
GREEN ENGINEERING

Environmentally Conscious Design
of Chemical Processes

DAVID T. ALLEN
AND
DAVID R. SHONNARD



Prentice Hall PTR
Upper Saddle River, NJ 07458
www.phptr.com



11.3 TIER 3 METRICS FOR ENVIRONMENTAL RISK EVALUATION OF PROCESS DESIGNS

In this section, we learn how to combine emissions estimation, environmental fate and transport information, and environmental impact data to obtain an assessment of the potential risks posed by releases from chemical process designs. This methodology will be applied in a systematic manner for the quantitative evaluation of a completed flowsheet for a chemical process design. We use the multimedia compartment model described in Section 11.2 to calculate environmental concentrations that are used by several of the indices. Although no single methodology has gained universal acceptance, several useful methodologies for indexing environmental and health impacts of chemicals have recently appeared in the literature. Many of the indexing methods include metrics for abiotic as well as biotic impacts. In the abiotic category, global warming, stratospheric ozone depletion, acidification, eutrophication, and smog formation are often included. In the biotic category, human health and plant, animal, and other organism health are impacts of concern. For issues of environmental and economic sustainability, resource-depletion indexes reflect long-term needs for raw materials use. A review of several of these methodologies would indicate that many environmental metrics (indexes) have been constructed by employing separate parameters for the inherent impact potential (IIP) and exposure potential (EP) of an emitted chemical. The index is normally expressed as a product of inherent impact and exposure, following risk assessment guidelines (NRC, 1983; Heijungs et al., 1992; SETAC, 1993), although summation-based indexes have also been used (Davis et al., 1994; Mallick et al., 1996).

In this text, we define and use nine environmental and health-related indexes for chemical process impacts, as shown in Table 11.3-1. These impacts affect local, regional, and global environmental issues. Global warming and stratospheric ozone depletion are problems with potentially global implications for a large proportion of the earth's population. Smog formation and acid deposition are regional problems that can affect areas in size ranging from large urban basins up to a significant fraction of a continent. Issues of toxicity and carcinogenicity are often of highest concern at the local scale in the vicinity of the point of release.

The general form of a dimensionless environmental risk index is defined as;

$$(\text{Dimensionless Risk Index})_i = \frac{[(EP)(IIP)]_i}{[(EP)(IIP)]_B} \quad (\text{Eq. 11-1})$$

Table 11.3-1 Environmental Impact Index Categories for Process Flowsheet Evaluation.

<i>Abiotic Indexes</i>	<i>Health-Related Indexes</i>	<i>Ecotoxicity Indexes</i>
Global warming	Inhalation toxicity	Fish Aquatic Toxicity
Stratospheric ozone depletion	Ingestion toxicity	
Acid deposition	Inhalation carcinogenicity	
Smog formation	Ingestion carcinogenicity	

where B stands for the benchmark compound and i the chemical of interest. To estimate the index I for a particular impact category due to all of the chemicals released from a process, we must sum the contributions for each chemical weighed by their emission rate.

$$I = \sum_i (\text{Dimensionless Risk Index})_i \times m_i \quad (\text{Eq. 11-2})$$

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

11.3.1 Global Warming

A common index for global warming is the global warming potential (GWP), which is the cumulative infrared energy capture from the release of 1 kg of a greenhouse gas relative to that from 1 kg of carbon dioxide (IPCC, 1991):

$$GWP_i = \frac{\int_0^n a_i C_i dt}{\int_0^n a_{CO_2} C_{CO_2} dt} \quad (\text{Eq. 11-3})$$

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 its predicted concentration in the atmosphere (ppm), and n is the number of years over which the integration is performed, for example, 100 years. The concentration is a function of time (t), primarily due to loss within the troposphere by chemical reaction with hydroxyl radicals. For carbon dioxide, $n = 120$ years. Several authors have developed models to calculate GWP and as a result, some variation in GWP predictions have appeared (Fisher, 1990a; Derwent, 1990; Lashof & Ahuja, 1990; Rotmans, 1990). A list of "best estimates" for GWPs has been assembled from these model predictions by a panel of experts convened under the Intergovernment Panel on Climate Change (IPCC, 1991 and 1996) and have appeared on separate lists (Heijungs et al., 1992; Goedkoop, 1995).

In Appendix D, Table D-1 is a list of global warming potentials for several important greenhouse gases. The global warming potential for each chemical is influenced mostly by the chemical's tropospheric residence time and the strength of its infrared radiation absorbance (band intensities). All of these gases are extremely volatile, do not dissolve in water, and do not adsorb to soils and sediments. Therefore, they will persist in the atmosphere after being released from sources. The product of the GWP and the mass emission rate of a greenhouse chemical results in the equivalent emission of carbon dioxide, the benchmark compound. The global warming index for the entire chemical process is the sum of the emissions-weighted GWPs for each chemical,

$$I_{GW} = \sum_i (GWP_i \times m_i) \quad (\text{Eq. 11-4})$$

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 greenhouse chemicals in the form of the benchmark compound, CO_2 .

