Environmental Management and Safety Issues

INTRODUCTION

In the last four decades, people have become aware of a wide range of environmental issues. All sources of air, land, and water pollution are under constant public scrutiny. Increasing numbers of professionals are being confronted with problems related to environmental management. Because many of these issues are of concern, practicing engineers must develop a proficiency and an improved understanding of technical and scientific issues regarding environmental management and safety issues in order to cope with these challenges.

The problem of what to include and what to omit has been particularly difficult for this chapter. However, every attempt has been made to offer material to the reader at a level that should enable them to better cope with some of the complex problems encountered in environmental management today.

The chapter is divided into the following five sections:

Introduction Environmental Issues of Concern Health Risk Assessment Hazard Risk Assessment Illustrative Examples

The next section provides a broad overview of all the key environmental issues. This is followed by two sections on risk assessment—one concerned with health and the other concerned with hazards. The chapter concludes with a section that contains 19 Illustrative Examples.

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ENVIRONMENTAL ISSUES OF CONCERN⁽¹⁾

The degradation of the environment is not a problem that is restricted to the United States or even to developed countries. On the contrary, under-developed countries are also struggling with several environmental issues that have already been resolved in many developed countries. In the United States, the Environmental Protection Agency (EPA) as well as individual states are working hard to implement regulations addressing areas of environmental concern. Generators and sources of pollutants are being identified so that solutions may be targeted to specific areas.

There are several different areas of concern related to air pollutants and their control. Atmospheric dispersion of pollutants can be mathematically modeled to predict where pollutants emitted from a particular source, such as a combustion facility stack, will settle to the ground and at what concentration. Pollution control equipment can be added to various sources to reduce the amount of pollutants before they are emitted into the air. Acid rain, the greenhouse effect, and global warming (climate change) are all indicators of adverse effects to the air, land, and sea, which result from the excessive amount of pollutants being released into the air. Two topics that few people are aware of are the issue of indoor air quality and vapor intrusion. Inadequate ventilation systems in homes and businesses directly affect the quality of health of the people within the buildings. For example, the episode of Legionnaires' disease that occurred in Philadelphia in the 1970s was related to microorganisms in the cooling water of the air-conditioning system. Noise pollution, although not traditionally an air pollution topic, is included in this topic area. The effects of noise pollution are not generally noticed until hearing is impaired. And, although impairment of hearing is a commonly known result of noise pollution, few people realize that stress is also a significant result of excessive noise exposure. The human body enacts its innate physiologic defensive mechanisms under conditions of loud noise and the fight to control these physical instincts causes tremendous stress on the individual.

Pollutants entering rivers, lakes, and oceans come from a wide variety of sources, including stormwater runoff, industrial discharges, and accidental spills. It is important to understand how these substances disperse in order to determine how to control them. Municipal and industrial wastewater treatment systems are designed to reduce or eliminate problem substances before they are introduced into natural water systems, industrial use systems, drinking water supply, and other water systems. Often, wastewater from industrial plants must be pretreated before it can be discharged into a municipal treatment system.

Programs to reduce and dispose of municipal waste include reuse, reduction, recycling, and composting, in addition to incineration and landfilling. Potentially infectious waste generated in medical facilities must be specially packaged, handled, stored, transported, treated, and disposed of to ensure the safety of both the waste handlers and the general public. Radioactive waste may have far more serious impacts on human health and the environment, and treatment and disposal requirements for radioactive substances must be strictly adhered to.

Incineration has been a typical treatment method for hazardous waste for many years. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, was enacted to identify and remedy uncontrolled hazardous waste sites. It also attempts to place the burden of cleanup on the generator rather than on the federal government. Asbestos, household hazardous wastes, used oil, metals, and underground storage tanks either contain, or inherently are, hazardous materials that require special handling and disposal. Furthermore, it is important to realize that small quantity generators of hazardous wastes are regulated as well as large generators.

Pollution prevention, both domestic and industrial, can be accomplished through

- 1 proper residential and commercial building design,
- 2 proper heating, cooling, and ventilation systems,
- 3 energy conservation,
- 4 reduction of water consumption, and
- 5 attempts to reuse or reduce materials before they become wastes.

Domestic and industrial solutions to environmental problems result from considering ways to make homes and workplaces more energy-efficient as well as ways to reduce the amount of wastes generated within them.

Additional environmental concerns include electromagnetic fields that emanate from power distribution systems. Items related to both worker and community health and safety and training have been brought to the forefront by the increasingly stringent regulations developed by the Occupational Safety and Health Administration (OSHA) and other federal and state regulatory agencies. The best way to prevent a dangerous situation is to be informed of the possible outcomes ahead of time and to be prepared to respond to an emergency situation. Guidelines on how to monitor the results of an environmental action are needed to determine how well an existing cleanup effort is proceeding or how present background levels will affect discharges from new facilities. Economic considerations also play a large role in the implementation of an environmental strategy.

Three of the newer waste remediation technologies include:

- **1** *Bioremediation* is a process that utilizes microorganisms to transform harmful substances into nontoxic compounds. It may be used to treat contaminated soil or groundwater and it is one of the most promising new technologies for treating chemical spills and hazardous wastes.
- **2** *Soil vapor extraction* is used to remove volatile organic compounds from soil. A vacuum is applied to the soil, causing the movement of vapors toward extraction wells. Volatiles are then readily removed from the subsurface of the soil through the extraction wells.
- **3** *Biofiltration* is a process that exploits the ability of microorganisms to remove and treat biodegradable substances in air (gas) streams. In the past, it has been used successfully in Europe to remove odors from wastewater treatment plants and compost factories, and it is now being used to remove volatile organic compounds.

Practicing engineers need to be informed on how to make decisions about associated risks and how to communicate these risks and their effects on the environment to the public. Risk related topics include short-term and long-term threats to human health and the environment. Risk assessment is the most important consideration for remediation of harmful effects stemming from the presence of a hazardous substance and risk-based decision-making is a tool that is now routinely being used to select a clean-up alternative.

