Indirect Risks to Human Health and Welfare

The Roman goddess of the hearth, Vestal, was worshiped in a temple that contained a perpetual fire, tended by six virgins. The Vestal Virgins were highly respected and took on demigod status within the community. Mortals were not allowed even to touch them. Occasionally, one of the Vestal Virgins fell from grace and had a liaison. When this violation was discovered, the offending Virgin was led to a deep underground cell, given some bread and water, and left to die. This punishment seemed to be a compromise between two strict rules: Do not touch a Vestal Virgin, and each Vestal Virgin must remain chaste or be put to death. By leaving her in an the underground cell to die, she was not touched by anyone and yet she paid for her transgression.

The lore of the Vestal Virgins illustrates that there are two ways to kill, be it a human being or any other living thing: by harming it directly, or killing it indirectly by removing the sustaining environment. In this chapter we argue that just engineers must consider the protection of our environment as a means for protecting human health and welfare, for present as well as future people.

RISK TO THE ENVIRONMENT

As a cynic might put it, the Corps has hired technical experts to turn mission-oriented sows' ears into ecological silk purses.

Lynton K. Caldwell, during one of the early National Environmental Policy Act court proceedings, as best remembered by Caldwell's former student, Timothy Kubiak¹

You have to hand it to the bureaucrats! Some seem to stop at nothing when trying to implement the objectives of particular programs. This can be a good thing if you agree with the mission, but in many instances, any effort not seen to be directly associated with the bureaucracy's purposes will be ignored or may even become the target of hostilities. There are parallels between Caldwell's quote above and what has occurred since issuance of an Executive Order mandating federal government agencies to embrace and to encourage environmental justice. Both the National Environmental Policy Act of 1970 (NEPA) and the Executive Order were bold statements that federal "business as usual" was falling short. NEPA was a recognition that many major projects were causing significant adverse environmental impacts; and the EJ Executive Order recognized that fed-

eral agencies had allowed disproportionate harm to be done to certain segments of society and had not adequately involved people from these communities in decisions that could have major effects on their quality of life.

The parallel can be drawn further. People tend to be *xenophobic;* they fear that which is different. Scientists and engineers are not exempt. In fact, we may be some of the worst and most difficult to convince that something needs change. Thomas S. Kuhn's thesis in his groundbreaking work *The Structure of Scientific Revolutions*² was that scientific paradigms, such as the move from Newtonian physics to relativity, come only after great consternation (even "violence") within the scientific community. In other words, scientists can be some of the most closed-minded people when it comes to carrying out their missions. So when we are asked to consider whether the systems that we have supported may somehow be working unfairly, we may be tempted to put some spin on our response. We are in effect trying to turn an unjust "sow's ear" into an environmental "silk purse." This is doubly wrong for scientists, since we are expected to be objective. We are called to work from factually sound premises.

Further, since we are trained for many years in our disciplines, we may be tempted to ignore or at least not to give proper credence to the views of the lay public. We may be insensitive, unsympathetic, and certainly not empathetic to the situations being encountered by the people affected by our designs. It is perilous to perceive that a decision is "just too complicated" for the general public. It is our responsibility to disclose the facts and to describe completely the various alternatives available. Again, this attention to details and full disclosure of the potential adverse effects from each alternative grew out of the environmental impact statement. The law and its regulations did not excuse federal agencies from fully disclosing and ensuring that the consequences, actual and potential, were completely understood by the affected public. In other words, the courts held that agency "experts" could not condescend. They must consider the people who could be affected as peers (or at least as fellow sojourners).

Although profit or corporate mission may come to mind first as examples of deluding the public and poorly communicating risks, the physical and environmental sciences have their share of intellectual deception. At a recent workshop of the National Academy of Engineering, John Ahearne, who served for seven years as executive director of Sigma Xi, the scientific research society, warned that scientists should never be arguing about the facts. Facts simply exist. We certainly must debate their meanings and give appropriate attention to their various interpretations, but we must not redefine facts simply to fit our paradigms. We may not like what the facts are telling us, but we must be objective if we are to follow the scientific method. We have seen students debate the ethics of full disclosure. In one recent debate, a number of environmental science students at Duke questioned the ethics of the findings of a journal article regarding sea turtles. Some students sympathized with Stephen Schneider, a Stanford University climatologist and former government advisor, who argued some years ago that scientists ought to "offer up scary scenarios, make simplified dramatic statements, and make little mention of any doubts we may have. Each of us has to decide what the right balance is between being effective and being honest."³ Ahearne argues, and we agree, that a distorted version of "utilitarian science" is dangerous. It violates a first canon of science, honest inquiry and reporting. The English philosopher of science C. P. Snow articulated this principle some 50 years ago: "The only ethical principle which has made science possible is that the truth shall be told all the time. If we do not penalise false statements made in error, we open up the way, don't you see, for false statements by intention. And of course a false statement of fact made deliberately, is the most serious crime a scientist can commit."⁴

Not every scientist and environmental professional buys this. The recent debate that precipitated the Duke student's quandary was actually over the seemingly innocuous field of biological taxonomy. The dialogues exposed the acceptance by some of the justification of using morally unacceptable means to achieve the greater good.⁵ The journal Conservation Biology published a number of scientific, philosophical, and ethical perspectives on whether to misuse science to promote the larger goal (conservation) to protect the black sea turtle (since the black and green turtles together would have sufficient numbers so as no longer to be considered "endangered"). Even though the taxonomy is scientifically incorrect (i.e., the black sea turtle is not a unique species), some writers called for a "geopolitical taxonomy."⁶ The analogy of war was invoked as a justification, with one writer declaring that "it is acceptable to tell lies to deceive the enemy." The debate moderators asked a telling question: Should legitimate scientific results then be withheld, modified, or spun to serve conservation goals? Continuing with the war analogy, some scientists likened the deceptive taxonomy to propaganda needed to prevent advances by the enemy. The problem is that, as Snow would put it, once you stop telling the truth, you have lost credibility as scientists, even if the deception is for a noble cause.⁷ Two writers, Kristin Shrader-Frechette and Earl D. McCoy, emphasized that credible science requires that "... in virtually all cases in professional ethics, the public has the right to know the truth when human or environmental welfare is at issue."8

Another example of late is the debate about global climate change, discussed later in this chapter. A particularly troublesome topic for many scientists is the role of nuclear power generation. For decades, many in the scientific and engineering communities have argued vociferously against the use of nuclear energy for weapons and its use as a source of energy. Nuclear weapons often boils down to differences of opinion of geopolitical issues, such as proliferation and the appropriateness of mutual destruction. Nuclear power generation is a different matter. Some scientists and engineers have resisted while others have supported the nuclear power plants. The public seems to support existing plants and are neutral to wary of new plants.⁹ These technological optimists argue that nuclear power is a reliable energy source and, with sufficient fail-safe measures, can provide an alternative to the dirty and unsafe fossil fuel sources.

In the past decade or so, with the increasing links (intellectual, if not necessarily scientific) between anthropogenic sources of greenhouse gases, especially carbon dioxide (CO_2) and increasing mean global temperatures, many in the scientific community have argued for curtailing the use of fossil fuels, especially in developed nations. However, pro-nuclear scientists see these findings as a requisite to revisit the need for nuclear power, since fission produces no CO_2 (there is no combustion, i.e., oxidation of a hydrocarbon). As in the case of the sea turtle taxonomy debate, scientists all too often revert to an advocacy position rather than one of objectivity. They know that nuclear power will produce long-lived radioactive by-products that will need to be stored for thousands of years. They also remember Chernobyl and fear similar accidents. But do these justify a full and open debate on whether nuclear power is a viable means of reducing the

emission of greenhouse gases? It is a challenge even to get some scientists to consider the issue, not as a geopolitical decision, but as an engineering, science, or mathematical problem.

If it is the responsibility of government to protect the lives of its citizens against foreign invasion or criminal assault, it is equally responsible for protecting the health and lives of its citizens from other potential dangers, such as falling bridges and toxic air pollutants. Government has a limited budget, however, and we expect that this money is distributed so as to achieve the greatest benefits to health and safety. If two chemicals provide the same public benefit, but are placing people at risk, it is rational that funds and effort be expended to eliminate the chemical that results in the greatest risk.

But is this what we really want? Suppose, for example, it is cost-effective to spend more money and resources to make coal mines safer than it is to conduct heroic rescue missions if accidents occur. It might be more risk-effective to put the money we have into safety, eliminate all rescue squads, and simply accept the few accidents that will still inevitably occur. But since there would no longer be rescue teams, the trapped miners would then be left on their own. The net effect would be, however, that overall, fewer coal miners' lives would be lost.

Even though this conclusion would be risk-effective, we would find it unacceptable. Human life is considered sacred. This does not mean that infinite resources have to be directed at saving lives, but rather that one of the sacred rituals of our society is the attempt to save people in acute or critical need, such as crash victims and trapped coal miners. Thus, purely rational calculations, such as the coal miners example above, might not lead us to conclusions that we find acceptable.

In all such risk analyses, the benefits are usually to humans only, and they are shortterm benefits. Similarly, the costs determined in the cost-effectiveness analysis are real budgetary costs, money that comes directly out of the pocket of the agency. Costs related to environmental degradation and long-term costs that are very difficult to quantify are not easily included in these calculations. When long-term and environmental costs can nowhere be readily considered in these analyses, coupled with the blatant abuse of benefit–cost analysis by governmental agencies, it is necessary to bring into action another decision-making tool: the analysis of environmental impact.

ANALYZING RISK TO THE ENVIRONMENT

Projects receiving funding or regulatory action from the U.S. government require compliance with the National Environmental Policy Act (NEPA)¹⁰ of 1969 and the Council on Environmental Quality (CEQ) Guidelines.¹¹ NEPA serves as the nation's basic environmental protection charter. It is to ensure that federal agencies consider the environmental consequences of their actions and decisions as they conduct their respective missions. For "major federal actions significantly affecting the quality of the human environment," the federal agency must prepare a detailed environmental impact statement (EIS) that assesses the proposed action and all reasonable alternatives.¹² EISs must be broad in scope to address the full range of potential effects of the proposed action on public health and the environment. Regulations established by both the CEQ and the EPA require that socioeconomic impacts associated with significant physical environmental impacts be addressed in the EIS. The first step toward compliance is to determine whether an action is categorically excluded from NEPA. Compliance with NEPA requires public participation throughout the process, starting with initial meetings, public meetings, and presentations during the assessment process, and final public hearing(s). The process begins with an initial session involving interested federal, state, and local agencies. The environmental assessment follows, with the public involved. The key output of the assessment is a determination of whether or not the federal action will significantly affect the quality of the human environment. If the results indicate that the action has no significant impact or the impacts can be mitigated, a *finding of no significant impact* (FONSI) is issued. This is akin to a "negative declaration." The public has 30 days to review the FONSI. There is a public hearing during the review process, and comments are received and formal responses are prepared. If the FONSI is still deemed the appropriate action after the hearings and the comments, the lead agency formally approves the document, allowing the action (or project) to go forward.

If the FONSI is appropriate, this does not mean that the project will not be scrutinized for environmental impact. It will probably have to go through some form of *environmental assessment* (EA) for the state. Environmental assessments are most common for treatment plant upgrades and other modifications.

If the FONSI is not appropriate, which is the case for almost all wastewater treatment plants, an *environmental impact statement* must be prepared. This process starts with the filing of a notice of intent that is published by U.S. EPA in the *Federal Register*. Although there are not strict guidelines on how the EIS is to be prepared, the following discussion is a description of several alternatives within a general framework. The EIS should be in three parts: *inventory, assessment,* and *evaluation*.

The first duty in the writing of any EIS is the gathering of data, such as hydrological, meteorological, and biological information. A list of the species of plants and animals in the area of concern, for example, is included in the inventory. There are no decisions made at this stage, since everything properly belongs in the inventory.

The second stage is analysis, commonly called the *assessment*. This is the mechanical part of the EIS in that the data gathered in the inventory are fed to the assessment mechanism and the numbers are crunched accordingly. Numerous assessment methodologies have been suggested, only some of which are discussed here.

The *quantified checklist* is possibly the simplest quantitative method of comparing alternatives. It involves first listing those areas of the environment that might be affected by the proposed project, and then an estimation of the *importance* of the impact, the *magnitude* of the impact, and the *nature* of the impact (whether negative or positive). Commonly, the importance is given numbers such as 0 to 5, where 0 means no importance whatever and 5 implies extreme importance. A similar scale is used for magnitude. The nature of the impact is expressed simply as -1, negative (or adverse) impact, or +1, positive (or beneficial) impact. The environmental impact (EI) is then calculated as

$$EI = \sum_{i=1}^{n} I_i M_i N_i$$
(5.1)

where I_i is the importance of the *i*th impact; M_i is the magnitude of the *i*th impact; N_i is the nature of the *i*th impact, so that N = +1 if beneficial and N = -1 if detrimental;

and n is the total number of areas of concern. The environmental impact, which can be negative (detrimental) or positive (beneficial), is calculated for each alternative and tabulated. The following example illustrates use of the quantitative checklist.

Example:

Analyzing Environmental Impact I

A community has two alternatives: increase the refuse collection frequency from once to twice a week, or allow the burning of rubbish on premises. Analyze these two alternatives using a quantified checklist.

First, the areas of environmental impact are listed. In the interest of brevity, only five areas are shown below, while recognizing that a thorough assessment would include many other concerns. Following this, values for importance and magnitude are assigned (0 to 5) and the nature of the impact (+/-) is indicated. The three columns are then multiplied.

Area of	Importance	Magnitude (M)	Nature (N)	Total $(\mathbf{I} \times \mathbf{M} \times \mathbf{N})$
concern	(1)	(141)	(14)	$(\mathbf{I} \wedge \mathbf{W} \wedge \mathbf{N})$
Air pollution (trucks)	4	2	-1	-8
Noise	3	3	-1	-9
Litter in streets	2	2	-1	-4
Odor	2	3	-1	-5
Traffic congestion	3	3	-1	-9
Groundwater pollution	4	0	-1	0
(Note: No new refuse v	vill be landfilled)			
				EI = -35
Alternative 2: Burning	on premises	4	-1	-16
Noise	4	4	-1	10
Litter (present system) (Note: Present system c	2 auses litter)	1	+1	+2
Odor	2	4	-1	-8
Traffic congestion	0	0	-1	0
Groundwater pollution (<i>Note:</i> Less refuse will	4 be landfilled)	1	+1	+4
				EI = -18

Alternative 1: Increasing collection frequency

On the basis of this analysis, burning the refuse would result in the lowest adverse effect.