The global warming index as calculated above accounts for direct effects of the chemical, but most chemicals of interest are so short-lived in the atmosphere (due to the action of hydroxyl radicals in the troposphere) that they disappear (become converted to CO_2) long before any significant direct effect can be felt. However, organic chemicals of fossil fuel origin will have an indirect global warming effect because of the carbon dioxide released upon oxidation within the atmosphere and within other compartments of the environment. In order to account for this indirect effect for organic compounds with atmospheric reaction residence times less than 1/2 year, an indirect GWP is defined (Shonnard and Hiew, 2000) as

$$GWP_i(\text{indirect}) = N_C \frac{MW_{\text{CO}_2}}{MW_i} \quad (\text{Eq. 11-5})$$

where N_C is the number of carbon atoms in the chemical i and the molecular weights MW convert from a molar to a mass basis for GWP, as originally defined. Organic chemicals whose origin is in renewable biomass (plant materials) have no global warming impact because the CO_2 released upon environmental oxidation of these compounds is, in principle, recycled into biomass within the natural carbon cycle.

Example 11.3-1 Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

1,1,1-Trichloroethane (TCA) is used as an industrial solvent for metal cleaning, as a reaction intermediate, and for other important uses (US EPA, 1979-1991). A major processing route for TCA is by hydrochlorination of vinyl chloride in the presence of an FeCl_3 catalyst to produce 1,1-dichloroethane, followed by chlorination of this intermediate. Sources for air emissions include distillation condenser vents, storage tanks, handling and transfer operations, fugitive sources, and secondary emissions from wastewater treatment. We wish to estimate the global warming impact of the air emissions from this process, including direct impacts to the environment (from 1,1,1-TCA) and indirect impacts from energy usage (CO_2 and NO_x release) in the analysis. Data below show the major chemicals that impact global warming when emitted from the process.

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

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

Chemical	m_i (kg/hr)	GWP_i
TCA	10	100
CO_2	7,760	1
N_2O	.14	310

TCA emissions were estimated using data for trichloroethylene (US EPA, 1979-1991).

CO₂ and N₂O emission rates were estimated from a life cycle assessment of ethylene production (Allen and Rosselot, 1997; Boustead, 1993).

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

$$\begin{aligned} I_{GW} &= (10 \text{ kg/hr})(100) + (7,760 \text{ kg/hr})(1) + (.14 \text{ kg/hr})(310) \\ &= 1,000 + 7,760 + 43.4 \\ &= 8,803.4 \text{ kg/hr} \end{aligned}$$

The percent of the process I_{GW} for each chemical is;

$$1,1,1\text{-TCA: } (1,000/8,803.4) \times 100 = 11.4\%$$

$$\text{CO}_2: (7,760/8,803.4) \times 100 = 88.1\%$$

$$\text{N}_2\text{O: } (43.4/8,803.4) \times 100 = 0.5\%$$

Discussion: This case study demonstrates that the majority of the global warming impact from the production of 1,1,1-TCA is from the energy requirement of the process and not from the emission of the chemical with the highest global warming potential. This analysis assumes that a fossil fuel was used to satisfy the energy requirements of the process. If renewable resources were used (biomass-based fuels), the impact of CO₂ on global warming would be significantly reduced. Finally, the majority of the global warming impact of 1,1,1-TCA could very well be felt during the use stage of its life cycle, not the production stage. A complete life cycle assessment (see Chapter 13) of 1,1,1-TCA is necessary to demonstrate this.

11.3.2 Ozone Depletion

The ozone depletion potential (ODP) of a chemical is the predicted time- and height-integrated change $\delta[\text{O}_3]$ in stratospheric ozone caused by the release of a specific quantity of the chemical relative to that caused by the same quantity of a benchmark compound, trichlorofluoromethane (CFC-11, CCl₃F) (Fisher et al., 1990b).

$$ODP_i = \frac{\delta[\text{O}_3]_i}{\delta[\text{O}_3]_{\text{CFC-11}}} \quad (\text{Eq. 11-6})$$

Model calculations for ODP have been carried out using one- and two-dimensional photochemical models. A list of ODPs for a small number of chemicals has been assembled by a committee of experts (WMO, 1990b and 1992b) and have appeared on separate lists (Heijungs et al., 1992; Goedkoop, 1995). The product of the ODP and the mass emission rate of a chemical i results in the equivalent impact of an emission of CFC-11. Appendix D, Table D-2 shows a list of ozone depletion potential values for important industrial compounds. Data on the tropospheric reaction lifetimes (τ), stratospheric atomic oxygen reaction rate constant (k), and number of chlorines in each molecule (X) are also listed. Notice that the brominated compounds in this table have much larger ODPs than the chlorinated species. Also, it is thought that fluorine does not contribute to ozone depletion