There are four topics that are relatively new in the area of environmental management:

- **1** *ISO 14000* is an international certification standard for an organization's environmental management system. It ensures that the objectives, targets, procedures, and systems of the environmental management system are part of the organization's routine operations.
- 2 *Environmental audits* provide a means of assessing the environmental condition of the organization to prevent health risks.
- **3** *Environmental justice* is a new term for describing the disproportionate distribution of environmental risks in minority and low-income communities. Federal attention is now being focused on environmental and human health conditions in these areas, with the goal of achieving equality of environmental protection for all communities.
- 4 *Environmental ethics* relates to rules of proper environmental conduct (see previous chapter for details.)

This chapter is not intended to be all-encompassing. Rather, it is to be used as a starting point. References are provided throughout that provide more detailed information on each topic.

HEALTH RISK ASSESSMENT⁽²⁻⁴⁾

There are many definitions for the word *risk*. It can be described as a triplet combination of event, probability, and consequences. It can also be described as a measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury. People face all kinds of risks everyday, some voluntarily and others involuntarily. Therefore, risk plays a very important role in today's world. Studies on cancer caused a turning point in the world of risk because it opened the eyes of risk scientists and health professionals to the world of risk assessments.

Since 1970, the field of risk assessment has received widespread attention within both the scientific and regulatory committees. It has also attracted the attention of the public. Properly conducted risk assessments have received fairly broad acceptance, in part because they put into perspective the terms toxic, hazard, and risk. Toxicity is an inherent property of all substances. It states that all chemical and physical agents can produce adverse health effects at some dose or under specific exposure conditions. In contrast, exposure to a chemical has the capacity to produce a particular type of adverse effect. Risk, however, is the probability or likelihood that an adverse outcome will occur in a person or a group that is exposed to a particular concentration or dose of the hazardous agent. Therefore, risk is generally a function of exposure or dose. Consequently, health risk assessment is defined as the process or procedure used to estimate the likelihood that humans or ecological systems will be adversely affected by a chemical or physical agent under a specific set of conditions.⁽⁵⁾

The term risk assessment is not only used to describe the likelihood of an adverse response to a chemical or physical agent, but it has also been used to describe the likelihood of any unwanted event. This subject is treated in more detail in the next section. These include risks such as: explosions or injuries in the workplace; natural catastrophes; injury or death due to various voluntary activities such as skiing, sky-diving, flying, and bungee jumping; diseases; death due to natural causes; and many others.⁽⁶⁾

Risk assessment and risk management are two different processes but they are intertwined. Risk assessment and risk management give a framework not only for setting regulatory priorities but also for making decisions that cut across different environmental areas. Risk management refers to a decision-making process that involves such considerations as risk assessment, technology feasibility, economic information about costs and benefits, statutory requirements, public concerns, and other factors. Therefore, risk assessment supports risk management in that the choices on whether and how much to control future exposure to the suspected hazards may be determined.

Regarding both risk assessment and risk management, this section will primarily address this subject from a health perspective. The next section will primarily address this subject from a safety and accident perspective.

The reader should note that two general types of potential health risk exist. These are classified as:

- 1 *Acute.* Exposures that occur for relatively short periods of time, generally from minutes to one or two days. Concentrations of (toxic) air contaminants are usually high relative to their protection criteria. In addition to inhalation, airborne substances might directly contact the skin, or liquids and sludges may be splashed on the skin or into the eyes, leading to adverse health effects. This subject area falls, in a general sense, in the domain of hazard risk assessment (HZRA).
- **2** *Chronic.* Continuous exposure occurring over long periods of time, generally several months to years. Concentrations of inhaled (toxic) contaminants are usually relatively low. This subject area falls in the general domain of health risk assessment (HRA) and it is this subject that is addressed in this section. Thus, in contrast to the acute (short-term) exposures that predominate in hazard risk assessment, chronic (long-term) exposures are the major concern in health risk assessments.

Health risk assessments provide an orderly, explicit, and consistent way to deal with scientific issues in evaluating whether a problem exists and what the magnitude of the problem may be. This evaluation typically involves large uncertainties because the available scientific data are limited and the mechanisms for adverse health impacts or environmental damage are only imperfectly understood. When one examines risk, how does one decide how safe is safe or how clean is clean? To begin with, one has to look at both sides of the risk equation; that is, both the toxicity of a pollutant and the extent of public exposure. Information is required at both the current and potential exposure, considering all possible exposure pathways. In addition to human health risks, one needs to look at potential ecological or other environmental effects. In conducting a comprehensive risk assessment, one should remember that there are always uncertainties and these assumptions must be included in the analysis.

Risk Evaluation Process for Health

In recent years, several guidelines and handbooks have been produced to help explain approaches for doing health risk assessments. As discussed by a special National Academy of Sciences committee convened in 1983, most human or environmental health hazards can be evaluated by dissecting the analysis into four parts: health (problem) identification, dose-response assessment or toxicity assessment, exposure assessment, and risk characterization (see Figure 22.1). For some perceived problems, the risk assessment might stop with the first step, identification, if no adverse effect is identified or if an agency elects to take regulatory action without further analysis. Regarding identification, a problem is defined as a toxic agent or a set of conditions that has the potential to cause adverse effects to human health or the environment. Identification involves an evaluation of various forms of information in order to identify the different problems. Dose-response or toxicity assessment is required in an overall assessment: responses/effects can vary widely since all chemicals and contaminants vary in their capacity to cause adverse effects. This step frequently requires



Figure 22.1 The health risk evaluation process.

that assumptions be made to relate experimental data for animals and humans. Exposure assessment is the determination of the magnitude, frequency, duration, and routes of exposure of human populations and ecosystems. Finally, in risk characterization, toxicology and exposure data/information are combined to obtain a qualitative or quantitative expression of risk.

Risk assessment involves the integration of the information and analysis associated with the above four steps to provide a complete characterization of the nature and magnitude of risk and the degree of confidence associated with this characterization. A critical component of the assessment is a full elucidation of the uncertainties associated with each of the major steps. Under this broad concept of risk assessment are encompassed all of the essential problems of toxicology. Risk assessment takes into account all of the available dose-response data. It should treat uncertainty not by the application of arbitrary safety factors, but by stating them in quantitatively and qualitatively explicit terms, so that they are not hidden from decision-makers. Risk assessment, defined in this broad way, forces an assessor to confront all the scientific uncertainties and to set forth in explicit terms the means used in specific cases to deal with these uncertainties.⁽⁷⁾

HAZARD RISK ASSESSMENT^(2-4,8)

Risk evaluation of accidents serves a dual purpose. It estimates the probability that an accident will occur and also assesses the severity of the consequences of an accident. Consequences may include damage to the surrounding environment, financial loss, or injury to life. This section is primarily concerned with the methods used to identify hazards and the causes and consequences of accidents. Issues dealing with health risks have been explored in the previous section. Risk assessment of accidents provides an effective way to help ensure either that a mishap does not occur or that the likelihood of an accident is reduced. The result of the risk assessment allows concerned parties to take precautions to prevent an accident before it happens.

