

1. Educational goals and topics covered in the module
2. Review of risk assessment concepts
3. Introduction to environmental multimedia models
4. Tier III environmental impact assessment for chemical process flowsheets
Educational goals and topics covered in the module

Students will:
1. learn to apply a systematic risk assessment methodology to the evaluation of chemical process designs

1. integrate emission estimation, environmental fate and transport calculation, and relative risk assessment to rank process design alternatives

Review of the hierarchical design process for pollution prevention

<table>
<thead>
<tr>
<th>Design Stage</th>
<th>P2 Tools</th>
<th>Environmental Evaluation</th>
<th>Book Chapter</th>
</tr>
</thead>
</table>
| 1. Earliest Design Stage | • Green Chemistry  
• atom efficiency                                                   | Tier 1 (persistence, bioaccumulation, toxicity)                                           | 7, 8         |
| 2. Preliminary Design Stage | Release estimation, optimum choice of  
• mass separating agents  
• process units  
• processing conditions                                          | Tier 2 (material usage, energy consumption, emission of targeted pollutants)           | 8, 9         |
| 3. Detailed Design Stage       | • Process integration methods  
• multimedia environmental fate modeling  
• relative risk assessment                         | Tier 3 (environmental fate and transport, relative risk assessment)               | 10, 11       |
Essential features of environmental impact assessment for process design

Computationally efficient
- Environmental performance indices to be quickly calculated using output from commercial process simulators
- Multiple environmental impacts considered

Link waste generation and release to environmental impacts
- Environmental indices linked to process parameters

Impacts based on a systematic risk assessment methodology
- Release estimates → fate and transport → exposure → risk

Systematic risk assessment methodology

National Academy of Sciences, 1983

1. Hazard Identification (which chemicals are important?)
2. Exposure assessment (release estimation, fate and transport, dose assessment)
3. Toxicity assessment (chemical dose - response relationships)
4. Risk Characterization (magnitude and uncertainty of risk)

Result: Quantitative risk assessment (e.g. excess cancers)

Atmospheric dispersion Model, $C_2 (mg/m^3)$

Thibodeaux, L.J. 1996, Environmental Chemodynamics, John Wiley & Sons
Quantitative risk calculation

Carcinogenic Risk Example (inhalation route)

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

- **CR** - contact rate (m³ 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 10⁶ 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

Carcinogenic Risk Example (inhalation route)

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

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

**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
Tier 3 Relative risk index formulation for one environmental impact category

**Chemical Specific**

\[
I_i = \frac{[(EP)(IIP)]_i}{[(EP)(IIP)]_B}
\]

**Process**

\[
I = \sum_{i=1}^{N} (I_i') \times (m_i)
\]

Airborne emissions estimation – chapter 8

- Unit Specific EPA Emission Factors
  - Distillation/stripping column vents
  - Reactor vents
  - Fugitive sources

- Correlation (AP-42, EPA)
  - Storage tanks, wastewater treatment
  - Fugitive sources (pumps, valves, fittings)

- Criteria Pollutants from Utility Consumption
  - Factors for CO₂, CO, SO₂, NOx
  - AP-42 (EPA) factors

- Process Simulators (e.g. HYSYS®)
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, $D_{ij}$
- reaction loss, $D_R$

Multimedia compartment model formulation - Chapter 11.2


Multimedia compartment model – fugacity

Fugacity - a thermodynamic property of a chemical and represents the “escaping tendency” of the chemical from an environmental phase (air, water, or solid) and has units of pressure (Pa).