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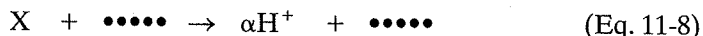
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(Ravishankara, et al., 1994). Like the global warming chemicals in Appendix D Table D-1, the chemicals in Appendix D, Table D-2 will exist almost exclusively in the atmosphere after being emitted by sources. The ozone depletion index for an entire chemical process is the sum of all contributions from emitted chemicals multiplied by their emission rates. The equivalent emission of CFC-11 for the entire process is then;

$$I_{OD} = \sum_i (ODP_i \times m_i) \quad (\text{Eq. 11-7})$$

11.3.3 Acid Rain

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



where X is the emitted chemical substance that 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:

$$\eta_i = \frac{\alpha_i}{MW_i} \quad (\text{Eq. 11-9})$$

where MW_{*i*} is the molecular weight of the emitted substance (moles i/kg i). As before, we can introduce a benchmark compound (SO₂) and express the acid rain potential (ARP_{*i*}) of any emitted acid-forming chemical relative to it (Heijungs et al., 1992):

$$ARP_i = \frac{\eta_i}{\eta_{SO_2}} \quad (\text{Eq. 11-10})$$

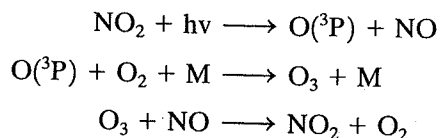
The number of acidifying compounds emitted by industrial sources is limited to a rather small number of combustion byproducts and other precursor or acidic species emitted directly onto the environment. Appendix D, Table D-3 lists the acid rain potentials for several common industrial pollutants. The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

$$I_{AR} = \sum_i (ARP_i \times m_i) \quad (\text{Eq. 11-11})$$

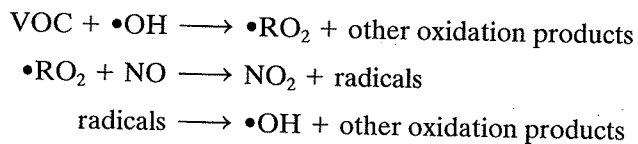
11.3.4 Smog Formation

The most important process for ozone formation in the lower atmosphere is photo-dissociation of NO₂:





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 $[\text{NO}_2]/[\text{NO}]$. The role of VOCs in smog formation is to form radicals which convert NO to NO_2 without causing O_3 destruction, thereby increasing the ratio $[\text{NO}_2]/[\text{NO}]$, and increasing O_3 .



The tendency of individual VOCs to influence O_3 levels depends upon its hydroxyl radical ($\bullet\text{OH}$) rate constant and elements of its reaction mechanism, including radical initiation, radical termination, and reactions which remove NO_x . Simplified smog formation potential indexes have been proposed based only on VOC hydroxyl radical rate constants, but these have not correlated well with model predictions of photochemical smog formation (Allen, et al., 1992; Japar, et al., 1991).

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). Several computer models have been developed to evaluate incremental reactivity (Bufalini and Dodge, 1983; Carter and Atkinson, 1989; Carter, 1994; Chang and Rudy, 1990; Dodge, 1984). In general, predicted VOC incremental reactivities are greatest when NO_x levels are high relative to reactive organic gases (ROG) and lowest (or even negative) when NO_x is relatively low. Therefore, the ratio ROG/NO_x is an important model parameter. Lists of incremental smog formation reactivities for many VOCs have been compiled (Carter, 1994; Heijungs et al., 1992). An estimation methodology has also been developed which circumvents the need for computer model predictions, though the practical use of this method is limited due to lack of detailed smog reaction mechanisms for a large number of compounds (Carter and Atkinson, 1989). Although several reactivity scales are possible, the most relevant for comparing VOCs is the maximum incremental reactivity (MIR), which occurs under high NO_x conditions when the highest ozone formation occurs (Carter, 1994).

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

$$SFP_i = \frac{MIR_i}{MIR_{ROG}} \quad (\text{Eq. 11-12})$$

where MIR_{ROG} is the average value for background reactive organic gases, the benchmark compound for this index. This normalized and dimensionless index is similar to the one proposed by the Netherlands Agency for the Environment (Heijungs et al., 1992). Appendix D, Table D-4 contains a listing of calculated MIR values for many common volatile organic compounds found in fuels, paints, and solvents. Most of the chemicals in Appendix D, Table D-4 are volatile and will maintain a presence in the atmosphere after release into the air, with the exception of the higher molecular weight organics. The total smog formation potential is the sum of the MIRs and emission rates for each smog-forming chemical in the process. The process equivalent emission of ROG is;

$$I_{SF} = \sum_i (SFP_i \times m_i) \quad (\text{Eq. 11-13})$$

Example 11.3-2 Solvent Recovery from a Gaseous Waste Stream: Effect of Process Operation on Indexes for Global Warming, Smog Formation, and Acidification