Regarding definitions, the first thing an individual needs to know is what exactly is an accident. An accident is an unexpected event that has undesirable consequences. The causes of accidents have to be identified in order to help prevent accidents from occurring. Any situation or characteristic of a system, plant, or process that has the potential to cause damage to life, property, or the environment is considered a hazard. A hazard can also be defined as any characteristic that has the potential to cause an accident. The severity of a hazard plays a large part in the potential amount of damage a hazard can cause if it occurs as noted earlier. Risk is the probability that human injury, damage to property, damage to the environment, or financial loss will occur. An acceptable risk is one whose probability is unlikely to occur during the lifetime of the plant or process. An acceptable risk can also be defined as an accident that has a high probability of occurring but with negligible consequences. Risks can be ranked qualitatively in categories of high, medium, and low. Risk can also be ranked quantitatively as an annual number of fatalities per million affected individuals. This is normally denoted as a number per one million, for example, 3×10^{-6} . This number indicates that on average, three workers will die every year

out of one million individuals. Another quantitative approach that has become popular in industry is the Fatal Accident Rate (FAR) concept. This determines or estimates the number of fatalities over the lifetime of 1000 workers. The lifetime of a worker is defined as 10^5 hours, which is based on a 40-hour work week for 50 years. A reasonable FAR for a chemical plant is 3.0 with 4.0 usually taken as a maximum. A FAR of 3.0 means that there are 3 deaths for every 1000 workers over a 50-year period. Interestingly, the FAR for an individual at home is approximately 3.0. Some of the Illustrative Examples in this chapter compliment many of the hazard concepts described below with technical calculations and elaborations.

Risk Evaluation Process for Accidents

As with Health Risk Assessment (HRA), there are four key steps involved in a Hazardous Risk Assessment (HZRA). These are presented in Figure 22.2. A more detailed flowchart is presented in Figure 22.3 if the system in question is a chemical plant. These steps are detailed below:

- 1 A brief description of the equipment and chemicals used in the plant is needed.
- **2** Any hazard in the system has to be identified. Hazards that may occur in a chemical plant include:
 - a Fire
 - b Toxic vapor release
 - c Slippage
 - d Corrosion
 - e Explosions
 - f Rupture of a pressurized vessel
 - g Runaway reactions
- **3** The event or series of events that will initiate an accident has to be identified. An event could be a failure to follow correct safety procedures, improperly repaired equipment, or a safety mechanism.
- **4** The probability that the accident will occur has to be determined. For example, if a chemical plant has a given life, what is the probability that the temperature in a reactor will exceed the specified temperature range? The probability can be ranked from low to high. A low probability means that it is unlikely for the event to occur in the life of the plant. A medium probability suggests that there is a possibility that the event will occur. A high probability means that the event will probably occur during the life of the plant.
- **5** The severity of the consequences of the accident must be determined.
- **6** The information from steps 4 and 5 are combined. If the probability of the accident and the severity of its consequences are low, then the risk is usually deemed acceptable and the plant should be allowed to operate. If the probability of occurrence is too high or the damage to the surrounding area is too great, then the risk is usually unacceptable and the system needs to be modified to minimize these effects.



Figure 22.2 Hazard risk assessment flowchart.



Figure 22.3 Chemical plant hazard risk assessment flowchart.

The heart of the hazard risk assessment algorithm provided is enclosed in the dashed box of Figure 22.3. The algorithm allows for re-evaluation of the process if the risk is deemed unacceptable (the process is repeated starting with either step 1 or 2).

As is evident from the lessons of past accidents, it is essential for industry to abide by stringent safety procedures. The more knowledgeable the personnel, from the management to the operators of a plant, and the more information that is available to them, the less likely a serious incident will occur. The new regulations, and especially Title III of CERCLA, will help to ensure that safety practices are up to standard.^(1,8) However, these regulations should only provide a minimum standard. It should be up to the companies, and specifically the plants, to see that every possible measure is taken to ensure the safety and well-being of the community and the environment in the surrounding area. It is also up to the community itself, under Title III, to be aware of what goes on inside local industry, and to prepare for any problems that might arise.

APPLICATIONS

The remainder of this chapter is devoted to Illustrative Examples, many of which contain technical development material. A good number have been drawn from National Science Foundation (NSF) literature^(9–14) and two other sources.^(15,16) The last example provides a detailed analysis of both health and hazard risk assessment.

ILLUSTRATIVE EXAMPLE 22.1

Explain why a large open bottle of a liquid waste with a finite vapor pressure ultimately fills the room with the odor of that waste.

SOLUTION: Through the process of mass transfer, the waste evaporates from the open bottle because of its vapor pressure. Then it diffuses through the air in the room from locations of high concentrations (e.g., at the mouth of the open bottle), to locations of lower concentrations (e.g., at the far ends of the room). Diffusion will continue throughout the room. Given the sensitivity of the human nose plus the nature of the waste evaporated, the odor of waste would then be detected throughout the room.

ILLUSTRATIVE EXAMPLE 22.2

A 10^6 gal/day (1.0 MGD) wastewater from a treatment plant contains 0.2 mg suspended solids (SS) per cubic meter of wastewater. The separated sludge from the plant consists of the SS. If 10% by weight of lime is required to stabilize the sludge treatment and 80% of the solids are captured, calculate the daily and annual lime requirements.