For simple projects, the quantified checklist is an adequate assessment technique, but it gets progressively unwieldy for larger projects, such as the construction of a dam, where there are many smaller actions all combining to produce the overall final product. The effect of each of these smaller actions should be judged separately with respect to impact. Such an interaction between the individual actions and areas of concern gives rise to the *interaction matrix*,¹³ where once again the importance and the magnitude of the interaction are judged (such as by the 0 to 5 scale used previously). There seems to be no agreement on what calculation should be made to produce the final numerical quantity. In some cases, the interaction value is multiplied by the magnitude, and the products summed as before, whereas other procedures are simply to add all the numbers on the table. In the example below, the products are summed into a grand sum shown on the lower right corner of the matrix.

Example:

Analyzing Environmental Impact II

Continuing the preceding example: Use the interaction matrix assessment technique to decide on the alternatives presented.

Figure 5.1 shows the calculations using the matrix technique. Note again that these are incomplete lists used only for illustrative purposes. The results indicate that once again it makes more sense to burn the paper.

Before moving on to the next technique, we want to emphasize again that the method illustrated in the example above can have many variations and modifications, none of



Figure 5.1 Interaction matrix.

which are "right" or "wrong" but which depend on the type of analysis conducted, for whom the report is prepared, and what is being analyzed. Individual initiative is often a most valuable component in the development of a useful EIS. However, whichever approach is used, it must be fully described and supported technically.

The *common parameter checklist* is a third technique for environmental impact assessment. It differs from the quantified checklist technique only in that instead of using arbitrary numbers for importance and magnitude, the importance term is called the effect (E) and is calculated from actual environmental data (or predicted quantitative values), and the magnitude is expressed as weighting factors, W.

The basic objective of this technique is to reduce all data to a common parameter, thus allowing the values to be added. The data (actual or predicted) are translated to the effect term by means of a function that describes the relationship between the variation of the measurable value and the effect of that variation. This function is commonly drawn for each interaction on a case-by-case basis. Three typical functions are illustrated in Figure 5.2. The curves show that as the value of the measured quantity increases, the effect on the environment (*E*) also increases, but that this relationship can take several forms. The value of *E* ranges from 0 to ± 1.0 , with the positive sign implying beneficial impact and the negative detrimental.

Consider, for example, the presence of a toxic waste on the health and survival of a certain aquatic organism. The concentration of the toxin in the stream is the quantity measured, and the health of the aquatic organism is the effect. The effect (detrimental) increases as the concentration increases. A very low concentration has no detrimental effect, whereas a very high concentration can be disastrous. But what type of function (curve) makes the most sense for this interaction? The straight-line function (linear portion of Figure 5.3A) implies that as the concentration of the toxin increases from zero, the detrimental effects are felt immediately. This is seldom true. At very low concentrations, most toxins do not show a linear relationship with effect, and thus this function does not appear to be useful. For the same reasons, Figure 5.3B, the next curve, is also clearly incorrect. But Figure 5.3 seems much more reasonable, since it shows that a number of substances are actually beneficial (Figure 5.3A) at certain concentrations (e.g., vitamins and essential metals) and also implies that the effect of the toxin is very small at lower concentrations, but when it reaches a threshold level, it becomes very toxic quickly (Figure 5.3B). As the level increases above the toxic threshold, there can be no further damage since the organisms are all dead and the effect levels off at 1.0 (i.e., 100%).

The conditions in Figure 5.3, where the safe dose is also the efficacious dose, is ideal for drugs and food additives, for example. Often, however, real-world exposures are more like that depicted in Figure 5.4, where the efficacious dose carries with it commensurate risk, with the positive and harmful effects increasing together (e.g., vaccines, cancer treatments, lipophilic vitamins, and metals). If the adverse effect (Figure 5.4B) is a relatively innocuous side effect (e.g., skin rash) compared to a lifesaving beneficial effect (hemophilia treatment), the risk-benefit conclusions are easy. However, when the benefits are dramatic but the harm is also substantial (e.g., applying DDT to eliminate malaria-bearing mosquitoes, with the possibility of causing endocrine disorders), the risk-benefit relationship becomes quite complicated.



Figure 5.2 Three specific functions of environmental effect.

Once the effect (E) terms are estimated for each characteristic, they are multiplied by weighting factors (W) which are distributed among the various effects according to the importance of the effect. Typically, the weighting terms add up to 100, but this is not important as long as an equal number of weighting terms are used for each alternative considered.

The final impact is then calculated by adding up the products of the effect terms (E) and weighing factors (W). Thus, for each alternative considered,

$$EI = \sum_{i=1}^{n} E_i \times W_i$$
(5.2)

Remember that E terms can be negative (detrimental) or positive (beneficial).



Figure 5.3 Hypothetical dose–response curve comparing exposure to a substance that can be either beneficial or adverse, depending on the dose. In this case, risk assessment is straightforward since the efficacious dose (about 7 units) is well below the unsafe level (greater than 8 units). This demonstrates a substance where the greatest efficacy is realized at the lowest dose. (Adapted from W. W. Lowrance, *Of Acceptable Risk: Science and the Determination of Safety,* William Kaufmann, Los Altos, CA, 1976, p. 97.)



Arbitrary dose units

Figure 5.4 Hypothetical dose–response curve comparing exposure to a substance that can be either beneficial or adverse, depending on the dose. In this case, risk assessment is complicated since the dose–response relationship has a large area with both efficacy and risk. This demonstrates a substance where the risk–benefit determination will rest on the weight of the gain *versus* that of the harm. (Adapted from W. W. Lowrance, *Of Acceptable Risk: Science and the Determination of Safety*, William Kaufmann, Los Altos, CA, 1976, p. 98.)

Example:

Analyzing Environmental Impact III

Continuing the preceding example: Considering only litter, odor, and airborne particulates as an example of air quality, calculate the environmental impact of rubbish burning using the common parameter–weighted checklist. (This is only a very small part of the total impact assessment that would be necessary when using this technique.)

Assume that the three curves shown in Figure 5.2 are the proper functions relating the environmental characteristics of litter, odor, and airborne particulates, respectively. Assume that it has been estimated that the burning of rubbish will result in a litter level of 2 on a scale of 0 to 4, an odor number of 3 on a scale of 0 to 9, and a airborne particulate increase to 180 g m⁻³ on a concentration scale. Entering Figure 5.2A, B, and C at 2, 3, and 180, respectively, the effects (*E*) are read off as -0.5, -0.8, and -0.9. (*Note:* We are assuming that the litter function looks like the curve in Figure 5.2A, the odor function looks like the curve in Figure 5.2B, and the air pollution function looks like the curve in Figure 5.2C; however, the actual functions could all be the same curve or three functions other than those shown in Figure 5.2.) It is now necessary to assign weighting factors, and out of a total of 10 it is decided to assign 2, 3 and 5, respectively, implying that the most important effect is the air quality, and the least important is the litter. Then

$$EI = (0.5 \cdot 2) + (0.8 \cdot 3) + (-0.9 \cdot 5) = -7.9$$

A similar calculation would be performed for other alternatives, and the EI values would be compared.

Clearly, this technique is wide open to individual modifications and interpretations, and the example above should not be considered in any way a standard method. It does, however, provide a numerical answer to the question of environmental impact, and when this is done for several alternatives, the numbers can be compared. This process of comparison and evaluation represents the third part of an EIS.

The comparison of the results of the assessment procedure and the development of the final conclusions is all covered under evaluation. It's important to recognize that the previous two steps, inventory and assessment, are simple and straightforward procedures compared to the final step, which requires judgment and common sense. During this step in writing the EIS, the conclusions are drawn up and presented. Often, the reader of the EIS sees only the conclusions and never bothers to review all the assumptions that went into the assessment calculations, so it is important to include in the evaluation the flavor of these calculations and to emphasize the level of uncertainty in the assessment step.

But even when the EIS is as complete as possible, and the data have been gathered and evaluated as carefully as possible, conclusions concerning the use of the analysis are open to severe differences. For example, the EIS written for the Alaska oil pipeline, when all the pages in the volumes are stacked, represents 14 feet of work. At the end of all that effort, good people on both sides drew diametrically opposite conclusions on the effect of the pipeline. The trouble was, they were arguing over the *wrong thing*. They may have been arguing about how many caribou would be affected by the pipeline, whereas their disagreement was actually how deeply they cared that the caribou were affected by the pipeline. For a person who does not care one twit about the caribou, the impact is zero, whereas those who are concerned about the herds and the long-range effects on the sensitive tundra ecology care very much. What, then, is the solution? How can engineering decisions be made in the face of conflicting values? Such decisions require engineers to make value judgments, and this is where the concepts of justice enter the analysis of environmental impact.

Once the draft EIS has been published in the *Federal Register*, a formal comment period begins that leads to preparation of the final environmental impact statement, another comment period, and finally, a record of decision. This process is time consuming, particularly if the project is controversial or the environmental documentation is challenged. This needs to be factored into the project implementation schedule. Also, many permits are contingent on having an approved environmental document (e.g., an NPDES permit); this can affect the entire project time line because the permits themselves are time intensive.

EISs are all about balance and fairness. Various aspects of the human and natural environment must be protected. Similarly, the environmental justice goal of "fair treatment" is not to shift risks among populations, but rather, to identify potential disproportionately elevated and harmful effects and to identify alternative approaches that may ameliorate and mitigate these effects. This makes the EIS an ideal environmental justice mechanism. EISs have been used as tools for three decades, striving for the best option among many, just as environmental justice concerns should engage in serious considerations of credible alternatives, including "no action" and modified designs to consider how a publicly funded project may affect minority and disadvantaged communities disproprotionately. The designers of NEPA called for community education and participation, much as environmental fairness calls for involvement. This is not to say that the guidance and existing approaches for community input are sufficient. Although many of the NEPA methods for public involvement and education have been honed for three decades, special situations brought on by historical disenfranchisement will undoubtedly need new tools, such as that shown in Figure 5.5. Note that neither the need for credible science nor the need for continuous involvement with those potentially affected by the project is sacrificed. There are key points in the critical path where the needs of the public and those of the professional intersect.

The preparation of an EIS or an environmental assessment of any type provides an opportunity to incorporate environmental justice into project design. Determining the distributional dimensions of environmental impacts on particular populations is entirely consistent with the NEPA process since socioeconomics and other "human" factors are components of the environment. Credible assessments heighten awareness of environmental justice issues within NEPA analyses and aid in considering the full potential for disproportionately adverse human health or environmental effects on minority and low-income populations. Assessments also identify situations early in the design phase where environmental justice issues may be encountered, laying out options for addressing disproportionately high and adverse effects. The assessment process also provides approaches for communicating with the affected population throughout the design, siting, building, and operation of projects. Thus, the application of many of the same tools currently intrinsic to the NEPA process applies directly to environmental justice.¹⁴



Figure 5.5 Possible process for incorporating community input into an environmental assessment process. (Adapted from D. A. Vallero, *Environmental Contaminants: Assessment and Control*, Elsevier Academic Press, Burlington, MA, 2004.)

MAJOR AREAS OF ENVIRONMENTAL CONCERN

Although there can be an almost infinite number of areas of concern on a regional or global basis for the effect of contaminants on environmental quality, in this section we concentrate on but a few, not so much because they pose the greatest actual or potential risks to the environment or health, but because they vividly illustrate the complexity of the science, technology, and social perspectives. They illustrate the difference in risk endpoints. For example, smog can affect ecosystems but is addressed principally as a human health issue. Acid rain is predominantly a threat to ecosystems. Global climate change would affect human health and welfare (e.g., a greater number of tropical diseases shifting to presently temperate climates). These global- and regional-scale problems provide a template for addressing complex problems by using a systematic approach (i.e., gathering reliable information, understanding and explaining the scientific processes, and characterizing potential adverse outcomes *before* recommending and designing solutions to environmental problems). Environmental systems from the molecular (popularly known as "nano") to the planetary scales are seldom linear and are often chaotic

Biographical Sketch: Eliza Sanderson

Sometimes people become heroes by standing up for what is right, losing, and then being remembered for generations for their unwillingness to submit to defeat. The name of Eliza Sanderson is not well known to the public, but in the world of personal rights law, her fame lives on.

In 1868 when Eliza Sanderson bought land in a town now known as Green Ridge, PA, near Scranton, PA, all she wanted to do was build a house and run a small farm. She and her husband, J. Gardner Sanderson, had by all accounts a successful and comfortable home. Running through their property was a small stream, Meadow Brook, and the brook was one of the reasons she bought the land. The water was sufficient for their rural use and was of high quality.

In 1870, the powerful Pennsylvania Coal Company sunk a deep vertical shaft at their mine north of the Sandersons' property, but this filled with water, and they started to pump it out. Unfortunately, the only place this water could flow was into Meadow Brook, making the water in the brook so foul that it could not be used for human consumption or for watering livestock.

Since Pennsylvania was a riparian law state, the property owner had every right to use the water that flowed through their property, and upstream property owners could not use or contaminate the water. It had to flow into their property "unimpaired in quality and undiminished in quantity", according to the law. Mrs. Sanderson thought she had a pretty good case and went to court.

But she did not count on the power of the Pennsylvania coal industry. The judge presiding on the case decided that the needs of the coal company exceeded the rights of the Sandersons to have their creek back. The judgment was that since "the coal could only be mined where it was, the contamination of the water was part of the mining operation." In other words, the mine could not move, but the Sandersons could. Personal rights be damned.

The willingness of Eliza Sanderson to stand up to the Pennsylvania Coal Company, even though she lost, will long be remembered. She will continue to be a hero of the environmental justice movement.

More information of the case can be found in *The Pennsylvania Coal Company v. Sanderson and Wife*, Supreme Court of Pennsylvania, No. 389, 113 Pa. 126; 6 A. 453; 1886 Pa. LEXIS 343

and ill posed. Their solutions must be matched to these conditions. We certainly recognize that experience and scientific knowledge will provide new and unanticipated problems in the future, but firmly believe the systematic approach will be needed to address them.

Photochemical Smog

The components of automobile exhaust are particularly important in the formation of secondary pollutants. The well-known and much discussed Los Angeles smog is a case of secondary pollutant formation. Photochemical smog starts with high-temperature, high-

pressure combustion such as occurs within the cylinders of an internal combustion (gasoline) engine. The first reaction is

$$N_2 + O_2 - high temperature and pressure \rightarrow 2NO$$
 (5.3)

which immediately oxidizes to NO_2 , as

$$2NO + O_2 \rightarrow 2NO_2 \tag{5.4}$$

Nitrogen dioxide, NO_2 , is very active photochemically and breaks apart as the first reaction in the sequence of photochemical smog formation:

$$NO_2 + h\nu \to NO + O \tag{5.5}$$

where h is Planck's constant [6.62 \times 10⁻³⁴ joule-second (J-s)] and ν is the frequency (s⁻¹). The atomic oxygen molecule, being quite unstable, reacts as

$$O + O_2 + M \rightarrow O_3 + M \tag{5.6}$$

where M is some radical that catalyzes the reaction. The ozone thus created is a strong oxidant, and it will react with whatever it finds to oxidize. From the reaction (5.6), NO is available, and thus

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{5.7}$$

and we are back where we started, with NO_2 . Since all of these reactions are fast, there is no way that high levels of ozone could build up in the atmosphere. This puzzled early air pollution researchers, until Arie Haagen-Smit came up with the answer. The answer is that one of the other constituents of polluted urban air is hydrocarbons, and some of these can oxidize the NO to NO_2 , leaving ozone in excess. For example,

$$HCO_3^0 + NO \rightarrow HCO_2^0 + NO_2$$
(5.8)

This explanation allowed for the possibility of ozone buildup as well as the formation of other components of photochemical smog.