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

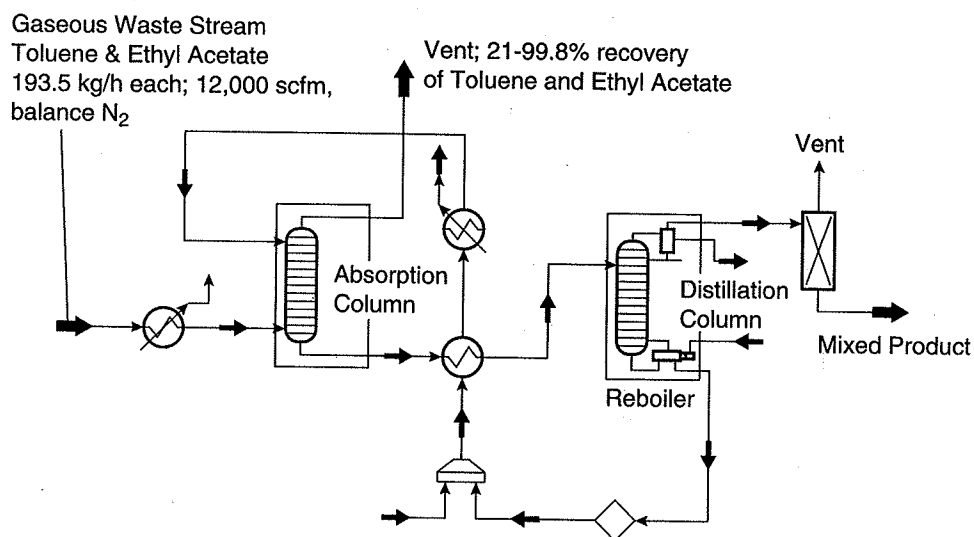


Figure 11.3-1 Schematic diagram (from HYSYS, Hyprotech, Calgary, Canada) of a solvent recovery and recycle process using absorption into heavy oil (n-tetradecane) followed by distillation.

the film process (Sangwichien, 1998). Since the waste stream may already meet environmental regulations for smog formation and human toxicity, the key issue is how much of the VOCs to recover and how much savings on solvent costs can be realized. In this problem, we do not deal with the economic issues, but rather show that when considering environmental impacts, there are trade-offs for several impacts depending on the percent recovery of the VOCs.

The gaseous waste stream enters the absorption column where the VOCs (toluene and ethyl acetate) transfer from the gas phase to the absorption oil (tetradecane). The effectiveness of this transfer depends largely on the oil flow rate, as the percent recovery of VOCs increases 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 after cooling. The VOCs are recovered as a mixed product from the condenser of the distillation column and stored in a tank for re-use in the plastic film process. The main emission sources are the absorption column, the vent on the distillation column, the vent on the storage tank (not shown), utility related pollutants, and fugitive sources.

Solution: Table 11.3-2 shows the effect of absorber oil flow rate on the emissions from the solvent recovery process. A commercial process simulator (HYSYS) was used to generate mass and energy balances and to calculate the VOC emission rates from the absorber unit. Within the Environmental Fate and Risk Assessment Tool (EFRAT,[®] refer to Appendix F for a list of software resources.) EPA emission factors and correlations were used to calculate VOC emission rates from the distillation column, storage tank, and fugitive sources. CO₂, CO, TOC, NO_x, and SO_x emission rates were also calculated within EFRAT based on the energy requirements of the process and an assumed fuel type (fuel oil no. 4). Figure 11.3-2 shows the recovery of toluene and ethyl acetate as a function of absorption oil flow rate in the process. As the absorber oil flow rate is increased, the emissions of toluene and ethyl acetate from the absorber unit decrease, reflecting an increased percent recovery from the gaseous

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

Absorber Oil Flow Rate (kgmol/hr)	Emission Rate (kg/hr)							
	Toluene	Ethyl Acetate	CO ₂	CO	TOC	NO _x	SO _x	n-C14
0	193.55	193.55	0	0.0	0.0	0.0	0.0	0.0
10	119.87	185.87	37	0.013	0.001	0.05	0.41	4.28
20	53.11	178.37	74	0.027	0.001	0.11	0.81	4.83
50	0.97	160.4	183	0.066	0.003	0.26	1.99	4.67
100	0.02	128.07	360	0.129	0.007	0.52	3.39	4.23
200	0.02	59.95	714	0.257	0.013	1.03	7.82	4.13
300	0.02	12.87	1,067	0.385	0.019	1.54	11.69	4.06
400	0.03	1.70	1,420	0.512	0.026	2.05	15.56	4.05
500	0.03	0.27	1,773	0.639	0.032	2.56	19.42	4.04

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

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0.81	4.83
1.99	4.67
3.39	4.23
7.82	4.13
1.69	4.06
5.56	4.05
9.42	4.04