SOLUTION: The sludge flow rate is

 $\dot{m}_{\rm S} = (0.2)(10^6)(8.34)/(1000)$ = 1668 lb/day

The treated sludge is

$$\dot{m}_{\rm TS} = (0.8)(1668)$$

= 1334 lb/day

The lime requirement is therefore

$$\dot{m}_{\rm L} = (0.1)(1334)$$

= 133.4 lb/day

The annual requirement is

$$\dot{m}_{\rm L} = (133.4)(365)$$

= 48,691 lb/yr

ILLUSTRATIVE EXAMPLE 22.3

Estimate the required landfill area for a community with a population of 260,000. Assume that the following conditions apply:

- 1 Solid waste generation = $7.6 \text{ lb/capita} \cdot \text{day}$
- 2 Compacted specific gravity (density) of solid wastes in landfall = 830 lb/yd^3
- **3** Average site depth of compacted solid wastes = 20 ft

SOLUTION: Determine the daily solid wastes generation rate in tons per day:

Generation rate =
$$\frac{(260,000 \text{ people})(7.6 \text{ lb/capita} \cdot \text{day})}{2000 \text{ lb/ton}}$$
$$= 988 \text{ ton/day}$$

The required area is determined as follows:

Volume required/day =
$$\frac{(988 \text{ ton/day})(2000 \text{ lb/ton})}{830 \text{ lb/yd}^3}$$
$$= 2381 \text{ yd}^3/\text{day}$$

Area required/yr =
$$\frac{(2381 \text{ yd}^3/\text{day})(365 \text{ day/yr})(27 \text{ ft}^3/\text{yd}^3)}{(20 \text{ ft})(43,650 \text{ ft}^2/\text{acre})}$$
$$= 26.88 \text{ acre/yr}$$

Area required/day =
$$\frac{(2381 \text{ yd}^3/\text{day})(27 \text{ ft}^3/\text{yd}^3)}{(20 \text{ ft})(43,650 \text{ ft}^2/\text{acre})} = 26.88/365$$

= 0.074 acre/day

The actual site requirements will be greater than the value computed because additional land is required for a buffer zone, office and service building, access roads, utility access, etc. Typically, this allowance varies from 20–40%. Thus, if an allowance of 30% over the lifetime of the facility is employed, the daily area requirement becomes

Area required/day =
$$(0.074)(1.3)$$

= 0.096 acre/day



Figure 22.4 Flow diagram for Illustrative Example 22.4.

A more rigorous approach to the determination of the required landfill area involves consideration of the contours of the completed landfill and the effects of gas production and overburden compaction.

ILLUSTRATIVE EXAMPLE 22.4

A liquid stream contaminated with a pollutant is being cleansed with a stripping control device. If the liquid has 600 ppm of pollutant and it is permissible to have 50 ppm of this pollutant in the discharge stream, what fraction of the liquid can bypass the control device?

SOLUTION: Using a basis of 1 lb of liquid fed to the control device, the flow diagram in Figure 22.4 applies.

Note that:

B = fraction of liquid bypassed 1 - B = fraction of liquid treated

Performing a pollutant balance around point 2 in Figure 22.4 yields

$$(1 - B)(0) + 600B = (50)(1.0)$$

Solving gives

$$B = 0.0833$$

Note that in some operations, a process does a more complete job than is required. For example, if moist air is passed through a fresh silica gel dryer, the air will leave the system almost bone dry. If it were desirable to have air containing some moisture, one would have to reintroduce water vapor into the air. This would be a wasteful process compared to bypassing the proper amount of original moist air. In general, a finished product is made only as good as it has to be to meet competition and/or to satisfy the user. "Product quality giveaway" is costly and is often minimized by bypassing.

ILLUSTRATIVE EXAMPLE 22.5

A municipality in the Midwest has a population of 50,000 and generates 100,000 yd³ of municipal waste annually. The waste is made up of 30% compacted waste and 70% uncompacted waste. Assume that the waste has a density of 1000 lb/yd³ compacted and 400 lb/yd³ uncompacted. How many pounds of waste are generated by this city each year and by each person each year?

SOLUTION: Based on the waste densities given in the problem statement, the following generation rates are determined:

Waste generated/yr =
$$(0.3)(100,000 \text{ yd}^3)(1000 \text{ lb/yd}^3)$$

+ $(0.7)(100,000 \text{ yd}^3)(400 \text{ lb/yd}^3)$
= $30,000,000 \text{ lb} + 28,000,000 \text{ lb}$
= $58,000,000 \text{ lb/yr}$
Per capita generation rate = $\frac{58,000,000 \text{ lb/yr}}{50,000 \text{ people}}$
= $1160 \text{ lb/person} \cdot \text{yr}$
= $3.2 \text{ lb/person} \cdot \text{day}$

ILLUSTRATIVE EXAMPLE 22.6

An incinerator burns mercury-contaminated waste. The waste material has an ash content of 1%. The solid waste feed rate is 1000 lb/h and the gas flow rate is 20,000 dscfm. It is reported that the average mercury content in the particulates was $2.42 \,\mu g/g$ when the vapor concentration was 0.3 mg/dscm. For the case where incinerator emissions meet the particulate standard of 0.08 gr/dscf (0.1832 g/dscm) with a 99.5% efficient electrostatic precipitator (ESP), calculate the amount of mercury bound to the fly ash that is captured in the ESP in lb/day.

SOLUTION: The amount of ash leaving the stack is

$$\left(\frac{0.08 \text{ gr}}{\text{dscf}}\right) \left(\frac{1 \text{ lb}}{7000 \text{ gr}}\right) \left(\frac{20,000 \text{ dscf}}{1 \text{ min}}\right) \left(\frac{60 \text{ min}}{h}\right) \left(\frac{24 \text{ h}}{\text{day}}\right) = 329 \text{ lb/day}$$

The amount of ash collected in the ESP is

(329 lb/day)/(1 - 0.995 collected) = 65,800 lb/day

ILLUSTRATIVE EXAMPLE 22.7

Refer to the previous example. Calculate the amount of mercury leaving the stack as a vapor and with the fly ash in grams/day.