Ozone is an eye irritant and can cause severe damage to plants and to materials such as rubber. The peroxyacetyl nitrates (PANs) are also effective in damaging crops and materials. Other hydrocarbons can cause breathing problems and also damage plants. Finally, NO_2 itself is an irritant and has a brownish orange color. Anyone who has ever flown into the Los Angeles airport on a sunny day would have seen the dramatic contrast between the blue sky above and the orange crud below into which the plane was heading.

Photochemical smog is possible if a series of conditions exits:

- · High-temperature, high-pressure combustion of fossil fuels such as gasoline
- Plentiful sunlight (source of photo energy)
- · Stable atmospheric conditions, which would allow time for the reactions to occur
- Hydrocarbon emissions, which would scavenge the NO from the mix and allow for the buildup of ozone

Cities in the United States that have these conditions include some of the largest urban areas, such as Los Angeles, Denver, and Houston, and even some rapidly growing areas such as Raleigh–Durham, North Carolina. Reducing photochemical smog has been a challenge to environmental scientists and managers for many years. Many different schemes for reducing the smog in Los Angeles, for example, have been suggested, such as boring a huge tunnel through the surrounding mountains and blowing the polluted air into the valleys on the other side. Never mind what the people on the other side of the mountain might say. Also, rough calculations show that the tunnel large enough to be able to exchange the air over Los Angeles needs to be about 2 miles in diameter! So other solutions have been sought, the most reasonable being not producing NO_2 in the first place by reducing the number of cars in the city and/or clearing up their emissions. The cars exhaust is already very clean compared to earlier models, and the people of LA are not keen on giving up their driving privilege, so this solution is not useful. Another proposed solution is to replace all the gasoline-powered vehicles with electric cars, also a nonstarter, at least for the next few decades, although hybrid gasoline-electric cars are having some impact. As of this writing, no clear solution is in sight.

Acid Rain

Normal, uncontaminated rain has a pH of about 5.6. This low pH can be explained by its adsorption of carbon dioxide, CO_2 . As the water droplets fall through the air, the CO_2 in the atmosphere becomes dissolved in the water, setting up an equilibrium condition:

$$CO_2$$
 (gas in air) \leftrightarrow CO_2 (dissolved in the water) (5.9)

The CO_2 in the water reacts to produce hydrogen ions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
(5.10)

$$\mathrm{HCO}_{3}^{-} \leftrightarrow 2\mathrm{H}^{+} + \mathrm{CO}_{3}^{2-} \tag{5.11}$$

Thus, the more CO_2 that is dissolved in the rain, the lower the pH will be. But this reaction will, at equilibrium, produce rainwater with a pH of 5.6, and no lower. How is it, then, that some rain can have a pH value less than 2 (i.e., 100,000 times more acidic than neutral water).

This pH reduction occurs as the result of interactions with air contaminants. For example, sulfur oxides produced in the burning of fossil fuels (especially coal) is a major contributor to low pH in rain. In its simplest terms, SO_2 is emitted from the combustion of fuels containing sulfur, the reaction being

sunlight

$$S + O_2 \xrightarrow{heat} SO_2$$
 (5.12)

$$SO_2 + O \longrightarrow SO_3$$
 (5.13)

$$SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow 2H^+ + SO_4^{-2-}$$
 (5.14)

 H_2SO_4 is, of course, sulfuric acid. Sulfur oxides do not literally produce sulfuric acid in the clouds, but the concept and environmental impact are the same.¹⁵ The precipitation from air containing high concentrations of sulfur oxides is poorly buffered and readily drops its pH.

Biographical Sketch: Arie Haagen-Smit



In the 1940s, as the number of clear days in southern California became fewer and fewer, concern was being expressed as to what the cause of this bad visibility might be. But during World War II, little was done until a butadiene plant was built in downtown Los Angeles. When the plant went online, it had severe upsets and produced noxious fumes that caused office buildings to be evacuated. Although we now know that the butadiene plant had little to do with the poor visibility, the event caused a public outcry and a demand to do something about the air pollution. Experts were sent for, arriving with their instruments for measuring SO₂ and smoke, but these were

worthless since the levels of sulfur oxides were very low. In 1947 the County of Los Angeles got the police power to do something about the air pollution, and the LA County Air Pollution District was formed. Early efforts to reduce air pollution in Los Angeles centered on the reduction of SO_2 from such sources as backyard burning, but to no avail. Finally, it was decided that some research was necessary.

Arie Haagen-Smit, a Dutch-born biologist working at Cal Tech on the fumes emitted by pineapples, decided to distill the contents of the Los Angeles air and discovered peroxyorganic substances, which were no doubt the source of the eye irritation. The source, if this were true, had to have been the gasoline-powered automobile, and the publication of this research set off a firestorm of protest by these industries. Scientists at the Stanford Research Institute, which had been doing smog research on behalf of the transportation industry, presented a paper at Cal Tech accusing Haagen-Smit of bad science. This made him so angry that he abandoned his pineapple work and began to work on the smog problem.

Some of his previous research had been on plant damage caused by ozone, and he discovered that the effect of automobile exhaust on plants produced a similar injury, suggesting that the exhaust contained ozone. But ozone was not emitted by automobiles, so where did it come from? By mixing automobile exhaust with hydrocarbons in a large air chamber, and subjecting the mixture to strong light, he was able to demonstrate that ozone is formed by reactions in the atmosphere. The ozone in the Los Angeles smog was created by reactions that began with the oxides of nitrogen in automobile exhaust.

The powerful automobile and gasoline industries denied that this could be the cause of the smog, and suggested instead that the ozone had to be in the smog because it somehow descended from the stratosphere, which of course was non-sense. Haagen-Smit's courageous work, taking on the most powerful political forces in California, paved the way for an eventual (but not yet present) solution to the smog problem in Los Angeles.

Nitrogen oxides, emitted mostly from automobile exhaust but also from any other high-temperature combustion, contribute to the acid mix in the atmosphere. The chemical reactions that apparently occur with nitrogen are

$$N_2 + O_2 \rightarrow 2NO \tag{5.15}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{5.16}$$

$$2NO_2 + O_3 + H_2O \rightarrow 2HNO_3 + O_2 \rightarrow 2H^+ + 2NO_3^- + O_2$$
(5.17)

where HNO_3 is nitric acid. However, like everything else in environmental science, acid rain formation and its effects are far more complicated than these reactions. A major complication is buffering. If soils have a large buffering capacity (i.e., they keep pH from changing significantly even when acidic water is added), the lakes are not severely impacted. Thus, in the United States, acid rain is not nearly as much a problem west of the Mississippi River than it is to the east (see Figure 5.6). A major reason for this difference in buffering capacity is the availability of carbonates in the soil from parent rock materials. The carbonic acid in rain will release some bicarbonate into the water (see Figure 5.7). This is why soils underlain by limestone (CaCO₃) and dolomite [CaMg(CO₃)₂] resist pH change much more than the granite and basaltic (noncarbonated) based soils in the eastern part of the United States and much of Scandinavia.



Figure 5.6 Hydrogen ion concentration as pH from measurements made at field laboratories, 2003. (Source: National Atmospheric Deposition Program/National trends Network, http://nadp.sws.uiuc.edu.)



Limestone and Dolomite Parent Rock

Figure 5.7 Process of releasing carbonates and providing natural soil buffers against acid rain.

The effect of acid rain has been devastating. Hundreds of lakes in North America and Scandinavia have become so acidic that they no longer can support fish life. In a recent study of Norwegian lakes, more than 70% of the lakes having pH less than 4.5 contained no fish, and nearly all lakes with pH 5.5 and above contained fish. The low pH not only affects fish directly, but contributes to the release of potentially toxic metals such as aluminum, thus magnifying the problem. For example, much of the fish toxicity can be attributed to the release of aluminum into the water. Aluminum does not readily become dissolved in neutral waters. However, the trivalent ion (Al^{3+}) , which is highly toxic to most aquatic fauna, is released when the pH of water drops.

In North America, acid rain has already wiped out all fish and many plants in 50% of the high mountain lakes in the Adirondacks. The pH in many of these lakes has reached such levels of acidity as to replace the trout and native plants with acid-tolerant mats of algae.

The deposition of atmospheric acid on freshwater aquatic systems prompted the U.S. EPA to suggest a limit of from 10 to 20 kg SO_4^{2-} per hectare per year. If Newton's law of air pollution is used (what goes up must come down), it is easy to see that the amount of sulfuric and nitric oxides emitted is vastly greater than this limit. For example, for the state of Ohio alone, the total annual emissions are 2.4×10^6 metric tons of gaseous

sulfur dioxide (SO₂) per year. If all of this is converted to SO_4^{2-} and is deposited on the state of Ohio, the total would be 360 kg per hectare per year.¹⁶

But not all of this sulfur falls on the folks in Ohio, and much of it is exported by the atmosphere to places far away. Similar calculations for the sulfur emissions for the northeastern United States indicates that the rate of sulfur emission is four to five times greater than the rate of deposition. Where does it all go?

The Canadians have a ready and compelling answer. They have for many years blamed the United States for the formation of most of the acid rain that invades across the border. Similarly, much of the problem in Scandinavia can be traced to the use of tall stacks in Great Britain and the lowland countries of continental Europe. For years British industry simply built taller and taller stacks as a method of air pollution control, reducing the local, immediate ground-level concentration, but emitting the same pollutants into the higher atmosphere. The air quality in the United Kingdom improved, but at the expense of acid rain in other parts of Europe.

CASE STUDY: THE MYSTERY OF THE DISAPPEARING FISH

In the 1960s, the mountain lakes of Norway were full of cold-water game fish, but the populations of these fish seemed to be decreasing. Studies conducted by the Norwegian Institute for Water Research showed a steady decline in fish. The lakes were in remote areas, far away from sources of pollution, and various nonpollution causes were considered for the declining fish populations. Using water quality samples, the institute found that the pH in the lakes had been steadily decreasing. More important, rain gauges set up around the lakes showed a wide variation in the pH of the rain. But where was the acid rain coming from? The mystery was solved by tracking the paths of storms that produced particularly low-pH rainwater and determining where these storms had been prior to dumping the rainwater in Norway. Knowing what was happening to the fish in Norwegian lakes was one thing, of course, and quite another was trying to do something about it.

Acid rain is an indicator of another, larger societal problem. Pollution across political boundaries is a particularly difficult regulatory problem. The big stick of police power is no longer available. Why *should* the UK worry about acid rain in Scandinavia? Why *should* the Germans clean up the Rhine before it flows through The Netherlands? Why *should* Israel stop taking water out of the Dead Sea, which it shares with Jordan? Laws are no longer useful, and threats of retaliation are unlikely. What forces are there to encourage these countries to do the right thing? Is there such a thing as *international ethics*?

One of the difficulties in dealing with acid rain and global climate change is that they in essence are asking that society cut back on combustion; and to many, combustion is tantamount to progress and development. This a but another example of risk tradeoffs.

Discussion: Where There's Fire, There's Smoke

Fire may not be one of the first things to come to mind when thinking about environmental justice. After all, humans have been around fire throughout our existence. We need it, yet we fear it. Combustion is a relatively simple phenomenon: oxidation of a substance in the presence of heat. Chemically, efficient combustion is

$$a(CH)_{x} + bO_{2} \rightarrow cCO_{2} + dH_{2}O$$
(5.18)

where *a*, *b*, *c*, and *d* are stoichiometric constants depending on the hydrocarbon combusted.

Following are additional complex combustion reactions, balanced combustion reactions for selected organic compounds:

Chlorobenzene	$C_6H_5CI + 7O_2 \rightarrow 6CO_2 + HCI + 2H_2O$
Tetrachloroethene (TCE)	$C_2CI_4 + O_2 + 2H_2O \rightarrow 2CO_2 + HCI$
Hexachloroethane (HCE)	$C_2CI_6 + \frac{1}{2}O_2 + 3H_2O \rightarrow 2CO_2 + 6HCI$
Postchlorinated polyvinyl	
chloride (CPVC)	$C_4H_5CI_3 + 4\frac{1}{2}O_2 \rightarrow 4CO_2 \cdot 3HCI + H_2O$
Natural gas fuel (methane)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
PTFE teflon	$C_2F_4 + O_2 \rightarrow CO_2 + 4HF$
Butyl rubber	$\mathrm{C_9H_{16}+13O_2 \rightarrow 9CO_2+8H_2O}$
Polyethylene	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Wood is considered to have the composition $C_{6.9}H_{10.6}O_{3.5}$. Therefore, the combustion reactions are simple carbon and hydrogen combustion:

$$C + O_2 \rightarrow CO_2$$
$$H + 0.25O_2 \rightarrow 0.5H_2O$$

Most fires, however, do not reach complete combustion of all of the compounds in the fuel being oxidized. They are usually oxygen-limited, so that a large variety of new compounds, many that are toxic, is released. Decomposition of a substance in the absence of oxygen is known as *pyrolysis*. So a fire consists of both combustion and pyrolytic processes; and the fire itself is not homogeneous, with temperatures varying in both space and time. Plastic fires, for example, can release over 450 different organic compounds.¹⁷ The relative amount of combustion and pyrolysis in a fire affects the actual amounts and types of compounds released. Temperature is also important, but there is no direct relationship between temperature and pollutants released. As evidence, Figure 5.8 shows that in a plastics fire (i.e., low-density polyethylene pyrolysis), some compounds are generated at lower temperatures, whereas for others the optimal range is at higher temperatures. However, the aliphatic compounds in this fire (i.e., 1-dodecene, 9-nonadecane, and 1-hexacosene) are generated in higher concentrations at lower temperatures (about 800°C), while the aromatics



Figure 5.8 Selected hydrocarbon compounds generated in a low-density polyethylene fire (pyrolysis) in four temperature regions. (Data from R. A. Hawley-Fedder, M. L. Parsons, and F. W. Karasek, Products Obtained During Combustion of Polymers Under Simulated Incinerator Conditions, *Journal of Chromatography*, 314:263–272, 1984.)

need higher temperatures (see Figure 5.9). This may be because with increasing temperature, the chains are being transformed to aromatic rings. Also, there appears to be a general trend toward heavier molecular weight compounds with increasing temperature (probably because the increased heat energy allows for more synthesis or combination chemical reactions).