At equilibrium, the fugacity of a chemical in one phase is equal to the fugacity of the chemical (i) in the adjoining phase for example:

$$f_i \text{ (air)} = f_i \text{ (water)}$$

Also, the fugacity is related to the molar concentration using the fugacity capacity, $Z$

$$C_i \text{ (air)} = f_i \cdot Z(\text{air})$$
Fugacity capacity of the air

Fugacity of a chemical in air

\[ f = y \phi P_T = P \]

- \( y \) = mole fraction of the chemical in air
- \( \phi \) = fugacity coefficient - accounts for non-ideal behavior (≈ 1)
- \( P_T \) = total pressure in the air (Pa)
- \( P \) = partial pressure of the chemical in air (Pa)

Ideal Gas Law

\[ C_i = n_i/V = P_i/(RT) = f_i/(RT) = f_i Z_i \]

\[ Z_i = 1/(RT) \]

Table 11.2-1 Fugacity Capacities (Z) Values for the Various Phases and Compartments

<table>
<thead>
<tr>
<th>Environmental Phases</th>
<th>Phase Densities (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Phase</td>
<td>( Z_1 = 1/(RT) ) 1.2</td>
</tr>
<tr>
<td>Water Phase</td>
<td>( Z_2 = 1/H ) 1,000</td>
</tr>
<tr>
<td>Soil Phase</td>
<td>( Z_3 = [1/H] K_{oc} \phi \rho_i/1000 ) 2,400</td>
</tr>
<tr>
<td>Sediment Phase</td>
<td>( Z_4 = [1/H] K_{oc} \phi \rho_i/1000 ) 2,400</td>
</tr>
<tr>
<td>Suspended Sediment Phase</td>
<td>( Z_5 = [1/H] K_{oc} \phi \rho_i/1000 ) 2,400</td>
</tr>
<tr>
<td>Fish Phase</td>
<td>( Z_6 = [1/H] 0.048 \rho_i K_{oc} ) 1,000</td>
</tr>
<tr>
<td>Aerosol Phase</td>
<td>( Z_7 = 6 \times 10^6/PS )</td>
</tr>
</tbody>
</table>

where

- \( R \) = gas constant (8.314 Pa·m³/(mol·K))
- \( T \) = absolute temperature (K)
- \( H \) = Henry's constant (Pa·m³/mole)
- \( K_{oc} \) = organic-carbon partition coefficient
- \( K_{ow} \) = octanol-water partition coefficient
- \( \rho_i \) = phase density for phase \( i \) (kg/m³)
- \( \phi \) = fraction of organic carbon in phase \( i \) (g/g)

Environmental Compartments

- Air Compartment (1) \( Z_{c1} = Z_1 + 2 \times 10^{-11} Z_7 \)
- Water Compartment (2) \( Z_{c2} = Z_2 + 5 \times 10^6 Z_1 + 10^6 Z_4 \)
- Soil Compartment (3) \( Z_{c3} = 0.2 Z_1 + 0.3 Z_2 + 0.5 Z_3 \)
- Sediment Compartment (4) \( Z_{c4} = 0.8 Z_2 + 0.2 Z_4 \)
Intermedia transport

**Diffusion**

\[ N_{ij} = D_{ij} \left( f_i \right) \text{ (moles/h)} \]

- \( D_{ij} \) = diffusion transport parameter from compartment \( i \) to \( j \) (moles/(Pa•hr))
- \( f_i \) = fugacity of a chemical in environmental compartment \( i \) (Pa)

**Convection**

\[ N = GZf \text{ (moles/h)} \]

- \( G \) = volumetric flow rate of material (rainwater, suspended sediment,)
- \( f \) = fugacity of a chemical in the transported phase \( i \) (Pa)