SOLUTION: The amount of mercury leaving the stack with the fly ash is

$$(329 \text{ lb ash/day})(2.42 \times 10^{-6} \text{ g Hg/g ash}) = 7.96 \times 10^{-4} \text{ lb Hg/day}$$

= 0.361 g Hg/day

The amount of mercury leaving the stack as vapor is

$$\left(\frac{0.3 \times 10^{-3} \text{ g Hg}}{\text{dscm}}\right) \left(\frac{20,000 \text{ dscf}}{1 \text{ min}}\right) \left(\frac{1 \text{ m}^3}{35.3 \text{ ft}^3}\right) \left(\frac{60 \text{ min}}{\text{h}}\right) \left(\frac{24 \text{ h}}{\text{day}}\right) = 244.8 \text{ g/day}$$

Total mercury leaving the stack = 244.8 + 0.361
= 245.2 g/day

ILLUSTRATIVE EXAMPLE 22.8

Some wastewater and water standards and regulations are based on a term defined as *parts per million* (ppm) or *parts per billion* (ppb). Define the two major classes of these terms and describe the inter-relationship from a calculational point-of-view. Also convert 10 calcium parts per million parts of water on a mass basis to parts per million on a mole basis.

SOLUTION: A water stream seldom consists of a single component. It may also contain two or more phases (a dissolved gas and/or suspended solids), or a mixture of one or more solutes. For mixtures of substances, it is convenient to express compositions in mole fractions or mass fractions. The following definitions are often used to represent the composition of component A in a mixture of components:

$$w_{A} = \frac{\text{mass of A}}{\text{total mass of water stream}} = \text{mass fraction of A}$$
$$y_{A} = \frac{\text{moles of A}}{\text{total moles of water stream}} = \text{mole fraction of A}$$

Trace quantities of substances in water streams are often expressed in parts per million (ppmw) or as parts per billion (ppbw) on a mass basis. These concentrations can also be provided on a mass per volume basis for liquids and on a mass per mass basis for solids. Gas concentrations are usually represented on a mole or volume basis (e.g., ppmm or ppmv). The following equations apply:

$$ppmw = 10^{6} w_{A}$$
$$= 10^{3} ppbw$$
$$ppmv = 10^{6} y_{A}$$
$$= 10^{3} ppbv$$

The two terms ppmw and ppmm are related through the molecular weight.

To convert 10 ppmw Ca to ppmm, select a basis of 10^6 g of solution. The mass fraction of Ca is first obtained by the following equation:

Mass of Ca = 10 g
Moles Ca =
$$\frac{10 \text{ g}}{40 \text{ g/mol}} = 0.25 \text{ mol}$$

Moles H₂O = $\frac{10^6 \text{ g} - 10 \text{ g}}{18 \text{ g/mol}} = 55,555 \text{ mol}$
Mole fraction Ca = $y_{Ca} = \frac{0.25 \text{ mol}}{0.25 \text{ mol} + 55,555 \text{ mol}} = 4.5 \times 10^{-6}$
ppmm of Ca = $10^6 y_{Ca}$
= $(10^6)(4.5 \times 10^{-6})$
= 4.5

ILLUSTRATIVE EXAMPLE 22.9

Calculate the Theoretical Chemical Oxygen Demand (ThCOD) of a 100 mg/L solution of glucose. Also calculate the total organic content.^(15,16)

SOLUTION: First, balance the chemical equation for the reaction of glucose and oxygen:

 $C_6H_{12}O_6+6O_2\rightarrow 6CO_2+6H_2O$

Second, determine the oxygen/substrate stoichiometric ratio for the oxygen reaction:

Ratio = (6)(32)/[(1)(180)]= 0.067 mg O₂/mg glucose

Third, calculate the ThCOD for a 100-mg/L solution of glucose. This is equal to the product of the mass concentration of glucose and the stoichiometric ratio:

$$ThCOD = (100 \text{ mg glucose/L})(1.067 \text{ mg } O_2/\text{mg glucose})$$
$$= 106.7 \text{ mg } O_2/\text{L or } 106.7 \text{ mg COD/L}$$

ILLUSTRATIVE EXAMPLE 22.10

The following 5-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS) data were collected from a clarifier at a local municipal wastewater treatment plant over a 7-day period.^(15,16) The National Pollutant Discharge Elimination System (NPDES)^(15,16) permit limitations for BOD₅ and TSS effluent concentrations from this wastewater treatment plant are 45 mg/L on a 7-day average. Based on this information (see Table 22.1), is the treatment plant within its NPDES permit limits?

SOLUTION: The BOD₅ 7-day average concentration based on the data tabulated in the problem statement is

$$(BOD_5)_7 = (45 + 79 + 64 + 50 + 30 + 25 + 21)/7$$

= 44.9 mg/L

Concentration Data Collected Over a 7-Day Period at a Municipal Wastewater Treatment Plant		
Day	BOD (mg/L)	TSS (mg

 Table 22.1
 Daily BOD₅ and TSS Effluent

Day	BOD (mg/L)	TSS (mg/L)	
1	45	20	
2	79	100	
3	64	50	
4	50	42	
5	30	33	
6	25	25	
7	21	15	

The 7-day average concentration for TSS is

$$(TSS)_7 = (20 + 100 + 50 + 42 + 33 + 25 + 15)/7$$

= 40.7 mg/L

The wastewater treatment plant is still within its NPDES permit limit (but only marginally) of an average 7-day maximum concentration of 45 mg/L for both BOD_5 and TSS.

ILLUSTRATIVE EXAMPLE 22.11

The average gasoline tank in an automobile has a 14-gal capacity. Every time the gas tank is filled, the vapor space in the tank is displaced to the environment. Since all forms of hydrocarbons in the atmosphere contribute to the formation of ozone and need to be controlled, this problem attempts to quantify some of these emissions.

Assume the automobile tank vapor space, the air, and the gasoline supply is all at 20° C. The vapor space is saturated with gasoline. The vapor-phase mole fraction of gasoline under these conditions is approximately 0.4. The lost vapor has a molecular weight of about 70 g/gmol and a *liquid* specific gravity of 0.62.

- 1 Calculate the amount of gasoline (in gallons of liquid) that is lost to the air during a 10-gal fill.
- **2** How much is lost annually from 50 million cars filled once each week with 10 gal of gasoline.