All societies depend on fire. The way that a nation addresses burning is an important measure of how advanced it is, not only in dealing with pollution, but in the level of sophistication of its economic systems. For example, many poorer nations are confronted with the choice of saving sensitive habitat or allowing large-scale biomass burns. And, the combustion processes in developing countries are usually much less restrictive than those in more developed nations. For example, it may be surprising that in Latin America, some of the



Figure 5.9 Total aliphatic (chain) hydrocarbons *versus* polycyclic aromatic hydrocarbons (PAHs) generated in a low-density polyethylene fire (pyrolysis) in four temperature regions. (Data from R. A. Hawley-Fedder, M. L. Parsons, and F. W. Karasek, Products Obtained During Combustion of Polymers Under Simulated Incinerator Conditions, *Journal of Chromatography*, 314:263–272, 1984.)

largest sources of chlorinated dioxins are in brickmaking. Refractories in developing nations are often small-scale neighborhood operations (see Figure 5.10). Often, the heat source used to reach refractory temperatures are furnaces with scrapped materials as fuel, especially petroleum-derived substances such as automobile tires.

Even within developed countries, there are still remnants of such processes. El Paso, Texas, and Ciudad Juarez, Mexico, with a combined population of 2 million, are located in a deep canyon between two mountain ranges, which can contribute to thermal inversions in the atmosphere (see Figure 5.11). The air quality has been characterized by the U.S. EPA as seriously polluted, with brickmaking on the Mexican side identified as a major source.¹⁸

The workers who make bricks are called *ladrilleros*. Nearly 400 of them live in unregulated shantytowns known as *colonias* on the outskirts of Ciudad Juarez. The kilns, which are of the same design as that used in Egypt thousands of years ago, are located within these neighborhoods, next to the small houses. The *ladrilleros* are not particular about the fuel they use, burning anything with caloric value, including scrap wood and old tires as well as more conventional fuels such as methane and butane. The dirtier fuels (e.g., tires), release large black plumes of smoke that contain a myriad of contaminants.

Children are at an elevated risk of health problems when exposed to these plumes, since their lungs and other organs are undergoing prolific tissue



Figure 5.10 Large urban city in Mexico showing the effects (loss of visibility and smog) of air pollution.



Figure 5.11 Two types of thermal inversions that contribute to air pollution.

growth. Thus, the *ladrilleros*' families are at particularly elevated risks, due to their frequent and high-dose exposures. "The health impact is not only of concern to the worker but also the entire family, especially pregnant women and children who, because of their socioeconomic status, tend to be undernour-ished," according to Beatriz Vera, project coordinator for the U.S.-Mexico Border Environment and Health Projects. She adds that "many times the entire family participates in the process. Sometimes children are put directly into the area where the kiln is fired."

The two nations' governments are at least somewhat cognizant of the problem, as are numerous *nongovernmental organizations* (known as NGOs). These have included Environmental Defense, Physicians for Social Responsibility, the Federación Mexicana de Asociaciónes Privadas de Salud y Desarrollo Comunitario (FEMAP), and El Paso Natural Gas (EPNG). FEMAP and EPNG, for example, offer courses to the *ladrilleros* from throughout the region on ways to use higher-quality fuel, together with improved safety and business practices. Often, however, even if the brickmakers know about cleaner fuels, they cannot afford them. For example, they have used butane, but in 1994 the Mexican government started to phase out its subsidy, and at about the same time, the peso was devalued, leading to a sharp increase in butane costs. The *ladrilleros* were forced to return to using cheaper fuels. In the meantime the Mexican government banned the burning of tires, so much of the more recent tire burning has been done at night surreptitiously.

A number of solutions to the problem have been proposed, including more efficient kilns. However, arguably the best approach is to prevent the combustion in the first place. In fact, many of the traditional villages where bricks are now used had previously been constructed with adobe. A return to such a noncombustion approach could hold the key. The lesson here is that often in developing countries, the simpler, "low-tech" solutions are the most sustainable.

In the mid-1990s, the U.S. EPA and the Texas Natural Resource Conservation Commission conducted a study in the Rio Grande valley region to address concerns about the potential health impact of local air pollutants, especially since little air quality information was available at the time. There are numerous "cottage industries," known as *maquiladoras*,¹⁹ along both sides of the Texas– Mexico border. In particular, the study addressed the potential for air pollution to move across the U.S.–Mexican border into the southern part of Texas. Air pollution and weather data were collected for a year at three fixed sites near the border in and near Brownsville, Texas. The study found overall levels of air pollution to be similar to or even lower than in other urban and rural areas in Texas and elsewhere and that transport of air pollution across the border did not appear to impact air quality adversely across the U.S. border. Although these "technical" findings may not be particularly surprising, the study provided some interesting results in how to work with local communities, particularly those with much cultural diversity and richness.

Scientists, engineers, and planners must be sensitive to specific challenges in addressing EJ issues. The National Human Exposure Assessment Survey and Lower Rio Grande Valley Transboundary Air Pollution Project evaluated total human exposure to multiple chemicals on community and regional scales from 1995 to 1997. Lessons learned from this research²⁰ apply to most EJ studies:

- 1. Develop focused study hypotheses and objectives and develop the linkages between the objectives, data requirements to meet the objectives, and available resources.
- 2. Ensure that questionnaires address study objectives and apply experiences of previous studies. Wording must apply to the study participants and reflect differences in demographics (e.g., language, race, nationality, gender, age).
- **3.** Develop materials and scripts to address potential concerns that participants may have about the study (e.g., time burden, purpose and value of study, collection of biological samples, legitimacy of the study).

Before recruiting, build knowledge of the study and support in the community, including support, sponsorship, and advertising from a range of organizations.

- **1.** Plan and conduct follow-up visits with community leaders and stakeholders for timely dissemination of information learned in the study.
- **2.** Integrate recruitment staff into the research team for continuity with participants and to build on experience.
- **3.** Limit field teams to two people per visit (about 1 to 1.5 hours) and have the same staff member work with the study participant at all visits.
- **4.** Ensure that laboratories have the expertise and capacity for planned analyses.
- **5.** Establish a format for reporting data before any field samples are collected.

Also, the way the information is conveyed to the public must be understandable, with a minimum possibility for misinterpretation. Obviously, when dealing with a largely Latino population, technical information must be presented in Spanish (see Figure 5.12). Ongoing EJ research is extending this knowledge. For example, it is becoming painfully obvious that without a readily understandable "benchmark" of environmental measurements, citizens in EJ communities can be left with possible misunderstandings, ranging from a failure to grasp a real environmental problem that exists (a false negative) to perceiving a problem even when values are better than or do not differ significantly from those of the general population (a false positive).

Not too long ago in the United States, the standard means of getting rid of household trash was the daily burn. Each evening, people in rural areas, small towns, and even larger cities made a trip into the backyard, dumped the trash they had accumulated into a barrel,²¹ and burned the contents. Also, burning was a standard practice elsewhere, such as intentional fires to remove brush,



Figure 5.12 Sitios 1, 2, y 3 de Monitoreo de Aire usados en este estudio y en otros sitios establecidos por laTNRCC en el Valle Bajo del Río Grande. Los parques de maquiladoras industriales listados e identificados se identifican con flechas para mostrar sus lugares con relación a los sitios de monitoreo

Figure 5.12 Map annotated in Spanish used to help to explain the Lower Grande Study to community members. English translation: Air monitoring sites 1, 2, and 3 used in this study and other sites established by TNRCC in the Lower Rio Grande Valley. Maquiladora industrial parks listed and identified by arrows to show location relative to monitoring sites. (From S. Mukerjee, D. Shadwick, and K. Dean, *Lower Rio Grande Valley Transboundary Air Pollution Project,* EPA/600/R-99/047, U.S. EPA, Washington, DC, April 1999.)

and even in cottage industries such as backyard smelters and metal recycling operations. Beginning in the 1960s and 1970s, the public acceptance and tolerance for open burning was waning. Local governments began to restrict and eventually to ban many fires. Often, these restrictions had multiple rationales, especially public safety (fires becoming out of control, especially during dry seasons) and public health (increasing awareness of the association between particulate matter in the air and diseases such as asthma and lung cancer).

This new intolerance for burning was a type of paradigm shift. What one did in one's own yard was no longer the sole primacy of the homeowner; the action had an effect on a larger area (i.e., wherever the plume migrated). It also

had a cumulative effect. A fire or two may not cause considerable harm, but when large numbers of fires occur, health thresholds could easily be crossed. In fact, the paradigm was new to environmental regulation—but not to ethics. Immanuel Kant is credited with the deontological (i.e., duty-based) view of ethics. A metric used by Kant to determine the morality of an action or decision is whether that action or decision, if universalized, would lead to a better or worse society. This is known as the *categorical imperative*. Somewhere in the 1960s and early 1970s, environmental science and policy shifted toward the categorical imperative. Slogans like "Think globally and act locally," and "We all live in Spaceship Earth" are steeped in the categorical imperative. Our duty and obligation to our fellow human beings, now and in the future, must drive our day-to-day decisions.

So, then, what is so bad about open burning? Vallero recalls as a teenager working with his Uncle Joe in his salvage business. Uncle Joe was truly amazing in his ability to identify sources of profit. He would drive by residences and see yards in need of cleaning, offer for a fee to clean up the site, load the "junk" into his 2-ton truck, and haul it to his "recycling facility," which for some reason not clear to Vallero, he called "the Ponderosa." When they arrived at the site, they would separate the various items by their material makeup. The motors, such as those from washing machines and tools, would be placed in one pile, wires in another, cast iron and bulk metals in another, and "trash" in another. The trash would be burned.

It is instructive to understand the vertical and horizontal integration of the salvage business to its possible environmental benefits and problems. In addition to cleaning up sites, Uncle Joe would visit local junkyards. East St. Louis, Illinois is a rail center and, as such, has been a prime location for rail-side salvage businesses. Often, the salvages had more unclaimed and dumped cargo than they could handle internally, so they often "contracted out" with wildcatters like Vallero's uncle. So we would visit a number of junkyards and buy motors, armatures, and wire at a bulk rate, take them back to the Ponderosa, and separate the valuable materials (e.g., No. 1 and 2 copper from the armatures) from the bulk materials (the cast iron housings from the armatures). Profit was the difference between the few dollars that Uncle Joe paid per hundreds of pounds of bulk material and the 60 cents per pound he received from the same salvage yards (or another if they paid more) for the clean copper. Unfortunately, not all of the copper that was removed and handled was bare wire. Much of it contained insulation, usually made of compounds and polymers similar to polyvinyl chloride (PVC). At the time, the only way available to remove the sheathing insulation en masse was by burning the wire. In addition, some of the materials contained dielectric fluids, probably with high concentrations of polychlorinated biphenyls (PCBs). Let us consider what happens when both PVC and PCBs are burned.

Like polyethylene, polyvinyl chloride is a polymer. However, rather than a series of ethylenes in the backbone chain, a chlorine atom replaces the hydrogen on each of the ethylene groups by free-radical polymerization of vinyl chloride (see Figure 5.13). The first thing that can happen when PVC is heated





is that the polymers become unhinged and chlorine is released. Also, dioxins and furans can be generated from the thermal breakdown and molecular rearrangement of PVC in a heterogeneous process [i.e., the reaction occurs in more than one phase (in this case, in the solid and gas phases)]. The active sorption sites on the particles allow for the chemical reactions, which are catalyzed by the presence of inorganic chloride compounds and ions sorbed to the particle surface. The process occurs within the temperature range 250 to 450°C, so most of the dioxin formation under the precursor mechanism occurs away from the high temperatures of the fire, where the gases and smoke derived from combustion of the organic materials have cooled. Dioxins and furans may also form de novo, wherein dioxins are formed from moieties different from those of the molecular structure of dioxins, furans, or precursor compounds. The process needs a chlorine donor (a molecule that "donates" a chlorine atom to the precursor molecule). This leads to the formation and chlorination of a chemical intermediate that is a precursor to dioxin.

In addition, PVC is seldom in a pure form. In fact, most wires have to be pliable and flexible. On its own, PVC is rigid, so plasticizers must be added, especially phthalates. These compounds have been associated with chronic effects in humans, including endocrine disruption. Also, since PVC catalyzes its own decomposition, metal stabilizers have been added to PVC products. These have included lead, cadmium, and tin (e.g., butylated forms). Another very common class of toxic compounds released when plastics are burned are the polycyclic aromatic hydrocarbons (PAHs).

The change in the attitude and the acceptance of pollution has been dramatic, but since it has occurred incrementally, it may be easy to forget just how much the baseline has changed. For example, like the open burning that was the norm, emissions from industrial stacks were pervasive and contained myriad toxic components. Vallero recalls his despair as a child walking by a chemical plant in Washington Park, Illinois and riding in a car near the coke ovens in Granite City, Illinois. He believes that the plant in Washington Park processed zinc and released compounds that apparently displaced the oxygen in the air downwind. He remembers coughing and gasping for air as he neared the plant. Vallero also recalls holding his nose when passing the Granite City coke ovens, which had a constant plume of obnoxious smelling compounds, probably metallic and sulfur compounds that volatilized during the conversion of coal to coke needed for steel manufacturing. He also remembers, even as a young child, wondering how people could live so close (within a few meters) of these facilities their entire lives. They had grown familiar with the depressed oxygen or odors. While these areas continue to be industrialized, such ambient air quality as that in the 1960s is no longer tolerated.

Coke remains an important component in steel making around the world. It is produced by blending and heating bituminous coals in coke ovens to 1000 to 1400°C in the absence of oxygen.²² Lightweight oils and tars are distilled from the coal, generating various gases during the heating process. Every half hour or so, the flows of gas, air, and waste gas are reversed to maintain uniform temperature distribution across the wall. In most modern coking systems, nearly half of the total coke oven gas produced from coking is returned to the heating flues for burning after having passed through various cleaning and coproduct recovery processes. Coke oven emissions are the benzene-soluble fraction of the particulate matter generated during coke production. What Vallero intuited as a child has since been borne out by scientific research. Coke oven emissions are known to contain human carcinogens. These emissions are truly an awful concoction.

Coke oven emissions are actually complex mixtures of gas, liquid, and solid phases, usually including a range of about 40 PAHs, as well as other products of incomplete combustion: notably, formaldehyde, acrolein, aliphatic aldehydes, ammonia, carbon monoxide, nitrogen oxides, phenol, cadmium, arsenic, and mercury. More than 60 organic compounds have been collected near coke plants. A metric ton of coal yields up to 635 kg of coke, up to 90 kg of coke breeze (large coke particulates), 7 to 9 kg of ammonium sulfate, 27.5 to 34 L of coke-oven gas tar, 55 to 135 L of ammonia liguor, and 8 to 12.5 L of light oil. Up to 35% of the initial coal charge is emitted as gases and vapors. Most of these gases and vapors are collected during by-product coke production. Coke oven gas is comprised of hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke-oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction. Coke production in the United States increased steadily between 1880 and the early 1950s, peaking at 65 million metric tons in 1951. In 1976, the United States was second in the world, with 48 million metric tons of coke, 14.4% of the world production. By 1990, the United States produced 24 million metric tons, falling to fourth in the world. A gradual decline in production has continued; production has decreased from 20 million metric tons in 1997 to 15.2 million metric tons in 2002. Demand for blast furnace coke has also declined in recent years because technological improvements have reduced the amount of coke consumed per amount of steel produced by as much as 25%.