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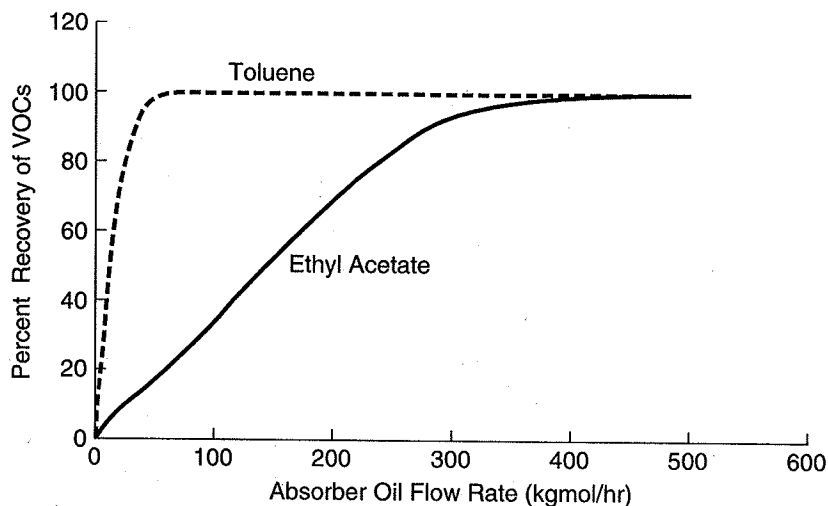


Figure 11.3-2 VOC recovery efficiency for the solvent recovery process of Figure 11.3-1. Adapted from Hiew (1998) and Shonnard and Hiew (2000).

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. Emissions of the utility-related pollutants (CO₂, CO, TOC, NO_x, and SO_x) increase in proportion to the oil flow rate. The emissions of the absorption oil (n-C14) remains relatively constant with oil flow rate.

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

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

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

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

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

		SFP, • m _i
Toluene:	(0.87)(0.97 kg/hr)	0.84 kg/hr
Ethyl Acetate:	(0.32)(160.4 kg/hr)	51.33 kg/hr
Tetradecane:	(0.1)(4.67 kg/hr)	0.47 kg/hr
Total:		52.64 kg/hr

Shown in Figures 11.3-3 through 11.3-5 are the relative impact indexes for the solvent recovery process of Figure 11.3-1. We observe in Figure 11.3-3 that the global warming index is minimized by operating the process at approximately 50 kgmole/hr. An explanation for this behavior follows next. 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 CO₂. 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. 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 11.3-4, 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 (SO_x and NO_x), 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 oil flow rate. The smog formation index (Figure 11.3-5) shows a significant 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 flow rate for minimizing the smog formation index is therefore about 500 kgmole/hr.

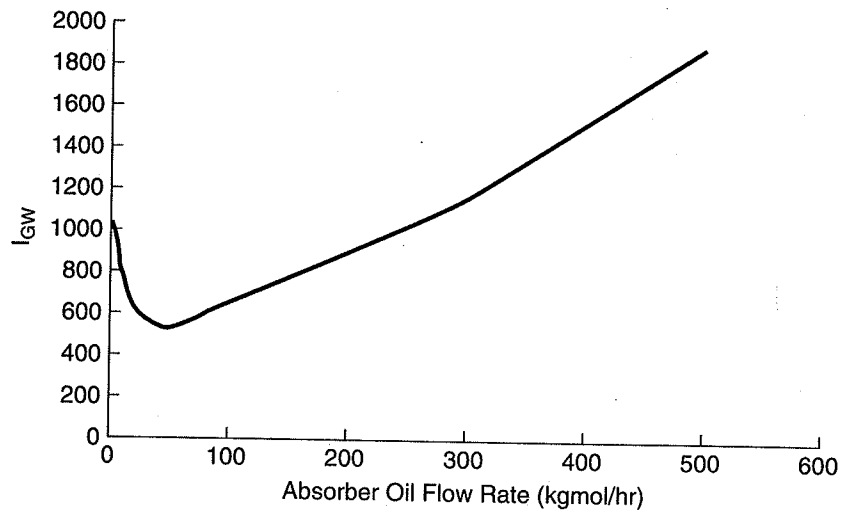


Figure 11.3-3 The global warming index for the solvent recovery process of Figure 11.3-1. Adapted from Hiew (1998) and Shonnard and Hiew (2000).