SOLUTION: The vapor specific volume in m³/kgmol is

$$\frac{V}{n} = \frac{RT}{P}$$

= $\frac{(8.314)(293)}{101.3}$
= 24.05 m³/kgmol

The amount of gasoline vapor in the tank in kgmol is

$$n = \frac{(0.4)(10 \text{ gal})}{(264.1 \text{ gal/m}^3)(24.05 \text{ m}^3/\text{kgmol})}$$
$$= 6.298 \times 10^{-4} \text{ kgmol}$$

The liquid volume of the gasoline vapor in the tank in gallons is

$$V_1 = \frac{(6.298 \times 10^{-4} \text{ kgmol})(70 \text{ kg/kgmol})(264.1 \text{ gal/m}^3)}{(0.62 \times 1000 \text{ kg/m}^3)}$$

= 0.01878 gal

The gasoline loss in gallons per car per year can now be calculated:

$$Lost = (0.01878 \text{ gal/fill})(52 \text{ fills/yr})$$
$$= 0.976 \text{ gal/car} \cdot \text{yr}$$

The estimated annual loss (AL) arising because of the vapor displaced during filling is

$$AL = [0.976 \text{ gal/(car \cdot yr)}](50,000,000 \text{ cars})$$
$$= 4.88 \times 10^7 \text{ gal/yr}$$

ILLUSTRATIVE EXAMPLE 22.12

Describe the two methods utilized to perform an exposure assessment.

SOLUTION: The two methods by which an exposure assessment is performed are by direct measurement and computer modeling. Direct measurement involves using receptors or analyzers placed at various locations around a specific area to measure the time-averaged concentration of an agent. Computer models are utilized to predict possible pathways of exposure, generally from a point source release.

ILLUSTRATIVE EXAMPLE 22.13

Discuss the significance of Figure 22.5.

SOLUTION: The figure below allows one to compare the relative cost of the detriment (associated with an accident) with the cost of improved protection. As can be seen on the graph, for low levels of cost protection, the costs are unreasonably high. However, for high levels of cost protection, the cost of detriment is significantly low. Therefore, a cost-benefit analysis should be performed in order to determine a reasonable cost for an acceptable level of protection while keeping the detrimental costs to a minimum. From a plant's perspective, the level of protection should be set in or around A. From a purely economic point-of-view, this point roughly represents the minimum cost. Other factors such as regulatory requirements, good will, and so on, can change this. See Chapter 18 for additional details on economic considerations.



Level of protection; adsorber explosion



ILLUSTRATIVE EXAMPLE 22.14

Two factory workers at a nail polish manufacturering facility are exposed to acetone at the following concentrations and durations:

Employee A	Employee B	
1000 ppm for 180 minutes	2000 ppm for 120 minutes	
500 ppm for 120 minutes	700 ppm for 180 minutes	
200 ppm for 180 minutes		

The 8-hour time-weighted average (TWA) acetone exposure limits for the American Conference of Government Industrial Hygienists (ACGIH), Occupational Health and Safety Administration (OSHA), and the National Institute of Occupational Safety and Health (NIOSH) are 250 ppm, 750 ppm, and 250 ppm, respectively. Calculate each worker's respective 8-hour TWA exposure. What do these results indicate about the worker's exposure at the company?

SOLUTION: Determine the 8-hour TWA exposure, *E*, for each employee:

$$E \text{ (Employee A)} = (C_1T_1 + C_2T_2 + \cdots + C_nT_n)/8$$

= [(1000)(3) + (500)(2) + (200)(3)]/8
= 575 ppm
$$E \text{ (Employee B)} = (C_1T_1 + C_2T_2) + \cdots + C_nT_n)/8$$

= [(2000)(2) + (700)(3) + (0)(3)]/8
= 763 ppm

Compare each employee's calculated 8-hour TWA exposure to the limits established by each reference source.

Employee A's 8-hour TWA exposure level is below the OSHA permissible exposure level (PEL) and above both the ACGIH recommended exposure limit (REL) and NIOSH threshold limit value (TLV). Employee B's 8-hour TWA exposure level is above all three reference sources. Since the OSHA PELs are the only legally enforceable standards, administrative actions/engineering controls to reduce the air quality concentrations of acetone in the work area or to reduce the time of exposure are required by law. If the employee's time of exposure is reduced, consideration should also be given to exceedance of OSHA short-term exposure limit (STEL) concentrations.

ILLUSTRATIVE EXAMPLE 22.15

Discuss exposure guidelines.

SOLUTION: The exposure guidelines discussed above are primarily based on industrial custom, toxicological studies, human exposure data, or a combination of these. The guidelines were developed for workers in an industrial environment and, in certain states, for municipal employees. Thus, they are not meant to be used for general air quality levels for exposure to the public. Furthermore, there is a limitation on the use of the exposure guidelines as a relative index of toxicity because the exposure limits are based on different effects for different chemicals. For example, the TLV-TWA for acetone is chosen to prevent irritation to the eyes and respiratory system, while the TLV-TWA for acrylonitrile is chosen to reduce the risk of cancer.

Exposures to these chemicals at other concentration levels could lead to other deleterious effects. Thus, when evaluating the risk of chemical exposure, all toxicological data should be thoroughly reviewed and evaluated.

ILLUSTRATIVE EXAMPLE 22.16

Two large bottles of flammable solvent were ignited by an undetermined ignition source after being knocked over and broken by a janitor while cleaning a 10 ft \times 10 ft \times 10 ft research laboratory. The laboratory ventilator was shut off and the fire was fought with a 10 lb CO₂ fire extinguisher. As the burning solvent had covered much of the floor area, the fire extinguisher was completely emptied in putting the fire out.

The Immediate Danger to Life or Health (IDLH) level for CO_2 set by NIOSH is 50,000 ppm. At that level, vomiting, dizziness, disorientation, and breathing difficulties occur after a 30-minute exposure. At a 10% level (100,000 ppm), death can occur after a few minutes even if the oxygen in the atmosphere would otherwise support life.

Calculate the concentration of CO_2 in the room after the fire extinguisher is emptied. Does it exceed the IDLH value? Assume that the gas mixture in the room is uniformly mixed, that the temperature in the room is $30^{\circ}C$ (warmed by the fire above the normal room temperature of $20^{\circ}C$) and that the ambient pressure is 1 atm.