The junkyards of some decades ago had their own emissions as well. In fact, the combination of fires, wet muck (comprised of soil, battery acid, radiator fluids, motor oil, corroded metal, and water), and oxidizing metals created a rather unique odor around the yards. Neurophysiologists have linked the olfac-

tory center to the memory center of the human brain (olfactory bulb in the cerebellum; see Figure 5.14). In other words, when we smell something, it evokes a strong memory response. This was the case when Vallero was involved in air sampling in lower Manhattan shortly after the attacks on the World Trade Center on September 11, 2001. The smell from the burning plastics, oxidizing metal, semivolatile and volatile organic compounds, and particulate matter was very similar to what Vallero smelled as a teenager in the East St. Louis junkyards, and it brought back 35-year-old memories.

Odors have often been associated with environmental nuisances. In addition to the link between memory and olfactory centers, however, the nasalneural connection is important to environmental exposure. This goes beyond nuisance and is an indication of potential adverse health effects. For example, nitric oxide (NO) is a neurotoxic gas released from many sources, such as confined animal feeding operations, breakdown of fertilizers after they are applied to soil and crops, and emissions from vehicles. In addition to being inhaled



(b) Enlarged aspect of olfactory receptors

Figure 5.14 Human smell is initiated by sniffing, which transports air with concentrations of odorant molecules past curved bony structures (i.e., turbinates) in the nose. The turbinates generate turbulent airflow that mixes volatile compounds and particles and carries them to a thin mucus layer that coats the olfactory epithelium. The olfactory epithelium contains odor-sensing cells. (From S. G. Turtora and B. Derrickson, *Principles of Anatomy and Phyisology,* 11th edition, copyright 2006, courtesy of John Wiley & Sons.)

into the lungs, NO can reach the brain directly. That is, without having to travel through the lungs and circulatory system, the gas can pass through a thin membrane via the nose to the brain.

The nasal exposure is a different paradigm from that commonly used to calculate exposure. In fact, most sources do not have a means for calculating exposures other than dermal, inhalation, and ingestion. Research at Duke University, for example, linked people's emotional states (i.e., moods) to odors around confined animal feeding operations in North Carolina.²³ People who live near swine facilities are negatively affected when they smell odors from the facility. This is consistent with other research, which has found that people experience adverse health symptoms more frequently when exposed to livestock odors. These symptoms include eye, nose, and throat irritation, headache, nausea, diarrhea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, and drowsiness. There is quite a bit of diversity in response, with some people being highly sensitive even to low concentrations of odorant compounds, whereas others are relatively unfazed even at much higher concentrations. Actually, response to odors can be triggered by three different mechanisms. In the first mechanism, symptoms can be induced by exposure to odorant compounds at sufficiently high concentrations to cause irritation or other toxicological effects. The irritation, not the odor, evokes the health symptoms. The odor sensation is merely an exposure indicator. In the second mechanism, symptoms of adverse effects result from odorant concentrations lower than those eliciting irritation. This can be due to genetic predisposition or conditioned aversion. In the third mechanism, symptoms can result from a coexisting pollutant (e.g., an endotoxin), which is a component of the odorant mixture.

Therefore, to address this new paradigm, better technologies will be needed. For example, the Duke and other findings have encouraged some innovative research, including the development of "artificial noses."²⁴

During the aftermath of the World Trade Center attacks, odors played a key role in response. People were reminded daily of the traumatic episode, even when the smoke from the fire was not visible; and the odors were evidence of exposure to potentially toxic substances. In this instance, it was not NO, but volatile, semivolatile organic, and metallic compounds. The presence of the odors was one of many factors that kept New Yorkers on edge, and until the ordors subsided significantly, they continued to be a source of anxiety. Analysis of the samples had confirmed the brain's olfactory-memory connection. The plume from the World Trade Center fires contained elevated concentrations of PAHs, dioxins, furans, volatile organic compounds (e.g., benzene), and particles containing metals (see Figures 5.15 to 5.17).

Obviously, combustion still goes on in the United States, but the *open burning* paradigm has thankfully shifted quite far toward cleaner processes and better control technologies in recent decades. In fact, the past few decades have clearly shifted toward an appreciation for the common value of air sheds, notwithstanding Garrett Hardin's laments in "The Tragedy of the Commons."²⁵ This is not to say that Hardin was wrong (i.e., people *do* tend to favor their



Figure 5.15 Mean daily particulate matter concentrations (aerodynamic diameter ≤ 2.5 micrometers = PM_{2.5}) at the World Trade Center site in 2001 and 2002.



Figure 5.16 Lead concentrations (composition of PM_{2.5}) at the World Trade Center site in 2001.



Figure 5.17 Measurements of airborne dioxins and furans near the World Trade Center site in 2001 and 2002.

personal utilities). However, once society's members saw the problems being wrought by unchecked combustion, they willingly accepted restrictions and regulations, as long as they were effective and perceived to be fair. In this way, the open-burning paradigm shift can be seen as a codicil to Thomas Hobbes' social contract; that is, had we continued on the path of unbridled combustion and emissions, we would have reached a societal "state of nature" where the collective of "brutes" with fires would damage the entire population, including our personal and familial well-being.

Ozone Depletion

The atmosphere surrounding the Earth is conveniently divided into identifiable layers. More than 80% of the airmass is in the lowest layer, the *troposphere*, which is between 10 and 12 km deep. The fastest airlines fly at around 38,000 feet, which is about 11.6 km. The mass of air in the troposphere varies with distance from the equator. At the equator, the troposphere is about 18 km deep, whereas at the poles it is only about 6 km deep. The temperature decreases with elevation, and the air within the troposphere is in motion with significant mixing.

Above the troposphere is the *stratosphere*, which is stable and reaches to about 50 km. There is little movement in or out of the layer, and anything that gets to that layer can be expected to stay there for a long time. Taken together, the troposphere and the stratosphere account for about 99.9% of all the air, and everything above this remaining 0.1% layer is considered "space."

One of the major gases in the stratosphere is ozone. Ozone (O_3) is a pollutant, but is also beneficial. It is a matter of where the O_3 is. The O_3 in the stratosphere acts as an ultraviolet radiation shield, and there is concern that this protective shield is being destroyed, leaving Earth and its inhabitants vulnerable to the effects of ultraviolet radiation, which can result in an increased risk of skin cancer as well as producing changes in the global ecology in unpredictable ways.

Ozone in the stratosphere is created by the reaction of oxygen with light energy, first splitting the oxygen molecule into free oxygen atoms:

$$O_2 + h\nu \to O + O \tag{5.19}$$

where *h* is Planck's constant $[6.62 \times 10^{-34} \text{ joule-second (J-s)}]$ and ν is the frequency (s⁻¹). Think of the combination of *h* and ν as light energy. The important point is that this reaction can take place only if the light energy is in the ultraviolet wavelength region, below about 400 mn.

Because the oxygen atoms are highly unstable, they will seek out oxygen molecules to form ozone,

$$O + O_2 + M \rightarrow O_3 + M \tag{5.20}$$

where M is some third body used to carry away the heat generated.

Ozone is in turn destroyed by light energy as ultraviolet radiation:

$$O_3 + h\nu \to O_2 + O \tag{5.21}$$

and the atomic oxygen can then once again react with molecular oxygen to form ozone. The light energy responsible for this reaction has a wavelength between 200 and 320 nm, which is smack in the middle of the ultraviolet part of the spectrum, thus adsorbing the ultraviolet energy and preventing it from reaching Earth's surface. If the stratosphere does not contain ozone, a much larger percentage of the ultraviolet energy will pass through the stratosphere, causing damage to living tissues. In the stratosphere there is a balance with oxygen being broken down, forming ozone, and the ozone being destroyed returning to oxygen molecules, all the time using up the energy from the ultraviolet radiation. The presence of the ozone at some steady-state concentration has become immensely important in protecting all life on Earth from damaging ultraviolet radiation.

The problem with the depletion of upper atmospheric ozone is due to the manufacture and discharge of certain compounds, especially a class of chemicals called *chlorofluorocarbons* (CFCs). These compounds have been widely used as propellants and in refrigeration systems, but may also responsible for both global warming as well as the depletion of the protective ozone layer in the stratosphere. Before the synthesis of CFCs, refrigeration units used CO₂, isobutene, methyl chloride, or sulfur dioxide, all of which are toxic, flammable, or inefficient. CFCs are nontoxic, not water soluble, nonreactive, nonbiodegradable, and are easily liquefied under pressure.²⁶ When they evaporate they produce very cold temperatures, making them ideal refrigerants. Two of the most important CFCs are trichlorofluoromethane, CFCl₃ (industrial designation CFC-11) and dichlorodifluoromethane, CF₂Cl₂ [industrial designation CFC-12, also known as Freon (trade name of DuPont)]. Other chlorinated refrigerants include hydrochlorofluorocarbons (HCFCs) such as CHF₂Cl (industrial designation HCFC-22) and hydrofluorocarbons (HFCs), which do not contain chlorine. One HFC of importance is CH₂FCF₃ (HFC 134a) which is becoming widely used in automobile air conditioners. Both the HCFCs and HFCs are still potentially ozone-depleting gases, but they can be broken down by sunlight and thus their lifetime in the atmosphere is significantly shorter than that of the CFCs and they don't end up in the stratosphere, whirling around for hundreds of years.

The problematic CFCs are no longer manufactured, although many air-conditioning systems still have CFCs, and thus the potential for damage by CFCs remains high. The problem is that the coolants can escape from the refrigeration units and enter the atmosphere, where they are inert and non-water soluble and do not wash out. They drift into the upper atmosphere and are eventually destroyed by shortwave solar radiation, releasing chlorine, which can react with ozone.

The effect of the CFCs on this delicate balance can be devastating. Because the CFCs are so nonreactive and nonsoluble, once they have drifted into the atmosphere, they will stay there for a long time. Eventually, they will be broken down by ultraviolet radiation, forming other chlorinated fluorocarbons and releasing atomic chlorine. For example, CFC-12, a leading refrigerant, breaks down as

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$
 (5.22)

The atomic chlorine acts as a catalyst in breaking down ozone:

$$Cl + O_3 \rightarrow ClO + O_2 \tag{5.23}$$

$$ClO + O \rightarrow Cl + O_2 \tag{5.24}$$

with atomic chlorine again forming to continue to promote more destruction of ozone. The atomic oxygen, meanwhile, can also help in destroying ozone:

$$O + O_3 \rightarrow 2O_2 \tag{5.25}$$

Thus, a single Cl atom can make thousands of loops until it eventually reacts with something like methane and is tied up chemically. The reaction with methane produces HCl and ClO. The ClO then can react with nitrogen dioxide (another air pollutant):

$$ClO + NO_2 \rightarrow ClONO_2$$
 (chlorine nitrate) (5.26)

The chlorine in HCl and $CIONO_2$ is trapped and can no longer enter into the foregoing reactions. The problem is that under certain conditions, both of these chemicals, HCl and $CIONO_2$, can break up and re-release the chlorine so that it can continue to do damage. These reactions occur when surfaces are available for the reaction to take place, and these surfaces are provided by molecules such as sulfate aerosols. The breakup of HCl and $CIONO_2$ plays an important role in understanding the "ozone hole" over the Antarctic.

During the winter months there exists a polar vortex, formed as a whirling mass of very cold air. This vortex is so strong that it isolates air above the South Pole from the rest of the atmosphere. When spring comes, this exceedingly cold $(-90^{\circ}C)$ air forms clouds of ice crystals in the stratosphere. On the surfaces of these crystals, the "inert" chlorinated compounds react as follows:

$$CIONO_2 + H_2O \rightarrow HOCI + HNO_3$$
(5.27)

$$HOC1 + HC1 \rightarrow Cl_2 + H_2O \tag{5.28}$$

$$CIONO_2 + HCl \rightarrow Cl_2 + HNO_3$$
(5.29)

These reactions tie up the chlorine on the ice crystals so that it cannot enter into the reactions to break up ozone. But when spring comes, this large quantity of stored chlorine suddenly becomes available, and light energy breaks it apart:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (5.30)

The sudden dumping of all that chlorine into the stratosphere results in a high rate of ozone destruction, producing the "hole" in the ozone layer. In the southern hemisphere's later spring (November) air from other parts of the globe rushes in, replenishing the ozone and reducing the size of the hole. The effect of the annual depletion is strongly felt in countries such as Australia and New Zealand, which are close to the Antarctic continent.

CASE STUDY: DISCOVERY OF THE OZONE HOLE

Ozone levels in the stratosphere had been measured since the 1970s using satellites. In addition to satellite data, a British team of scientist in the Antarctic began to measure the concentration of ozone in the stratosphere using sophisticated instruments at the base near the South Pole. In 1985 the team discovered that there had been a dramatic drop in the ozone levels in the stratosphere, creating a large hole (i.e., O₃ concentration lower than the rest of the strastosphere) over the Pole. The satellite date did not show such a hole, however, and the scientists concluded that their instruments must be faulty. They had a new set of instruments flown in, and even with careful calibration, they had to conclude that this huge hole had indeed developed. The team studied the satellite data and found that the software being used was designed to ignore very low levels of ozone and reported this simply as "no data." The satellite had seen this hole for many years, but the data reduction did not recognize the presence of the hole. When the scientists adjusted the program to report low levels of ozone, the satellite data agreed with the data obtained on the ground. There indeed was this huge hole over the middle of the South Pole.

The size of the ozone layer has been increasing over the years, prompting increasing concern about the effect on the Earth of ultraviolet radiation. Calculations show that a 1% increase in UV radiation can result in a 0.5% increase in melanoma, a particularly aggressive form of skin cancer, and a 2.5% increase in other forms of skin cancer. Epidemiological statistics show that melanoma is, in fact, increasing at a rate of 2 to 3% annually in the United States. It must be pointed out, however, that much of this increase might be explained by a longer life span as well as more outdoor activities and recreation.

UV radiation can also cause eye damage and can suppress the immune system in humans. A very troublesome effect of UV radiation is the suppression of photosynthesis in aquatic plants. A slower rate of photosynthesis would result in a higher atmospheric concentration of CO_2 , exacerbating the problems associated with global warming.