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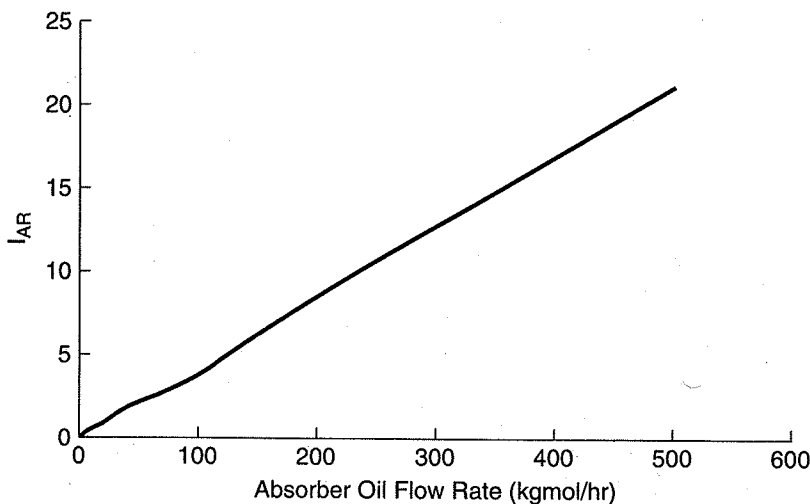


Figure 11.3-4 The acid rain index for the solvent recovery process of Figure 11.3-1. Adapted from Hiew (1998) and Shonnard and Hiew (2000).

Discussion: These indexes demonstrate the complexities in evaluating chemical processes using multiple indexes of environmental performance. It is not possible to identify a single absorption oil flow rate that simultaneously minimizes all three indexes. However, we can see that significant reductions in the global warming (42%) and the smog formation (82%) indexes are realized at an oil flow rate of 50 kgmole/hr, with only a relatively modest increase in the acid rain index. This observation suggests

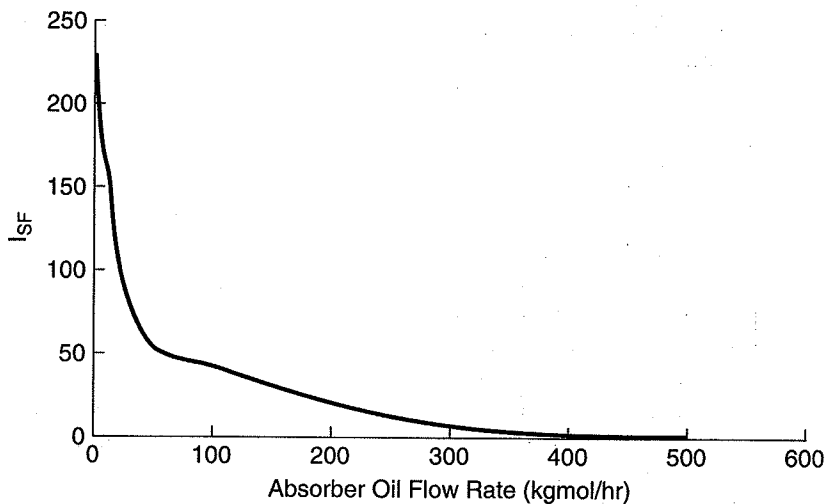


Figure 11.3-5 The smog formation index for the solvent recovery process of Figure 11.3-1. Adapted from Hiew (1998) and Shonnard and Hiew (2000).

11.3-1. Adapted

that a decision to operate the process at 50 kgmole/hr is 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.

11.3.5 Toxicity

As explained in Chapter 2, chemical toxicity to humans and ecosystems is a function of dose and response. The dose is dependent on a complex series of steps involving the manner of release, environmental fate and transport of chemicals, and uptake mechanisms. The final two steps dictate the extent of exposure. Key questions which affect the administered dose include: Where are the emissions released to—the air, water, or soil? Are the chemicals altered by environmental reactions or are the chemicals persistent? How are the chemicals taken up by the body? Through breathing contaminated air? Drinking contaminated water? By direct contact with and transfer through the skin? The effective dose is dependent on processes occurring in the body including absorption, distribution, storage, transformation, and elimination. The response by the target organ in the body is a very complex function of chemical structure and modes of action and is the purview of the field of toxicology.

Clearly, the complexity of toxicology precludes an exact determination of all adverse effects to human and ecosystem health from the release of a chemical. From an engineering point of view, an exact assessment may not be necessary. Similar to the potential impact indexes presented for global warming, stratospheric ozone depletion, smog formation, and acidification, we develop and use *toxicity potentials* for non-carcinogenic and carcinogenic health effects for ingestion and inhalation routes of exposure. Both inhalation and ingestion are thought to be the dominant routes of exposure for human contact with toxic chemicals in the environment.

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 its reference dose (RfD (mg/kg/d) or reference concentration (RfC (mg/m³)) for ingestion and inhalation exposure, respectively. Exposures to concentrations in the water or air which result in doses or concentrations above these reference levels is believed to cause adverse effects. Lists of RfD and RfC data are available in electronic or paper copy form (US EPA, 1997; US EPA, 1994). Because RfDs and RfCs are not available for all chemicals, we use lethal doses (LD₅₀) and concentrations (LC₅₀) as additional toxicological parameters for health assessments. Lists of LD₅₀ and LC₅₀ are tabulated in additional sources (NTP, 1997). Threshold Limit Values (TLVs), Permissible Exposure Limits (PELs), and Recommended Exposure Limits (RELs) are additional toxicity properties that, like RfD and RfC, are based on low-dose studies.