SOLUTION: First, calculate the number of moles of CO₂ discharged by the fire extinguisher:

moles of CO₂ = (10 lb CO₂)(454 g/lb)/(44 g/gmol CO₂) = 103 gmol CO₂

Calculate the volume of the room:

Room volume =
$$(10 \text{ ft})(10 \text{ ft})(10 \text{ ft})(0.0283 \text{ m}^3/\text{ft}^3)$$

= 28.3 m³

Next, calculate the total number of moles of gas in the room:

moles of gas =
$$PV/RT$$

= (1 atm)(28,300 L)/(0.08206 atm · L/gmol · K)(303 K)
= 1138 gmol gas

Calculate the concentration, or mole fraction, of CO_2 in the room:

mole fraction = gmol
$$CO_2/gmol$$
 gas
= 103 gmol $CO_2/1138$ gmol gas
= 0.0905

Convert this fraction to a percent and compare to the IDLH and lethal levels:

$$%CO_2 = (mole fraction)(100)$$

= (0.0905)(100)
= 9.05%

The IDLH level is 5.0% and the lethal level is 10.0%. Therefore, the level in the room of 9.05% does exceed the IDLH level for CO₂. It is also dangerously close to the lethal level. The person extinguishing the fire is in great danger and should take appropriate safety measures.

ILLUSTRATIVE EXAMPLE 22.17

Briefly describe HAZOP and HAZAN.

SOLUTION: A Hazard and Operability (HAZOP) Study is a systematic approach to recognizing and identifying possible hazards that may cause the failure of a piece of equipment or part of a process system in a new or existing facility. This qualitative enterprise is primarily conducted by a team of technical experts in plant design and operation. A HAZOP study may be applied to operating process plants or it may be performed at various stages throughout the design. An early start will lead to a safer, more efficient design, and ultimately, higher profits.

Before any action is taken, the goals of the study should be defined. There are five objectives to most HAZOP studies:

- 1 To identify areas of the design that may possess a significant hazard potential.
- **2** To identify and study features of the design that influence the probability of a hazardous incident occuring.
- **3** To familiarize the study team with the design information available.
- **4** To ensure that a systematic study is made of the areas of significant hazard potential.
- 5 To identify pertinent design information not currently available to the team.

The recommended procedure for implementing a HAZOP study is as follows. The section of the process to be studied is first identified; generally, the focus is on a major piece of equipment although a pump or a valve may be chosen depending on the hazardous nature of the materials being handled and the operating conditions. Once the intended operation has been defined, a list of possible deviations from the intended operations is developed. The degrees of deviation from normal operation are conveyed by the use of *guide words*, some of which are listed below. The purpose of these guide words is to develop the thought process and encourage discussion that is related to any potential deviations in the system. When a possible deviation is recognized, the possible causes and consequences are determined. Alterations and appropriate action to be taken are then recommended. Final steps in the methodology include issuing formal reports and following up on recommendations.

Guide words	Meaning	Examples
No or not	No part of the intention is achieved, but nothing else happens.	No flow, no agitation, no reaction.
More or less	Quantitative increases or decreases to the intended activity.	More flow, higher pressure, lower temperature, less time.
As well as	All of the intention is achieved, but some additional activity occurs.	There is an additional component, contaminant, extra phase.
Part of	Only part of the intended is achieved; part is not.	Component omitted, part of multiple destinations omitted.
Reverse	The opposite of the intention occurs.	Reverse flow, reverse order of addition.
Other than	No part of the intention is achieved. Something different happens.	Wrong component, startup, shutdown, utility failure.

After the serious hazards have been identified via a HAZOP study or some other qualitative approach, a quantitative examination should be performed. Hazard quantification or *hazard analysis* (HAZAN) involves the estimation of the expected frequencies or probabilities of events with adverse or potentially adverse consequences. It logically ties together historical occurrences, experience, and imagination. Once a hazard has been identified, an *event tree* and *fault tree* analysis may be used to evaluate the causes and consequences, and mitigate the possible effects.

Event tree analyses (ETA) are used to represent possible failure sequences and to analyze the sequence of events that lead to an accident or failure. When the potential hazard has been identified, an analysis of the consequences can be initiated by selecting an appropriate model. The event tree model is started from the initial occurrence and built upon by sequencing the possible events and safety systems that come into play. The model displays at a glance branches of events that relate the proper functioning or failure of a safety device or system and the ultimate consequence. The model also allows quick identification of the various hazards that can result from the single initial event.

Fault tree analysis (FTA) begins with the ultimate consequences and works backward to the possible cause and failures. It is based on the most likely or most credible events that lead to the accident. FTA demonstrates the mitigating or reducing effects and can include causes stemming from human error as well as equipment failure. The task of constructing a fault tree is tedious and requires a probability background to handle common failures.

ILLUSTRATIVE EXAMPLE 22.18

A storage tank at a refinery contains a large volume of contaminated oil waiting to be processed via distillation. The tank is protected against emissions of vapors by a nitrogen blanket. In the event that the nitrogen blanket fails, there is a vent system that includes a canister of activated carbon to adsorb toxic fumes from the vented gas. The tank itself is situated on a high-traffic plant area and is in danger of tank failure resulting from collisions with vehicles improperly operated by plant personnel. *Annual failure rate estimates* are given below for the (hazardous) oil storage tank subjected to a variety of scenarios:

From vent	
Nitrogen blanket, and	0.05/y
Adsorbent canister	0.05/y
Tank rupture, or	
Truck collision, or	
Driver on drugs out, or	0.1/y
Driver drunk, or	0.8/y
Brakes fail, or	0.2/y
Metal fatigue, or	0.05/y
Earthquake	0.01/y
Tank overfill, or	0.25/y
Miscellaneous tank failure	0.3/y

Prepare a fault tree^(14,16) and calculate the overall failure rate for emissions from the storage tank. Which failure mode(s) is (are) most important in terms of potential hazard mitigation and should be addressed first? Use the principle that the failure rate for the independent events (across branches) is the sum (OR gate) of the probabilities, while for dependent events (down branches), the failure rate is the product (AND gate) of the probabilities.



Figure 22.6 Fault tree, Illustrative Example 22.18.

SOLUTION: Prepare a fault tree. See Figure 22.6.

Calculate the overall failure rate (OFR) for the emissions from the storage tank:

$$OFR = (0.1 + 0.8 + 0.2) + (0.01 + 0.05) + (0.25 + 0.3) = 1.71$$

Determine which failure mode is most important in terms of potential hazard mitigation:

emission < tank rupture < truck collision < driver drunk

The most significant contribution to failure is seen to be the hazard associated with drunken truck drivers. Mitigation of this hazard is a good place to start in the process of overall hazard reduction. Alcohol and substance abuse programs can provide a positive step toward mitigation of driver generated accidents. In addition, construction of a physical barrier between

the tank and the roadway would lower the frequency of toxic emissions drastically by preventing the collisions.