---

**Table 11.2-3.** \( D \) Values in the Mackay Level III model (Adapted from Mackay and Paterson, 1991)

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Process</th>
<th>Individual ( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>air (1) - water (2)</td>
<td>diffusion</td>
<td>( D_{12} = 1/(1/(u_{11} A_W Z_1) + 1/(u_{22} A_W Z_2)) )</td>
</tr>
<tr>
<td></td>
<td>rain wash out</td>
<td>( D_{12} = u_{22} A_W Z_2 )</td>
</tr>
<tr>
<td></td>
<td>wet/dry deposition</td>
<td>( D_{12} = u_{22} A_W Z_2 )</td>
</tr>
<tr>
<td>air (1) - soil (3)</td>
<td>diffusion</td>
<td>( D_{13} = 1/(1/(u_{11} A_S Z_1) + 1/(u_{33} A_S Z_3)) )</td>
</tr>
<tr>
<td></td>
<td>rain wash out</td>
<td>( D_{13} = u_{33} A_S Z_3 )</td>
</tr>
<tr>
<td></td>
<td>wet/dry deposition</td>
<td>( D_{13} = u_{33} A_S Z_3 )</td>
</tr>
<tr>
<td>water (2) - sediment (4)</td>
<td>diffusion</td>
<td>( u_{44} A_S Z_4 )</td>
</tr>
<tr>
<td></td>
<td>deposition</td>
<td>( u_{44} A_S Z_4 )</td>
</tr>
<tr>
<td>sediment (4) - water (2)</td>
<td>diffusion</td>
<td>( u_{44} A_S Z_4 )</td>
</tr>
<tr>
<td></td>
<td>resuspension</td>
<td>( u_{44} A_S Z_4 )</td>
</tr>
<tr>
<td>soil (3) - water (2)</td>
<td>water runo ff</td>
<td>( u_{32} A_W Z_2 )</td>
</tr>
<tr>
<td></td>
<td>soil runo ff</td>
<td>( u_{32} A_Z Z_2 )</td>
</tr>
<tr>
<td>advection (bulk flow)</td>
<td>emissions and bulk flow in</td>
<td>( I_i = E_i + G_a C_i )</td>
</tr>
<tr>
<td></td>
<td>bulk flow out</td>
<td>( D_{32} = G_a Z_c )</td>
</tr>
<tr>
<td>reaction</td>
<td></td>
<td>( D_{32} = k_{32} V Z_c )</td>
</tr>
</tbody>
</table>
Table 11.2-4. Mole Balance Equations for the Mackay Level III Fugacity Model

<table>
<thead>
<tr>
<th>Component</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>[ I_1 + f_2D_2 + f_3D_3 = f_1D_1 ]</td>
</tr>
<tr>
<td>Water</td>
<td>[ I_2 + f_1D_1 + f_3D_3 + f_4D_4 = f_2D_2 ]</td>
</tr>
<tr>
<td>Soil</td>
<td>[ I_3 + f_1D_1 = f_3D_3 ]</td>
</tr>
<tr>
<td>Sediment</td>
<td>[ I_4 + f_2D_2 = f_4D_4 ]</td>
</tr>
</tbody>
</table>

where the left hand side is the sum of all gains and the right hand side is the sum of all losses, \( I_i = E_i + G_aiC_i \), usually being zero. The \( D \) values on the right hand side are:

\[
\begin{align*}
D_{T1} &= D_{13} + D_{41} + D_{12} + D_{11} \\
D_{T2} &= D_{23} + D_{22} + D_{32} + D_{42} \\
D_{T3} &= D_{33} + D_{32} + D_{31} + D_{34} \\
D_{T4} &= D_{43} + D_{42} + D_{41} + D_{44}
\end{align*}
\]

The solution for the unknown fugacities in each compartment is:

\[
\begin{align*}
f_2 &= \frac{(I_2 + J_1J_4 + I_3D_32 + I_4D_42)}{(DT_2 - J_2J_4 + D_{24}D_{42})} \\
f_1 &= \frac{(J_1 + f_2J_2)}{J_3} \\
f_3 &= \frac{(I_3 + f_1D_13)}{DT_3} \\
f_4 &= \frac{(I_4 + f_2D_42)}{DT_4}
\end{align*}
\]

where

\[
\begin{align*}
J_1 &= I_1 / DT_1 + I_3 / (DT_3DT_1) \\
J_2 &= D_{21} / DT_1 \\
J_3 &= 1 - D_{31}D_{13} / (DT_1DT_3) \\
J_4 &= D_{41} + D_{13}D_{13} / DT_3
\end{align*}
\]

Multimedia prediction for benzene, ethanol, and pentachlorophenol
## Multimedia compartment model input data