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

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

$C_{i,w}$ 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 of Section 11.2. The factor of 2 L/d and 70 kg are the standard ingestion rate and body weight used for risk assessment (Pratt, et al., 1993). The product of the concentration and the ingestion rate divided by the body weight provides the exposure dose. This exposure dose is divided by the reference dose to determine whether this dose poses a toxicological risk. The ratio of these risks for the chemical and the benchmark compound results in the ingestion toxicology potential for chemical i.

The toxicity potential for inhalation exposure is defined similarly as:

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

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. The doses are not shown in the equation because the inhalation rate (20 m³/d) and body weights (70 kg) cancel out. In this equation, the ratio of the risks for inhalation exposure is the potential for inhalation toxicity relative to the benchmark compound.

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

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

Similarly for inhalation route toxicity;

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

Carcinogenic Toxicity

In a similar method as outlined for non-carcinogenic toxicity, we develop two indexes for cancer-related risk, based on predicted concentrations of chemicals in the air and water from a release of 1000 kg/hr. The concentrations are converted to

doses using standard factors and then the risk for the chemical and a benchmark compound, benzene, is calculated. The carcinogenic potential for a chemical is determined by taking the ratio of the chemical's risk to that for the benchmark compound. The ingestion route carcinogenic potential for a chemical is:

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

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. 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 (US EPA, 1997; US 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 11.3-3 along with a numerical hazard value (HV). The value of HV can be used in Equations 11-18 and 11-19 in the absence of SF data. Data for WOE can be found in the following sources (NIHS, 1997; OSHA, 1997; IRIS, 1997).

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

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

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

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

and for inhalation,

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

Example 11.3-3 Toxicity Evaluation of the Solvent Recovery Process in Figure 11.3-1

Toxicity evaluation of the toluene and ethyl acetate recovery and recycle process design is conducted in a fashion similar to the previous example problem. We are concerned with three compounds in this analysis, toluene, ethyl acetate, and hexane (a surrogate for products of incomplete combustion in utility consumption). There are no carcinogenic compounds present in the design, therefore the two carcinogenic indexes will be ignored. This example illustrates how LD₅₀/LC₅₀ can be used interchangeably with RfDs and RfCs when data gaps occur.

Data and Results: The emission rates of these compounds appeared in the previous example problem and are used again here. The concentrations of these chemicals and

Table 11.3-3 Weight of Evidence (WOE) Classifications (IRIS, 1997; Davis et al., 1994).

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

the benchmark compound (toluene again) are calculated using the Mackay model of Section 11.2. The input data and the resulting concentrations are provided in the following table. The calculations were conducted using a standard emission of 1000 kg/hr of each compound into the air compartment when evaluating both ingestion toxicity and inhalation toxicity. 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 (°C)	Fugacity ratio	Vapor pressure @25°C (Pa)	Solubility (g/m ³)	Log K _{ow}
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	1.97×10 ⁻⁷	4.00×10 ⁻⁷
Ethyl acetate	55	55	170	550	4.36×10 ⁻⁷	5.00×10 ⁻⁶
Hexane	17	550	1700	5500	1.97×10 ⁻⁷	1.50×10 ⁻⁹

The toxicological properties (RfDs, RfCs) are incomplete for the three chemicals in this design. We are forced to use LD₅₀ and LC₅₀ data when gaps occur. The following table 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 11-14 and 11-15.

	Inhalation RfC (mg/m ³)	Oral RfD (mg/kg/day)	LC ₅₀ (ppm)	LD ₅₀ (mg/kg)	Toxicity Potentials	
					INHTP	INGTP
Toluene	0.4	0.2	4000	5000	1.0	1.0
Ethyl acetate		0.9	3200		2.8	2.8
Hexane	0.2			28700	2.0	6.5×10 ⁻⁴

Figures 11.3-6 and 11.3-7 show the change in process inhalation and ingestion toxicity index with absorption oil flow rate using the emission rate data tabulated in the previous example problem and concentrations calculated by the Mackay model.

Discussion: The inhalation toxicity is reduced with increasing absorption oil flow rate due to the removal of both toluene and ethyl acetate, and to a much lesser extent by hexane (TOC). The inhalation and ingestion index behavior is nearly identical since the inherent toxicity potentials, INHTP and INGTP, are virtually the same (as shown above). These toxicity indexes can be reduced by 39% by operating the process at 50 kgmoles/hr absorber flow rate. Keep in mind that interchanging RfCs with LC₅₀s will introduce additional uncertainties in the evaluation.