ILLUSTRATIVE EXAMPLE 22.19⁽¹⁸⁾

A risk assessment being conducted at a chemical plant is concerned with the consequences of two incidents that are defined as follows:

- **I.** A distillation column explosion resulting from detonation of an unstable chemical (ethylene oxide).
- **II.** A continuous 240 g/s release of the toxic chemical (ethylene oxide) at an elevation of 125 m.

Both incidents occur at approximately the same location in the plant.

Two weather conditions are envisioned, namely a northeast wind and a southwest wind (6.0 miles/h) with stability category "B". Associated with these two wind directions are events IIA, and IIB, respectively, defined as follows:

IIA: Toxic cloud to the southwest

IIB: Toxic cloud to the northeast

Based on an extensive literature search, the probabilities and conditional probabilities of the occurrence of the defined events in any given year are estimated as follows:

$$P(I) = 10^{-6}$$

$$P(II) = 1/33,333$$

$$P(IIA|II) = 0.33$$

$$P(IIB|II) = 0.67$$

The consequences of events I, IIA, and IIB, in terms of number of people killed, are estimated as follows:

- I: All persons within 200 meters of the explosion center are killed; all persons beyond this distance are unaffected.
- IIA: All persons in a pie-shaped segment 22.5 degrees width (downwind of the source) are killed if the concentration of the toxic gas is above 0.33 μ g/L; all persons outside of this area are unaffected.
- IIB: Same as IIA.

Three people are located within 200 m of the explosion center but not in the pie-shaped segment described above. Five people are located within the pie-shaped segment southwest of the discharge center; three are 350 m downwind, two are 600 m away at the plant fence (boundary). Another four people are located 500 m away outside the pie-shaped segment but within the plant boundary. All individuals are at ground level.

Calculate the average annual individual risk based on the number of individuals potentially affected. Also calculate the average risk based on all the individuals within the plant boundary. *Hint*: Perform atmospheric dispersion calculations at a distance of 300, 500, 800, 1000, 1500, and 2000 m from the emission source.



Figure 22.7 Plant personnel location.

SOLUTION: Draw a line diagram (see Figure 22.7) of the plant layout and insert all pertinent data and information.

An event tree for the process [including a possible (though negligible) vapor cloud explosion] is provided in Figure 22.8.

The probability of event IIA and event IIB occurring is:

$$P(IIA) = P(II)P(IIA|II) = (1/33,333)(0.33) = 1/100,000 = 10-5
$$P(IIB) = P(II)P(IIB|II) = (1/33,333)(0.67) = 2/100,000 = 2 × 10-5$$$$

Perform a dispersion calculation to determine the zones where the concentration of the nanochemical exceeds $0.33 \,\mu g/L$. Assume a continuous emission for a point source.



Figure 22.8 Event tree.

To maintain consistent units, convert wind speed from mi/h to m/s and concentration from $\mu g/$ L to g/m^3 :

$$\frac{0.33\,\mu\text{g}}{\text{L}} \frac{1\,\text{g}}{10^6\,\mu\text{g}} \frac{10^3\,\text{L}}{\text{m}^3} = 3.3 \times 10^{-4}\,\text{g/m}^3$$

$$\frac{6.0 \text{ mi}}{\text{h}} \quad \frac{5280 \text{ ft}}{\text{mi}} \quad \frac{\text{h}}{3600 \text{ s}} \quad \frac{0.3048 \text{ m}}{\text{ft}} = 2.68 \text{ m/s}$$

Set up the Pasquill-Gifford model using the data and calculations provided above.⁽¹⁷⁾

$$C(x, 0, 0, H) = m \exp[-0.5(H/\sigma_z)^2]/\pi \sigma_y \sigma_z u$$

	1			
<i>x</i> (m)	σ_{y} (m)	σ_{z} (m)	$C (g/m^3)$	
300	52	30	3.10×10^{-6}	
500	83	51	3.34×10^{-4}	
800	128	86	9.01×10^{-4}	
1000	156	110	8.71×10^{-4}	
1500	225	170	5.69×10^{-4}	
2000	295	235	3.57×10^{-4}	

Table 22.2 Dispersion Calculations

where

 $C = 3.3 \times 10^{-4} \text{ g/m}^3$ m = 240 g/su = 2.68 m/sH = 125 m $\sigma_y, \sigma_z = f(x)$

Employing the σ_y and σ_z values recommended in the literature for stability category "B",⁽¹⁷⁾ calculate the downwind concentrations that satisfy the Pasquill–Gifford equation. The results for the recommended downwind distances are shown in Table 22.2.

Note that the concentration goes through a maximum that is in excess of 0.33 μ g/L; thus, there are two solutions. A linear interpolation (or plotting the results on a graph) indicates that the maximum GLC is approximately 9.9×10^{-4} g/m³ and is located at a downwind distance of about 850 m. The "critical" zone is located between 500 m and 2175 m.

One may determine which individuals within the pie-shaped segment downwind from the source will be killed if either Accident I or II occurs. Refer to the problem statement or Figure 22.7. One can conclude that three individuals within the 200 m radius will die from Accident I. Two individuals located in the pie-shaped segment and 600 m southwest of the emission source will die from Accident II.

The total annual risk (TAR) for the process may now be determined. The total risk, measured in terms of the average annual total number of people killed, is obtained by multiplying the number of people in each impact zone by the sum of the probabilities of the events affecting that zone, and summing the results:

TAR = (3)P(I) + (2)P(IIA)
= (3)(10⁻⁶) + (2)(10⁻⁵)
=
$$2.3 \times 10^{-5}$$

The average annual risk (AAR) based only on the "potentially affected" people can be calculated. The average annual individual risk for the eight people in the impact zone is obtained by dividing the total annual risk by 8. Since only eight people are "affected,"

$$AAR = 2.3 \times 10^{-5}/8$$

= 2.9 × 10⁻⁶

Finally, calculate the average annual individual risk for all the individuals within the plant (fence) boundary. The average is now based on 12 rather than eight individuals.

$$AAR = 2.3 \times 10^{-5}/12$$

= 1.9×10^{-6}

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