The story with the ozone layer and CFCs is one of two environmental researchers who published a courageous paper in 1974 suggesting that the depletion of ozone was possible as a direct result of escaped refrigerants. Industrial interests at first contested these findings, and it might never have become a global concern were it not for the discovery of the Antarctic ozone hole. From that point on, international concern forced action, culminating in the Montreal Protocol on Substances That Deplete the Ozone Layer, with 23 nations, including the United States, agreeing to cut the use of CFCs by 50% by 1999, and eventually, to cease production totally. In 1988, DuPont, the largest manufacturer of CFCs, stopped making them, prompting a huge underground industry based on smuggling these refrigerants into the United States, since so many cooling systems depended on them. In 1990, the availability of new refrigerants, and the growing concern with the ozone hole in the Antarctic, prompted a revised schedule, with a new timetable calling for a complete phase-out of CFCs by 2000, with a few exceptional chemicals needed for medical and other uses to be phased out by 2010. A convention in Copenhagen in 1992 again accelerated the phase-out, with the production and importation of CFCs banned as of 1994. The U.S. EPA responded to these protocols by banning nonessential use of CFCs, such as in noise horns, requiring automobile mechanics to save and reuse CFC in air conditioners, and mandating the removal of CFCs from cars headed for demolition.

The Montreal Protocol was mainly the product of both UK and U.S. leadership, and was possible because the two largest manufacturers of refrigerants, DuPont in the United States and ICI in the United Kingdom, already had developed alternative coolants. The Protocol was therefore welcomed by these industries since this represented a way of increasing their market share in these chemicals.

Global Warming

The first question that comes to mind in a discussion global warming is: Is it happening? Is the Earth really getting warmer? Quite obviously, the average temperature of the earth is difficult to measure, but the measurements agree that the Earth is getting warmer. This is a very small overall change that would not be detectable to humans based solely on short-term and regional variations.

The second question, provided that we have convinced ourselves that the Earth is in fact getting warmer, is what might be causing this increase in temperature. One explanation would be that we are simply seeing a natural cycle of temperature fluctuations, such as has occurred on Earth for hundreds of thousands of years. Studies of ice cores in Russia have shown that, amazingly enough, the mean temperature of the Earth has not changed in over 200,000 years. There have been wide fluctuations, such as the ice ages, but on balance, the mean temperature has remained constant, prompting some scientists to speculate some whimsical causes for such consistency.

There is another explanation for the sudden (relative to geological time) increase we are presently experiencing, and that is that the presence of certain gases in the atmosphere are causing the Earth to become less efficient in returning the heat energy from the sun back into space. The Earth acts as a reflector of the sun's rays, receiving radiation from the sun, reflecting some of it into space (called *albedo*), and adsorbing the rest, only to reradiate this into space as heat. In effect, the Earth acts as a wave converter, receiving high-energy, high-frequency radiation from the sun and converting most of it into low-

Biographical Sketches: F. Sherwood Rowland and Mario J. Molina



Mario Molina was born and raised in Mexico. Following his university graduation with a degree in physical chemistry, he went to Berkeley, where he did research on photochemical reactions. In 1973 he joined a research group headed by Sherwood Rowland at the University of California at Irvine. Rowland, who had come to Irvine after an undergraduate degree from Ohio Wesleyan and a Ph.D. in

chemistry from the University of Chicago, offered several research opportunities to Molina, who chose the little-known problem of understanding the fate of chlorofluorocarbons in the atmosphere. In 1972, Rowland had heard a talk by the British scientist James Lovelock about detecting these chemicals in the atmosphere but not understanding their fate. At first the study was only one of scientific curiosity, but soon they began to realize that the presence of CFCs in the stratosphere would have profound environmental consequences. Other scientists had recognized the effect of chlorine on stratospheric ozone, but none had shown that the CFCs would have a dramatic impact on the ozone concentration. Molina and Rowland published their findings in Nature in 1974 and immediately became the targets of severe scientific criticism from industrial interests. The two scientists persevered, however, and went to great lengths to publicize their results and to testify at congressional hearings. Finally, the scientists at DuPont, the largest manufacturer of CFCs, acknowledged that Molina and Rowland were correct, and pledged to cease the manufacture of these compounds. (The fact that they had already developed an alternative refrigerant no doubt played a role in their decision.)

In 1974, Rowland and Molina, along with Paul Crutzen of the Max-Planck Institute, were awarded the Nobel Prize in Chemistry for their work in understanding the chemical processes involved in ozone depletion.

energy, low-frequency heat to be radiated back into space. In this manner, the Earth maintains a balance of temperature.

To better understand this balance, light and heat energy have to be defined in terms of their radiation patterns, as shown in Figure 5.18. The incoming radiation (light) wavelength has a maximum at around 0.5 nm, and almost all of it is less than 3 nm. The heat energy spectrum, the energy reflected back into space, has the maximum at about 10 nm, almost all of it at a wavelength higher than 3 nm.

As both light and heat energy pass through the Earth's atmosphere, they encounter the aerosols and gases surrounding the Earth. These can either allow the energy to pass through, or they can interrupt it by scattering or absorption. If the atoms in the gas molecules vibrate at the same frequency as the light energy, they will absorb the energy

Biographical Sketch: Charles Keeling



Charles Keeling thought that atmospheric chemists should study the atmosphere from the field, and not from the laboratory, and he took his instruments to Mauna Loa in Hawaii, where he began to measure carbon dioxide concentrations in the atmosphere using an infrared gas analyzer. Beginning in 1958, these data have provided the single most important piece of information on global warming. The data are referred to as the *Keeling curve* in honor of the scientist.

The Keeling curve shows that there has been more than a 15% increase in CO_2 concentration, which is a huge jump given the short time that the measurements have been taken. It is likely, if we extrapolate backward, that our present CO_2 levels are double what they were in pre–industrial revolution times, providing ample evidence that global warming is indeed occurring.

Keeling received an undergraduate degree from the University of Illinois and a Ph.D. from Northwestern University. He worked for many years at the Scripps Institute of Oceanography in La Jolla, California.



Figure 5.18 Patterns for heat and light energy.

and not allow it to pass through. Aerosols will scatter the light and provide "shade" for the Earth. It was this latter effect that caused many scientists in the 1970s to be concerned about the possibility of "global cooling."

The absorptive potential of several important gases is shown in Figure 5.19, along with the spectra for the incoming light (short-wavelength) radiation and the outgoing heat (long-wavelength) radiation. The incoming radiation is impeded by water vapor and oxygen and ozone, as discussed in the preceding section. Most of the light energy however, comes through unimpeded.

The heat energy, on the other hand, encounters several potential impediments. As it is trying to reach outer space, it finds that water vapor, CO_2 , CH_4 , O_3 , and N_2O all have absorptive wavelengths in the middle of the heat spectrum. An increase in the concentration of any of these will greatly limit the amount of heat transmitted into space. These heat-trapping gases are appropriately called *greenhouse gases* because their presence will limit the heat escaping into space, much like the glass of a greenhouse or even the glass in your car limits the amount of heat that can escape, thus building up the temperature under the glass cover on a sunny day.

The effectiveness of a particular gas to promote global warming (or cooling, as is the case with aerosols) is known as *radiative forcing*. The atmospheric gases of most importance in forcing are listed in Table 5.1 and Appendix 2 (Radiative Forcing and Global Warming).



Figure 5.19 Absorptive potential of several important gases in the atmosphere. Also shown are the spectra for the incoming solar energy and the outgoing thermal energy from the Earth. Note that the wavelength scale changes at 4 μ m. (From G. Masters, *Introduction to Environmental Engineering and Science*, Prentice Hall, Upper Saddle River, NJ, 1998.)

Gas	Percent of relative radiative forcing
Carbon dioxide, CO ₂	64
Methane, CH ₄	19
Halocarbons (mostly CFCs)	11
Nitrous oxide, N ₂ O	6

 Table 5.1
 Relative Radiative Forcing of Increased

 Global Temperature
 Provide State

Carbon dioxide is the product of decomposition of organic material, whether biologically or through combustion. The effectiveness of CO_2 as a global warming gas has been known for over 100 years, but the first useful measurements of atmospheric CO_2 were not taken until 1957. The data from Mauna Loa in Hawaii are exceptionally useful, since they show that even in the 1950s the CO_2 concentration had increased from the baseline 280 ppm to 315 ppm, and this has continued to climb over the last 50 years at a constant rate of about 1.6 ppm per year. The most serious problem with CO_2 is that the effects on global temperature due to its greenhouse effect are delayed. Even if we stopped emitting any new CO_2 into the atmosphere, what we have already done will increase CO_2 from our present 370 ppm to possibly higher than 600 ppm. Even if we stopped producing excess CO_2 now, we have already contaminated the global atmosphere to where we will have increased the CO_2 concentration to 450 ppm. The effect of this is discussed below.

Methane is the product of anaerobic decomposition and human food production. One of the largest producers of methane in the world is New Zealand, which has 80 million sheep. Methane is also emitted during the combustion of fossil fuels and cutting and clearing of forests. The concentration of CH_4 in the atmosphere has been steady at about 0.75 ppm for over 1000 years, but spiked to 0.85 ppm in 1900. Since then, in the space of only 100 years, CH_4 has skyrocketed to 1.7 ppm. Methane is removed from the atmosphere by reaction with the hydroxyl radical (OH'):

$$CH_4 + OH + 9O_2 \rightarrow CO_2 + 0.5H_2 + 2H_2O + 5O_3$$
 (5.31)

In so doing, it creates carbon dioxide, water vapor, and ozone, all of which are greenhouse gases, so the effect of one molecule of methane is substantial to the production of the greenhouse effect.

Halocarbons, the same chemical class involved in the destruction of atmospheric ozone, are also at work in promoting global warming. The most effective global warming gases are CFC-11 and CFC-12, both of which are no longer manufactured, and the banning of these substances has shown a leveling off in the stratosphere.

Nitrous oxide (N_2O , known as laughing gas) is also in the atmosphere, primarily as a result of human activities, especially the cutting and clearing of tropical forests. The greatest problem with nitrous oxide is that there appear to be no natural removal processes for this gas, so its residence time in the stratosphere is quite long.

The net effect of these global pollutants continues to be debated. Various atmospheric models used to predict temperature change over the next hundred years vary widely (about 1.5 to 5.5°C). They nevertheless agree that some increase will occur even if we do something drastic today (which does not seem likely). Even if we do not increase our production of greenhouse gases and if the Western nations were to agree to terms akin to those in the Kyoto Accord, which encourages the reduction in greenhouse gas production, the global temperature is likely to be between 0.5 and 1.5°C warmer by the year 2100. The effect of this seemingly small temperature increase on natural systems and ocean currents will be devastating, including shifts in biomass, altered habitats, and even changes in human disease transmission.

Emerging Health Endpoints of Concern

For most of the second half of the twentieth century, scientific research targeted cancer as its major chronic health endpoint. Environmental carcinogens received the most attention of the numerous etiologies addressed. As such, many of the toxic substances addressed by environmental professionals are carcinogenic. Recently, other health endpoints have also gained much attention. Since the 1970s a cascade of research has shown that lead (Pb), mercury (Hg), and other metals, as well as organophosphate and halogenated organic pesticides and other organics (e.g., PCBs, dioxins), are highly neurotoxic (i.e., they damage the brain and the peripheral and central nervous systems). This is particularly problematic for children, since the effects are more pronounced when tissue is proliferating and since neurotoxicity leads to learning disabilities and behavioral disorders.

More recently, numerous chemicals found in the environment have been linked to hormonal dysfunctions.²⁷ These chemicals, known as *endocrine disruptors* (see Table 5.2), act like natural hormones by binding to a cell's receptor, at which point they are known as *agonists*. Conversely, chemicals that inhibit the receptor are called *antagonists*. Environmental endocrine disruptors can be of either type. Another group of chemicals act as indirect disruptors, due to their effects on the immune or neural systems, such as the strong neurotoxin mercury, which does not bind to an estrogen or androgen site, but affects the neurological system, which in turn interferes with an organism's hormonal health. The neural, immunological, and endocrine systems are all chemical messaging systems that are so interconnected that a change in one can lead to changes to the others.

Environmental endocrine disruption was observed through much of the twentieth century. Abnormal mating patterns in bald eagles on the east coast of North America were observed in the 1940s. Rachel Carson in the classic 1962 book *Silent Spring* observed that predatory birds such as eagles accumulated chlorinated hydrocarbon pesticides. The eggshells of these birds were abnormally thin, and dichlorodiphenyltrichloroethane (DDT)-contaminated birds were less successful in hatching than those with lower concentrations of the pesticide. During the last two decades of the twentieth century, scientists increasingly found associations between exposure to chemical compounds and changes affecting endocrine systems in humans and animals. These compounds were first called *environmental estrogens*, but since other hormonal effects were found, the term *environmental hormone* gained usage. *Hormone mimicker* was sometimes used to

Compound ^a	Endocrine effect ^b	Potential source
2,2',3,4',5,5'-Hexachloro-4-biphenylol and other chlorinated biphenylols	Antiestrogenic	Degradation of PCBs released into the environment
4',7-Dihydroxydaidzein and other isoflavones, flavones, and flavonals	Estrogenic	Natural flora
Aldrin*	Estrogenic	Insecticide
Alkylphenols	Estrogenic	Industrial uses, surfactants
Bisphenol A and phenolics	Estrogenic	Plastics manufacturing
DDE [1,1-dichoro-2,2-bis(<i>p</i> -chlorophenyl)ethylene]	Antiandrogenic	DDT metabolite
DDT and metabolites	Estrogenic	Insecticide
Dicofol	Estrogenic or antiandrogenic in top-predator wildlife	Insecticide
Dieldrin	Estrogenic	Insecticide
Diethylstilbestrol (DES)	Estrogenic	Pharmaceutical
Endosulfan	Estrogenic	Insecticide
Hydroxy-PCB congeners	Antiestrogenic (competitive binding at estrogen receptor)	Dielectric fluids
Kepone (Chlorodecone)	Estrogenic	Insecticide
Lindane (γ -hexachlorocyclohexane) and other HCH isomers	Estrogenic and thyroid agonistic	Miticide, insecticide
Lutolin, quercetin, and naringen	Antiestrogenic (e.g., uterine hyperplasia)	Natural dietary compounds
Malathion*	Thryroid antagonist	Insecticide
Methoxychlor	Estrogenic	Insecticide
Octachlorostyrene*	Thryroid agonist	Electrolyte production
Pentachloronitrobenzene*	Thyroid antagonist	Fungicide, herbicide
Pentachlorophenol	Antiestrogenic (competitive binding at estrogen receptor)	Preservative
Phthalates and their ester compounds	Estrogenic	Plasticizers, emulsifiers
Polychlorinated biphenyls (PCBs)	Estrogenic	Dielectric fluid
Polybrominated diphenyl ethers (PDBEs)*	Estrogenic	Fire retardants, including <i>in utero</i> exposures
Polycyclic aromatic hydrocarbons (PAHs)	Antiandrogenic (aryl hydrocarbon–receptor agonist)	Combustion by-products
Tetrachlorodibenzo- <i>para</i> -dioxin and other halogenated dioxins and furans*	Antiandrogenic (aryl hydrocarbon–receptor agonist)	Combustion and manufacturing (e.g., halogenation) by- product
Toxaphene	Estrogenic	Animal pesticide dip
Tributyl tin and tin organometallic compounds*	Sexual development of gastropods and other aquatic species	Paints and coatings

Table 5.2 Some Compounds Found in the Environment That Have Been Associated with Endocrine Disruption,Based on In Vitro, In Vivo, Cell Proliferation, or Receptor-Binding Studies

Compound ^a	Endocrine effect ^b	Potential source
Vinclozolin and metabolites	Antiandrogenic	Fungicide
Zineb*	Thyroid antagonist	Fungicide, insecticide
Ziram*	Thyroid antagonist	Fungicide, insecticide

Table 5.2 (Continued)

Source: D. A. Vallero, Environmental Endocrine Disruptors, in *McGraw-Hill Yearbook of Science and Technology*, McGraw-Hill, New York, 2004. For a full list, study references, study types, and cellular mechanisms of action, see Chapter 2 of National Research Council, *Hormonally Active Agents in the Environment*, National Academies Press, Washington, DC, 2000. The source for asterisked (*) compounds is T. Colburn et al., http://www.ourstolenfuture.org/Basics/chemlist.htm.