<table>
<thead>
<tr>
<th>Environmental Property</th>
<th>Unit</th>
<th>Spreadsheet Location</th>
<th>Benzene</th>
<th>Ethanol</th>
<th>PCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>g/mole</td>
<td>C6</td>
<td>78.11</td>
<td>48.07</td>
<td>266.34</td>
</tr>
<tr>
<td>Melting Point</td>
<td>°C</td>
<td>C7</td>
<td>5.53</td>
<td>115</td>
<td>174</td>
</tr>
<tr>
<td>Dissociation Constant</td>
<td>log pKₐ</td>
<td>C8</td>
<td></td>
<td></td>
<td>4.74</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>g/m³</td>
<td>C11</td>
<td>1.78E+2</td>
<td>6.78E+5</td>
<td>14</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>Pa</td>
<td>C12</td>
<td>1.27E+4</td>
<td>7.80E+3</td>
<td>4.15E-3</td>
</tr>
<tr>
<td>Octanol-Water Coefficient</td>
<td>log Kₒw</td>
<td>C13</td>
<td>2.13</td>
<td>-0.31</td>
<td>5.05</td>
</tr>
<tr>
<td>Half-life in air</td>
<td>hr</td>
<td>C33</td>
<td>1.7E+1</td>
<td>5.5E+1</td>
<td>5.50E+2</td>
</tr>
<tr>
<td>Half-life in water</td>
<td>hr</td>
<td>C34</td>
<td>1.7E+2</td>
<td>5.5E+1</td>
<td>5.50E+2</td>
</tr>
<tr>
<td>Half-life in soil</td>
<td>hr</td>
<td>C35</td>
<td>5.5E+2</td>
<td>5.5E+1</td>
<td>1.7E+3</td>
</tr>
<tr>
<td>Half-life in sediment</td>
<td>hr</td>
<td>C36</td>
<td>1.7E+3</td>
<td>1.7E+2</td>
<td>5.50E+3</td>
</tr>
</tbody>
</table>

## Multimedia compartment model typical results

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(emission scenario)</td>
<td>Total mass (kg)</td>
</tr>
<tr>
<td>(a) 1000 kg/hr emitted into the air compartment</td>
<td>1.98x10⁴</td>
</tr>
<tr>
<td>(b) 1000 kg/hr emitted into the water compartment</td>
<td>1.41x10⁵</td>
</tr>
<tr>
<td>(c) 1000 kg/hr emitted into the soil compartment</td>
<td>6.86x10⁴</td>
</tr>
<tr>
<td>Ethanol (a)</td>
<td>4.56x10⁵</td>
</tr>
<tr>
<td>Ethanol (b)</td>
<td>7.35x10⁵</td>
</tr>
<tr>
<td>Ethanol (c)</td>
<td>7.84x10⁵</td>
</tr>
<tr>
<td>Pentachlorophenol (a)</td>
<td>2.07x10⁵</td>
</tr>
<tr>
<td>Pentachlorophenol (b)</td>
<td>4.59x10⁵</td>
</tr>
<tr>
<td>Pentachlorophenol (c)</td>
<td>2.39x10⁵</td>
</tr>
</tbody>
</table>

(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
   b) high $K_{OW}$ results in high soil concentrations
   c) high reactions half lives results in highest pollutant amounts

Tier 3 Relative risk index formulation for one environmental impact category - Ch 11.3

Chemical Specific

Exposure Potential

Dimensionless Risk Index ($I'_i$) = \[ \frac{(EP)(IIP)}{(EP)(IIP)_{B_i}} \]

Inherent Impact Parameter

Benchmark Compound Chemical “i”

Process

Process Index ($I$) = \[ \sum_{i=1}^{N} (I'_i) \times (m_i) \]

Emission Rate of Chemical, $i$
Nine Environmental Impact / Health Indexes

<table>
<thead>
<tr>
<th>Relative Risk Index</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td>$I^*_{GW_i} = GWP_i$</td>
</tr>
<tr>
<td></td>
<td>$I^*<em>{GW_i} = \frac{N_c \cdot MW</em>{CO_2}}{MW_i}$</td>
</tr>
<tr>
<td>Ozone Depletion</td>
<td>$I^*_{ODP} = ODP_i$</td>
</tr>
<tr>
<td>Smog Formation</td>
<td>$I^*<em>{SF} = \frac{MIR_i}{MIR</em>{ref}}$</td>
</tr>
<tr>
<td>Acid Rain</td>
<td>$I^*<em>{AR} = \frac{ARP_i}{ARP</em>{ref}}$</td>
</tr>
</tbody>
</table>

$GWP = \text{global warming potential}, N_c = \text{number of carbons atoms}, ODP = \text{ozone depletion potential}, MIR = \text{maximum incremental reactivity}, ARP = \text{acid rain potential}$.