SUMMARY

This chapter has outlined a systematic methodology for evaluating environmental and health-based impacts for chemical process designs. Multiple impact indexes are included for process evaluation because of the complexity of pollutant interactions

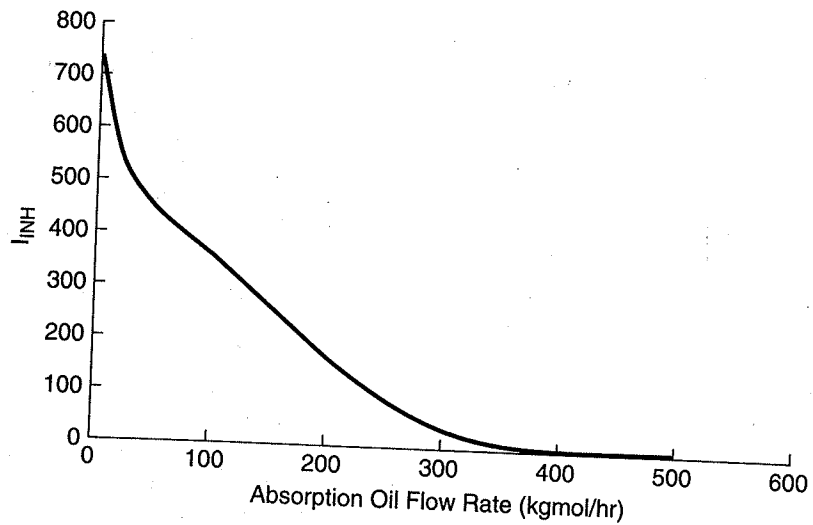


Figure 11.3-6 Inhalation toxicity index for the solvent recovery and recycle process.

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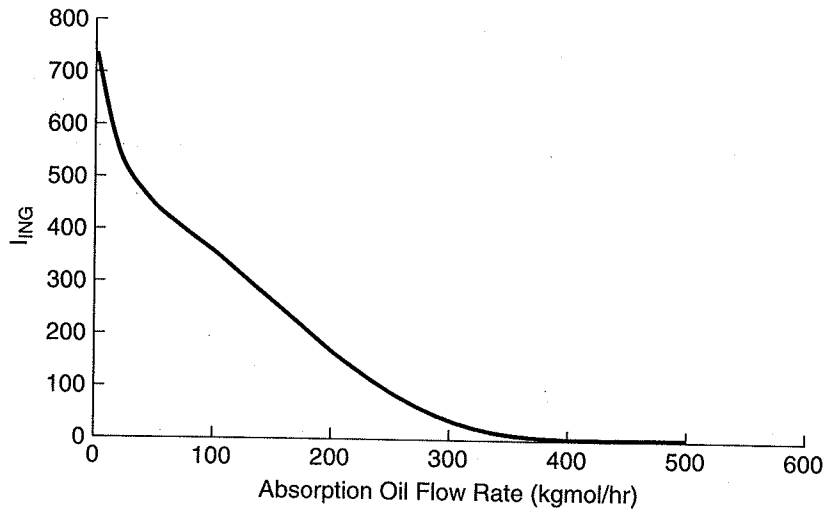


Figure 11.3-7 Ingestion toxicity index for the solvent recovery and recycle process.

with the environment and with human health. The methodology includes pollutant release or emission estimation (Chapter 8), environmental fate and transport of pollutants, and relative risk assessment using the benchmarking concept. The methodology was applied for the evaluation of air emissions from a process flow-sheet utilizing a commercial chemical process simulator to generate the material and energy balances for the process. From this analysis, we were able to assess the environmental performance of the process as one of the process parameters, the absorber oil flow rate, was varied over a wide range. This exercise provided insights into how energy consumption within the process drives up certain environmental impacts and how the recovery and recycle of VOCs drives down others. The trends for impact with respect to absorber oil flow rate are clear, but making a decision based on these trends is not straightforward. Since trade-offs do occur among these impact indexes, questions such as which impacts are most important need to be addressed. Nonetheless, the environmental information provided will allow for more sound process design decisions.

It is important to stress that the methodology is general, and can accommodate releases to the water and the soil as well as to the air, since the multimedia compartment model can predict environmental concentrations for all of these release mechanisms. Another issue to consider is the uncertainties involved in the assessment of environmental risk. There are many sources of uncertainty, particularly for emission estimation and environmental fate calculations. The magnitude of these uncertainties may be quite large, depending upon the emission estimation method and on chemical-specific environmental properties. It is important to understand the magnitude of these uncertainties in order to decide whether significant differences actually occur when comparing the environmental

impacts of process operating conditions or of various process technologies. Uncertainty analysis for environmental impact assessment is an active research area in chemical engineering and in environmental science and engineering. The topic is beyond the scope of this introductory textbook, but methods of evaluating uncertainty are available, and may include Monte Carlo simulation and propagation of error analysis.

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PROBLEMS

1. **Ethanol as a Substitute Octane-Boosting Additive to Automobile Fuels.** In response to requirements of the 1990 Clean Air Act Amendments, automobile fuels sold in some urban areas must contain 10% ethanol. The reasons for adding ethanol are 1)