^{*a*} Not every isomer or congener included in a listed chemical group (e.g., PAHs, PCBs, phenolics, phthlates, flavinoids) has been shown to have endocrine effects. However, since more than one compound has been associated with hormonal activity, the entire chemical group is listed here.

^b Note that the antagonists' mechanisms result in an opposite net effect. In other words, an antiandrogen feminizes and an antiestrogen masculinizes an organism.

describe compounds that could elicit a response like that of a natural hormone. For example, certain pesticides bind very easily to estrogen receptors, resulting in increased feminization of the organism. For example, male fish exposed to estrogenic components will start producing vitellogenin, an egg-laying hormone. A hormonally active agent and an endocrine disruptor are more general classifications of any chemical that causes hormonal dysfunction.

Endocrine effects can vary dramatically within a population, with some groups being highly susceptible to endocrine disruptors, while other seemingly go completely unscathed. Sensitive subpopulations, especially adolescents and children, may be particularly threatened. Considerable scientific uncertainty exists, but numerous chemicals, including organochlorine pesticides such as DDT and persistent organic chemicals such as the polychlorinated biphenyls (PCBs) have been shown in laboratory studies at very low concentrations to block or mimic hormones during prenatal development, giving rise to concerns about birth defects and changes in a child's growth and development. Endocrine disruptors have also been associated with certain reproductive cancers. Like other environmental contaminants, endocrine disruptors vary in physical and chemical forms. These differences result in distinct ways that chemicals resist breaking down in the environment, known as *persistence*. Chemicals also vary in their ability to bioaccumulate as well as in their toxicity. Persistent, bioaccumulating toxics easily build up in the food chain and lead to toxic effects: in this instance, hormonal dysfunction. Thus, endocrine disruptors can be organic compounds [known as persistent organic pollutants (POPs)], inorganic compounds (certain metals and their salts), or organometallic compounds, such as the butylated or phenalated forms of the metal tin (Sn).

Endocrine disruptors enter the environment in numerous ways. Wastes from households and medical facilities may contain hormones that reach landfills and wastewater treatment plants, where they pass through untreated or incompletely treated and enter waterways. Fish downstream from treatment plants have shown symptoms of endocrine disruption. Engineers designing treatment facilities must consider the possibility that wastes will contain hormonally active chemicals and find ways to treat them. In addition, manufacturers of pharmaceuticals, plastics, and other sources of endocrine disruptors must find ways to eliminate them. One means of doing this is to change the chemical structure of compounds (known as *green chemistry*) so that they do not bind or block receptor sites on cells. The addition or deletion of a single atom or the arrangement of the same set of atoms (i.e., an isomer) can significantly reduce the likelihood of hormonal effects elicited by a compound.

Hundreds of thousands of chemicals in current or past use are present in the environment, meaning that human populations and ecosystems are at risk of being exposed to them. The large number and various forms of chemicals preclude regulators from evaluating every chemical with the most rigorous testing strategies. Instead, standard toxicity tests have been limited to a small number of chemicals, with the hope that the "worst" chemicals receive specific attention; or the chemicals that are tested may represent large classes of compounds, such as certain types of pesticides. The good news is that computational biology offers the possibility that with advances in its subdisciplines (e.g., genomics, proteomics, metabolomics, metabonomics), scientists may have the ability to develop a more detailed understanding of the risks posed by a much larger number of chemicals pose to human health and the environment is termed *computational toxicology*. Computational toxicology applies mathematical and computer models to predict adverse effects and to better understand the mechanism(s) through which a given chemical induces harm (see Table 6.1).

Much of what is known about environmental problems and risks has been learned from laboratory or field studies, or from studies of exposures of populations. However, scientists are beginning to develop new "tools" to understand the processes that lead to environmental risks, including the blending of genomic technologies, sophisticated structure–activity analysis, and high-performance computer modeling of pharmacokinetic and pharmacodynamic pathways. Recent advances focus on breaking down the traditional dichotomy between approaches to evaluating cancer *versus* other disease endpoints, on addressing sensitive life stages, and on addressing aggregate and cumulative exposure to pollutants. The engineer and environmental professional will benefit from the new methods for predicting environmental problems and health threats.

Hazardous Waste Contamination

One of the biggest challenges to environmental professionals is what to do with contaminated sites. Over the past three millennia, civilization has generated wastes in exponentially increasing volumes. Engineering has its roots in these attempts at control. Knossos, Crete's burial program for solid wastes produced by the Minoan civilization (a precursor of the modern landfill where waste was buried in layers intermittently covered by soil), is one of the first recorded efforts at land disposal of wastes.²⁸ In the millennium before Christ, the city-state of Athens required that citizens be responsible for the refuse and garbage that they produced, and that they transport the wastes at least 1500 meters from the city walls for disposal. The ancient Greeks and Romans also addressed the need for potable water supplies.²⁹ Vitruvius, for example, recognized in the first century B.C. that water would become polluted in stationary ponds left to evaporate, a process we now refer to as *eutrophication*. He also noted the generation of "poisonous vapors," probably the generation of methane from the anaerobic, reduced conditions of eutrophic water bodies. Ironically, Vitruvius may well have avoided recommending that the neurotoxic lead be used for water supplies, not due to its toxicity (unknown until this century), but because bronze could better withstand the pressures on the closed pipe systems used to move water relatively long distances.³⁰

Incineration applied to wastes was led by Europeans, especially Britain and Germany, in the nineteenth century, with the first municipal garbage incineration program established in Nottingham, England, in 1874, followed in a couple of decades by a Britain's first "waste-to-energy" incinerator in the 1890s.³¹

For centuries, wastes that would now be categorized as hazardous, were simply stored above ground, in pits, ponds, and lagoons, or buried under thin layers of soil. In the 1950s and 1960s, initiatives to eliminate open dumps called upon engineers to begin designing sanitary landfills. These engineered systems were a response to public health concerns, but the concern has moved beyond infectious disease agents to a myriad of toxic chemicals.

Hazardous waste can be generated from many types of processes (see Table 5.3) and generally has been considered a subset of solid waste and has been distinguished from municipal wastes and nonhazardous industrial wastes. This characterization is not based completely on science and engineering, but also on the regulatory history of hazardous wastes. For example, in the United States in the mid-1970s, statutes already existed to control air and water pollution, as well as the design of landfills and other facilities to address solid wastes, but the problem of hazardous wastes was not being addressed. As a result, the U.S. Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976. The law's primary goals are to protect human health and the environment from the potential hazards of waste disposal, to conserve energy and natural resources, to reduce the amount of waste generated, and to ensure that wastes are managed in an environmentally sound manner.³² Of the 13 billion tons of industrial, agricultural, commercial, and household wastes generated annually in the United States, 2% (i.e., more than 279 million tons) are "hazardous" as defined by RCRA regulations.

One of the chief concerns from hazardous wastes is the potential to contaminate groundwater, which can be affected by any type of hazardous waste from numerous sources. Thus, hazardous wastes may be of any phase: solid, liquid, gas, or mixtures. Also, the hazardous of the waste can result from its inherent properties, such as its physicochemical properties, including its likelihood to ignite, explode, react, cause irritations, or elicit toxic effects. A waste's hazardous inherent properties can also be biological, such as that of infectious medical wastes.

Since wastes are transported by fluids (i.e., liquids and gases), especially in air and water, the likelihood of contamination depends strongly on physical properties, especially solubility, density, and vapor pressure. If the substances comprising the hazardous waste are quite soluble (i.e., easily dissolved in water under normal environmental conditions of temperature and pressure), they are known to be *hydrophilic*. If, conversely, a substance is not easily dissolved in water under these conditions, it is said to be *hydrophobic*. Since many contaminants are organic (i.e., consisting of molecules containing covalent carbon-to-carbon bonds and/or carbon-to-hydrogen bonds), the solubility can be further differentiated as to whether under normal environmental conditions of temperature and pressure, the substance is easily dissolved in organic solvents. Such substances are said

Waste generator	Types of wastes produced	
Chemical manufacturers	Strong acids and bases	
	Reactive wastes	
	Ignitable wastes	
	Discarded commercial chemical products	
Vehicle maintenance shops	Paint wastes	
	Ignitable wastes	
	Spent solvents	
	Acids and bases	
Printing industry	Photography waste with heavy metals	
	Heavy metal solutions	
	Waste inks	
	Spent solvents	
Paper industry	Ignitable wastes	
	Corrosive wastes	
	Ink wastes, including solvents and metals	
Construction industry	Ignitable wastes	
-	Paint wastes	
	Spent solvents	
	Strong acids and bases	
Cleaning agents and cosmetic manufacturing	Heavy metal dusts and sludges	
	Ignitable wastes	
	Solvents	
	Strong acids and bases	
Furniture and wood manufacturing and refinishing	Ignitable wastes	
	Spent solvents	
	Paint wastes	
Metal manufacturing	Paint wastes containing heavy metals	
-	Strong acids and bases	
	Cyanide wastes	
	Sludges containing heavy metals	

 Table 5.3
 Typical Hazardous Wastes Generated by Selected Industries

Source: U.S. Environmental Protection Agency, *RCRA: Reducing Risks from Wastes*, EPA/530/K-97/004, U.S. EPA, Washington, DC, September 1997.

to be *lipophilic* (i.e., readily dissolved in lipids). If, conversely, a substance is not easily dissolved in organic solvents under these conditions, it is said to be *lipophobic*. When a fluid that is dense and miscible (i.e., able to be mixed in any concentration without separation of physical phases) seeps underground through the vadose zone, below the water table, and into the zone of saturation, the dense contaminants move downward (see Figure 5.20). When these contaminants reach the bottom of the aquifer, the shape continued movement is determined by the slope of the underlying bedrock or other relatively impervious layer. Solution and dispersion near the boundaries of the plume will generate a secondary plume that will generally follow the direction of groundwater flow (see Figure 5.21). Organics more dense than water [called dense nonaqueous-phase liquids,



Figure 5.20 Dense nonaqueous-phase liquids (DNAPLs) can penetrate more deeply into the aquifer than do the light nonaqueous-phase liquids (LNAPLs). The density reference for whether a compound is a DNAPL or an LNAPL is whether it is denser or lighter than water, respectively. The DNAPL may even be against the general flow of the groundwater. (From D. A. Vallero, *Environmental Contaminants: Assessment and Control,* Elsevier Academic Press, Burlington, MA, 2004; and H. Hemond and E. Fechner-Levy, *Chemical Fate and Transport in the Environment,* Academic Press, San Diego, CA, 2000.)

(DNAPLs)] will penetrate more deeply, whereas the lighter organics [light nonaqueousphase liquids (LNAPLs)] will float near the top of the zone of saturation.

The physics of this system determine the direction of the contaminant plume's movement. For example, the movement is greatly affected by the solubility and density of the contaminants, but other factors also influence the rate of transport (e.g., sorption, presence of other solvents besides water, and the amount of organic matter in the soil). Figure 5.2 indicates the importance of vapor pressure. The volatile contaminants (i.e., those with relatively high vapor pressure), can move upward from the plume, often reaching the atmosphere. Thus, hazardous wastes can contaminate the air, soil, aquifers, and surface waters.

A promising development in recent years has been improvements in ways to reclaim previously contaminated sites. *Brownfields* are properties that have been polluted by a hazardous substance. Cleaning up and reinvesting in these properties takes development pressures off undeveloped open land, and both improves and protects the environment. In Houston, Texas, for example, the inner-city and downtown areas that were neglected as the city experienced an economic boom in the 1970s and 1980s precipitated the move of businesses and residents away from the urban core to the expanding development of outlying suburbs.³³ The abandoned properties downtown were feared to have environ-



Figure 5.21 Hypothetical plume of hydrophobic fluid. [From D. A. Vallero, *Environmental Contaminants: Assessment and Control*, Elsevier Academic Press, Burlington, MA, 2004; and M. N. Sara, Groundwater Monitoring System Design, in *Practical Handbook of Ground-Water Monitoring*, D. M. Nielsen (Ed.), Lewis Publishers, Chelsea, MI, 1991.]

mental contamination, which prevented efforts to redevelop these properties for several years. Houston's Brownfields Redevelopment Program has since led to these inner-city brownfields being assessed, cleaned up, and redeveloped for such uses as a major league baseball park, a 450-acre golf course, a performing arts center, an aquarium and enter-tainment complex, and nearly 1000 new housing units. March 30, 2000 saw the opening of Astros Field, a 42,000-seat baseball stadium built on a 38-acre former brownfield. The redeveloped site also includes a railroad station, an industrial facility, and a number of corrugated-metal buildings. The site's owner funded environmental assessments at the site, entered the property into the Texas Voluntary Cleanup Program, and funded the site's cleanup. Located on the east side of downtown Houston, the ballpark offers spectators a spectacular view of the Houston skyline. The Astros Field property also includes the renovated Union Station, with restaurants, shops, and a theater. The \$310 million redevelopment project has created 223 new jobs and is a leading force behind the revitalization of downtown Houston.

Before cleanup and redevelopment of a waste site begin, engineers must conduct site investigations to determine the degree and extent of contamination. These investigations are eligible for financial assistance from local, state, and federal agencies. A number of factors must be considered to determine if a contaminated site is a good candidate for redevelopment and whether to conduct a Brownfield investigation, including:

- · The surrounding neighborhood's economic status
- · The degree of uncertainty surrounding the site's contamination
- · The likelihood that the site investigation will reduce such uncertainty
- · The feasibility of proceeding with the assessment within the established time frame
- · Plans for reuse
- · Benefits to the community
- · General geographic diversity and financial need

Diversity, Productivity, and Sustainability of Ecosystems

The health of the global ecosystem depends on diversity, productivity, and sustainability. If a productive and highly diverse system of interlocking species shows sustainability, the ecosystem is able to withstand stresses or perturbations. If, on the other hand, species die out and diversity is reduced or the productivity is stunted, the ecosystem is susceptible to failure and collapse.