---

Nine Environmental Impact / Health Indexes

<table>
<thead>
<tr>
<th>Relative Risk Index</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human Toxicity Ingestion</td>
<td>$I^*<em>{ING} = \frac{C</em>{W_i, LD_{50, Tol}}}{C_{p, Tol}} \cdot LD_{50}$</td>
</tr>
<tr>
<td>Human Toxicity Inhalation</td>
<td>$I^*<em>{INH} = \frac{C</em>{A_i, LC_{50, Tol}}}{C_{p, Tol}} \cdot LC_{50}$</td>
</tr>
<tr>
<td>Human Carcinogenicity</td>
<td>$I^*<em>{CING} = \frac{C</em>{W_i, HV}}{C_{W, Benzene, HV}}$</td>
</tr>
<tr>
<td>Human Carcinogenicity</td>
<td>$I^*<em>{CINH} = \frac{C</em>{A_i, HV}}{C_{A, Benzene, HV}}$</td>
</tr>
<tr>
<td>Fish Toxicity</td>
<td>$I^*<em>{FT} = \frac{C</em>{W_i, LC_{50, PCP}}}{C_{W, PCP}} \cdot LC_{50}$</td>
</tr>
</tbody>
</table>

$LD_{50} = \text{lethal dose 50% mortality}, LC_{50} = \text{lethal concentration 50% mortality},$ and $HV = \text{hazard value for carcinogenic health effects}$. 
Software Structure

- HYSYS OLE programming (Object Linking and Embedding)
- HYSYS is acting as an OLE server
- OLE controller application can access the HYSYS objects
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
- Dr. Heriberto Cabezas and Dr. Douglas Young
- US Environmental Protection Agency
  National Risk Management Research Laboratory
  26 W. Martin Luther King Dr.
  Cincinnati, OH 45268

Absorption - distillation process: analysis of an existing separation sequence

Gaseous Waste Stream
- Toluene & Ethyl Acetate
  193.5 kg/h each; 12,000 scfm, balance N₂

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

Make-up oil
- Absorption oil (C-14)
  10 – 800 kgmole/h

HYSYS® Flowsheet
Unit-specific emission summary

**Where are the centers for energy consumption and emissions?**

100 kgmole/hr Oil Flow Rate;
Oil Temperature = 82˚F; \( \Delta T = 180˚F \)

<table>
<thead>
<tr>
<th>UNIT OPERATION</th>
<th>Mass Flow (kg/hr)</th>
<th>Emission rate (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Column</td>
<td>19.345</td>
<td>0.002 1.0 0.002 1.0 0.002 1.0</td>
</tr>
<tr>
<td>Distillation Column</td>
<td>259.1</td>
<td>0.010 0.010 0.010</td>
</tr>
<tr>
<td>Fugitive Emissions</td>
<td>259.1</td>
<td>0.062 0.062</td>
</tr>
<tr>
<td>Storage Tank</td>
<td>259.1</td>
<td>0.0014 0.0014</td>
</tr>
<tr>
<td>Reboiler</td>
<td>6.18</td>
<td>1.03 0.52 499 0.129 0.007</td>
</tr>
</tbody>
</table>

Total Emissions (kg/hr) 0.088 128.07 4.23 3.93 0.52 499 0.129 0.007

Risk index summary

**Which chemicals have the highest impact indexes?**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( I^*_\text{GW} )</th>
<th>( I^*_\text{OD} )</th>
<th>( I^*_\text{PF} )</th>
<th>( I^*_\text{FA} )</th>
<th>( I^*_\text{HI} )</th>
<th>( I^*_\text{MIC} )</th>
<th>( I^*_\text{HI} )</th>
<th>( I^*_\text{MIC} )</th>
<th>( I^*_\text{PF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>3.14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>2</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>SOx</td>
<td>40</td>
<td>0</td>
<td>0.7</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>NOx</td>
<td>1</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO2</td>
<td>4</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>C-14</td>
<td>3.1</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>TOC</td>
<td>3.1</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Process environmental summary