Ecosystems can be stressed by numerous human activities that introduce stressors to the environment. As is the case for human health risk assessments, the stressors may be chemicals, but physical and biological stressors also exist. For example, the placement of a roadway or the changes brought about by bulldozers and earthmovers are considered to be physical stressors to habitats. The accidental or intentional introduction of invasive biota [e.g., grass carp (fauna) and kudzu (flora) in the southern United States] are examples of biological stressors.

The identification of possible adverse outcomes is crucial. These outcomes alter essential structures or functions of an ecosystem. The severity of outcomes is characterized as to their type, intensity, and scale of the effect and the likelihood of an ecosystem to recover from the damage imposed by a single or multiple stressors. The characterization of adverse ecological outcomes can range from qualitative, expert judgments to statistical probabilities. The emergent fields of eco-toxicology and eco-risk have several things in common with human toxicology and risk assessment, such as concern about ambient concentrations of contaminants and uptake in water, air, and soil. In some ways, however, ecological dose–response and exposure research differs from that in human systems. First, ecologists deal with many different species, some more sensitive than others, to the effects of contaminants. Second, the means of calculating exposure are different, especially if one is concerned about the exposure of an entire ecosystem.

Ecosystems are complex. Ecologists characterize them by evaluating their composition, structure, and functions. Ecosystem composition is a list, a taxonomy if you will, of every living and nonliving part of the ecosystem. As the term implies, *ecological structure* is how all of the parts of the system are linked to form physical patterns of life-forms from single forest stands to biological associations and plant communities. A single wetland or prairie, for example, is a much simpler structure than a multilayered forest, which consists of plant and microbial life in the detritus, herbs, saplings, newer trees, and canopy trees. Ecosystem functions include cycles of nitrogen, carbon, and phosphorus that lead to biotic processes such as production, consumption, and decomposition.

Indicators of an ecosystem's condition include:

• *Diversity. Biodiversity* has been defined as the ". . . composition, structure, and function [that] determine, and in fact constitute, the biodiversity of an area. Composition has to do with the identity and variety of elements in a collection, and includes species lists and measures of species diversity and genetic diversity. Structure is the physical organization or pattern of a system, from habitat complexity as measured within communities to the pattern of patches and other elements at a landscape scale. Function involves ecological and evolutionary processes, including gene flow, disturbances, and nutrient cycling."³⁴

The diversity of this stream community can be found using the *Shannon–Weiner index:*

$$D = -\sum_{i=1}^{m} P_i \log_2 P_i$$
 (5.32)

or

$$D = -1.44 \sum_{i=1}^{m} \frac{n_i}{N} \ln \frac{n_i}{N}$$
(5.33)

where *D* is the index of community diversity; $P_i = n_i/N$; n_i is the number (i.e., density) of the *i*th genera or species; *N* is the total number (i.e., density) of all organisms in the sample; i = 1, 2, ..., m; and *m* is the number of genera or species. The higher the value of *D*, community diversity, the greater is the stability of the ecosystem.

• *Productivity.* This is an expression of how economical a system is with its energy. How much biomass is produced from abiotic (e.g., nutrients and minerals) and biotic resources (from microbial populations to canopy plant species to top predator fauna). One common measure is *net primary productivity*, which is the difference between two energy rates:

$$P_1 = k_p - k_e (5.34)$$

where P_1 is the net primary productivity, k_p is the rate of chemical energy storage by primary producers, and k_e is the rate at which the producers use energy (via respiration).

• *Sustainability.* How likely is it that the diversity and productivity will hold up? Even though an ecosystem appears to be diverse and highly productive, is there something looming that threatens the continuation of these conditions? For example, is an essential nutrient being leached out of the soil, or are atmospheric conditions changing that may threaten a key species of animal, plant, or microbe? Sustainability is difficult to quantify precisely.

Example:

Assessing Ecological Risk³⁴

In 2000, your environmental assessment of microbes in a small stream at your plant found a total of 1510 organisms, represented by seven different species. Your

actual number count of each microbial species in stream community was 10, 50, 75, 125, 200, 350, and 750 m L^{-1} .

Construct a table to derive the values needed to find D, using equation (5.33):

i	n_i	n_i/N	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	10	0.006623	7.224883	0.047847
2	50	0.033113	4.907292	0.162493
3	75	0.049669	4.323423	0.21474
4	125	0.082781	3.587834	0.297006
5	200	0.13245	2.911028	0.385567
6	350	0.231788	2.105182	0.487956
7	700	0.463576	1.10705	0.513202
Σ	1510	1		2.10881

$$D = -1.44 \sum_{i=1}^{m} \frac{n_i}{N} \ln \frac{n_i}{N}$$

So the diversity index is 2.1. The index is most useful when comparing systems. So if your stream is 2.1 and the surrounding streams are all around 4, you may have a problem. Generally, D values range from about 1.5 to 4.5.

What will happen if all of the numbers of species quadrupled?

Construct a new table with four times each species:

i	n_i	n_i/N	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	40	0.006623	7.224883	0.047847
2	200	0.033113	4.907292	0.162493
3	300	0.049669	4.323423	0.21474
4	500	0.082781	3.587834	0.297006
5	800	0.13245	2.911028	0.385567
6	1400	0.231788	2.105182	0.487956
7	2800	0.463576	1.10705	0.513202
Σ	6040	1		2.10881

So nothing changed; the index remains 2.1. The index indicates, correctly, that the total species abundance does not affect diversity.

You conducted a follow-up study in 2005 which indicates that the density of these species had changed to 3000, 50, 35, 40, 30, 70, and 15 L^{-1} of the same species of microbes as the early study. How had the numbers and diversity changed in five years?

i	n_i	n_i/N	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	3000	0.92593	0.11082	0.10261
2	50	0.01543	6.00668	0.0927
3	35	0.0108	6.52029	0.07044
4	40	0.01235	6.32801	0.07812
5	30	0.00926	6.74227	0.06243
6	70	0.0216	5.52216	0.11931
7	15	0.00463	7.7404	0.03584
Σ	3240	1		0.56144

Again, calculate D by constructing a new table:

This shows that in five years, the actual number of microbes is more than doubling, but the diversity has been reduced drastically (D = 0.6 versus 2.1). This may indicate that conditions favorable to one species [e.g., the presence of a toxic chemical or a change in habitat (e.g., a road)] are detrimental to the other six species.

A follow-up question must be asked: Were they conducted in the same season (some microbes grow better in warmer conditions, whereas others may compete more effectively in cooler waters)? If the studies are comparable, further investigation is needed, but this certainly is an indication that things are amiss, since Shannon values usually range from about 1.5 to 4.5. Diversity, like productivity, is often an important indicator of change. If diversity as measured by the index shows a decline, it may well indicate than an ecosystem is under increasing stress.

Ecological risk assessments may be prospective or retrospective, but often are both. The Florida Everglades provides an example of an integrated risk approach. The population of panthers, a top terrestrial carnivore in southern Florida, was found to contain elevated concentrations of mercury (Hg) in the 1990s. This was observed through retrospective eco-epidemiological studies. The findings were also used as scientists recommended possible measures to reduce Hg concentrations in sediment and water in Florida. Prospective risk assessments can help to estimate expected changes in Hg concentrations in panthers and other organisms in the food chain from a mass balance perspective. That is, as the Hg mass entering the environment through the air, water, and soil is reduced, how has the risk to sensitive species been reduced concomitantly? Integrated retrospective/prospective risk assessments are employed where ecosystems have a history of previous impacts and the potential for future effects from a wide range of stressors. This may be the case for hazardous waste sites.

The ecological risk assessment process embodies two elements: characterizing the adverse outcomes and characterizing the exposures. From these elements, three steps are undertaken:

- 1. Problem formulation
- 2. Analysis
- 3. Risk characterization

In problem formulation, the need to conduct the assessment is fully described, the specific problem or problems are defined, and the plan for analysis and risk characterization is laid out. Problem formulation includes integrating available information about the potential sources, the description of all stressors, the effects, and the characterization of the ecosystem and the receptors. Two basic products result from this stage of eco-risk assessment: assessment endpoints and conceptual models.

The analysis phase consists of evaluating the available data to conduct an exposure assessment (i.e., exposure to stressors is likely to occur or to have occurred). From these exposure assessments, the next step is to determine the possible effects and how wide-spread and severe these outcomes will be. During analysis, the engineer should investigate the strengths and limitations of data on exposure, effects, and ecosystem and receptor characteristics. Using these data, the nature of potential or actual exposure and the ecological changes under the circumstances defined in the conceptual model can be determined. The analysis phase provides an exposure profile and stressor–response profile, which together form the basis for risk characterization.

Thus, the ecological risk assessment provides valuable information to the engineer by:

- Providing information to complement the human health information, thereby improving environmental decision making
- Expressing changes in ecological effects as a function of changes in exposure to stressors, which is particularly useful to the decision maker who must evaluate trade-offs, examine different options, and determine the extent to which stressors must be reduced to achieve a given outcome
- Characterizing uncertainty as a degree of confidence in the assessment, which aid the engineer's focus on those areas that will lead to the greatest reductions in uncertainty
- Providing a basis for comparing, ranking, and prioritizing risks, as well as information to conduct cost-benefit and cost-effectiveness analyses of various remedial options
- Considering management needs, goals, and objectives, in combination with engineering and scientific principles to develop assessment endpoints and conceptual models during problem formulation

Environmental problems are complex. As we learn more about them, engineers and environmental professionals must find innovative ways to address them. Engineers play a particularly important role in helping society manage these risks.

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- 13. For example, the Leopold index is an interaction matrix developed by the U.S. Geological Survey for environmental assessment applications.
- 14. For an interesting application of the NEPA process in an area important to environmental justice communities (i.e., nuclear power facility siting), consider the Nuclear Regulatory Commission (NRC) environmental justice policy. The policy articulates the NRC's commitment to complying the requirements of the National Environmental Policy Act (NEPA) in all of its regulatory and licensing actions, especially as these actions may incur differential impacts greater than those of the general population, due to a community's distinct cultural characteristics or practices. See http://www.epa.gov/fedrgstr/EPA-IMPACT/2003/November/Day-05/i27805.htm.
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- 19. The Coalition for Justice in the Maquiladoras, a cross-border group that organizes maquiladora workers, traces the term *maquiladora* to *maquilar*, a popular form of the verb *maquinar*, which means roughly "to submit something to the action of a machine, as when rural Mexicans speak of *maquilar* with regard to the grain that is transported to a mill for processing. The farmer owns the grain; yet someone else, who owns the mill, keeps a portion of the value of the grain

for milling. So the origin of maquiladora can be found in this division of labor. The term has more recently been applied to the small factories opened by U.S. companies that provide laborintensive jobs on the Mexican side of the border. Thus, *maquilar* has changed to include this process of labor, especially assembling parts from various sources, and the maquiladoras are those small assembling operations along the border. While the maquiladoras have fueled the growth of entrepreneurs along the Mexico–U.S. border, they have also provided an opportunity for the workers and their families to be exploited in the interests of profit and economic gain.

- S. Mukerjee, Communication Strategy of Transboundary Air Pollution Findings in a US– Mexico Border XXI Program Project, *Environmental Management*, 29(1):34–56, 2002.
- 21. Often, these barrels were the 55-gallon drum variety, so the first burning probably volatilized some very toxic compounds, depending on the residues remaining in the drum. These contents could have been solvents (including halogenated compounds such as chlorinated aliphatics and aromatics), plastic residues (e.g., phthalates), and petroleum distillates. They may even have contained substances with elevated concentrations of heavy metals such as mercury, lead, cadmium, and chromium. The barrels (drums) themselves were often perforated to allow for higher rates of oxidation (combustion) and to take advantage of the smokestack effect (i.e., driving the flame upward and pushing the products of incomplete combustion out of the barrel and into the plume). Vallero recalls neighbors not being happy about burning trash while their wash was drying on the clothesline. They would complain of ash (aerosols) blackening their clothes and the odor from the incomplete combustion products on their newly washed laundry. Both of these complaints are evidence that the plume leaving the barrel contained harmful contaminants that were transported in the atmosphere.
- The principal source for this section is National Toxicology Program, Eleventh Report on Carcinogens, Coke Oven Emissions, Substance Profile, http://ntp.niehs.nih.gov/ntp/roc/ eleventh/profiles/s049coke.pdf, accessed May 11, 2005.
- 23. S. S. Schiffman and C. M. Williams, Science of Odor as a Potential Health Issue, *Journal of Environmental Quality*, 34:129–138, 2005.
- For a survey of the state of the science in electronic-odor-sensing technologies, see H. T. Nagle, S. S. Schiffman, and R. Gutierrez-Osuna, The How and Why of Electronic Noses, *IEEE Spectrum*, 35(9):22–34, 1998.
- 25. G. Hardin, Tragedy of the Commons, Science, 162. 1243-1248, Dec. 13, 1968.
- 26. A common reason for halogenating compounds is to reduce their flammability, making them safer to use than their nonhalogenated counterparts. Unfortunately, halogenation often increases chronic toxicity, such as carcinogenicity, and makes the compounds more persistent in the environment (i.e., more resistant to biodegradation).
- 27. The endocrine disruptor discussion is based on D. A. Vallero, Environmental Endocrine Disruptors, *McGraw-Hill Yearbook of Science and Technology*, McGraw-Hill, New York, 2004.
- 28. D. G. Wilson, History of Solid Waste Management, in *Handbook of Solid Waste Management*, Van Nostrand Reinhold, New York, 1997, pp. 1–9.
- 29. J. G. Landels, *Engineering in the Ancient World*, Barnes & Noble Books, New York, 1978. This book contains an excellent discussion of water supplies as recorded by the Roman architect/engineer Vitruvius in his eighth book of *De Architectura* in the first century B.C.
- 30. Landels, 1978. The two major challenges to delivering water in sprawling, ancient Rome were pressure and sediment. The large head needed to transport water over distances would split the lead and earthenware pipes, so the harder bronze was recommended. The siltation in the aqueducts was addressed using cisterns similar to sedimentation basins in modern wastewater treatment plants.
- 31. H. Tammenagi, *The Waste Crisis: Landfills, Incinerators, and the Search for a Sustainable Future*, Oxford University Press, Oxford, 1999, pp. 22–24.

- 32. The RCRA regulations are found in the *Code of Federal Regulations* at Title 40, Parts 260 through 280. In fact, RCRA is an amendment to the Solid Waste Disposal Act of 1956. The 1984 amendments to RCRA are known as the Hazardous and Solid Waste Amendments (HSWA). Subtitle C (hazardous waste) and Subtitle D (solid, primarily nonhazardous waste) provide the structure for comprehensive waste management programs. In addition, RCRA also regulates underground storage tanks under Subtitle I and medical waste under Subtitle J. Many other countries have similar programs to control hazardous wastes.
- 33. The source for this discussion is the U.S. Environmental Protection Agency's brownfield Web site, http://www.epa.gov/swerosps/bf/success/houston.pdf, accessed June 22, 2005.
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