100 kgmole/hr Oil Flow Rate;
Oil Temperature = 82˚F; ∆T=180˚F

<table>
<thead>
<tr>
<th>Process</th>
<th>All units in kg/yr</th>
<th>( \Delta T )</th>
<th>( \Delta T )</th>
<th>( \Delta T )</th>
<th>( \Delta T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission from</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>utility</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>1.44E+05</td>
<td>5.21E+06</td>
<td>1.70E+02</td>
</tr>
<tr>
<td>absorber</td>
<td>4.67E+04</td>
<td>6.43E+04</td>
<td>2.55E+02</td>
<td>3.95E+02</td>
<td>1.09E+00</td>
</tr>
<tr>
<td>distillation column</td>
<td>3.16E+00</td>
<td>6.43E+03</td>
<td>3.60E+02</td>
<td>6.32E+03</td>
<td>3.12E+00</td>
</tr>
<tr>
<td>fugitive</td>
<td>3.12E+01</td>
<td>5.30E+03</td>
<td>2.35E+02</td>
<td>2.90E+03</td>
<td>1.12E+00</td>
</tr>
</tbody>
</table>

VOC recovery by absorption into tetradecane (C14)

% Recovery of VOCs vs Absorber Oil Flow Rate (kgmole/hr)
Environmental Index Profiles

- **A**:
  - Absorber Oil Flow Rate (kgmoles/hr)
  - Index Values (kg/hr)
  - Lines labeled with different indices (GW, IR, IGF, IGW, IAR, ISF)

- **B**:  
  - Absorber Oil Flow Rate (kgmoles/hr) 
  - Index Values (kg/hr) 
  - Lines labeled with different indices (FT, KNO, INH)

Michigan Technological University
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

Normalization and Valuation of Indices

1. Normalized Index \( I_N^k = \frac{I_k}{I_k^N} \)

2. Weighting of Index Categories

\[
I_{PC} = \sum_k (I_N^k \times W_k)
\]

Weighting Factors
- global warming: 2.5
- ozone depletion: 100
- smog formation: 2.5
- acid rain: 10
- carcinogenic: 5
- noncarcinogenic: 5
- ecotoxicity: 10

Source: Eco-Indicator 95 framework for life cycle assessment, Pre Consultants, http://www.pre.nl
IPC and ISF and IING dominate the IPC index.

Use of EFRAT: evaluate the MA process

1. Basecase (Dibutyl phthalate absorber oil) with and without heat integration
2. Simulate 3 case studies using heat integrated flowsheet
   - Dibutyl phthalate absorber oil
   - Dibenzyl ether absorber oil
   - Diethylene glycol butyl ether acetate absorber oil
Heat integration of the MA flowsheet

Without Heat Integration

Maleic anhydride flowsheet with heat integration
Maleic anhydride from n-butane: effect of heat integration on risk indexes

Relative Risk Indexes

- No Heat Integration
  - IGW: 1.E+10
  - ISF: 1.E+09
  - IAR: 1.E+08
  - IING: 1.E+07
  - IINH: 1.E+06
  - IFT: 1.E+05

- Heat Integration
  - IGW: 30.4% reduction
  - ISF: 72.2% reduction
  - IAR: remaining indexes unchanged

Maleic anhydride from n-butane: effects of absorber oil choice

Relative Risk Index

- Dibutyl Phthalate: 1.E+10
- Dibenzyl Ether: 1.E+09
- DGBEA: 1.E+08

- IGW: 16.3% reduction
- ISF: 85.1% reduction
- IAR: 81.7% reduction
- IING: 42.1% reduction
Recap

1. Review of environmental impact assessment methods

2. Application of Tier 3 environmental impact assessment to a detailed flowsheet - Chapter 11
   » Heat integration of the Maleic Anhydride flowsheet
   » Effects of absorber oil choice for the MA flowsheet