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Sources and Types of Pollutants, Why We Need Modeling, and the Need to Study Historical Pollution Events

1.1 Introduction

A good starting point for our discussions and this book is to ask, "Is there a common sequence of events leading to the identification, characterization, and remediation of an old hazardous waste site?" There are a variety of answers to this question, but a general order of events often occurs as follows:

- First, a pollutant is observed to be present or the potential of a pollutant release from a proposed industrial site is identified. This can result from routine monitoring of a pollutant's concentration at the site, through the known manufacturing of the pollutant at the site, through research identifying the cause of an illness or cancer cluster in the community of a site, or during an environmental planning assessment (also called an environmental impact statement, EIS).
- Second, the source of the pollutant is identified at the hazardous waste site or a theoretical release can be simulated.
- Third, a remedial investigation is conducted to determine the mass/volume of pollutant released and responsible parties.
- Fourth, pollutant fate and transport modeling is completed to determine what pollutant concentrations will result at specific points at the site over time (referred to as receptor sites where humans are the receptors of the pollutants).
- Fifth, the results of the pollutant fate and transport modeling are used in risk assessment calculations to estimate health or environmental/ecological risks. A common use of modeling in the twentieth and twenty-first centuries is in air and water quality environmental management and related to compliance with ambient air or water quality standards (EPA 2017a). Essentially, the model purports the allowable discharge or emission rates to maintain acceptable air or water quality.
- And finally, a decision or plan of remediation is negotiated between the local citizens, local and federal governments, and the party responsible for the hazardous waste site.

Today, new pollutant releases from regulated industries take on a slightly different approach. In the Global North, previously referred to as developed countries, most industries act responsibly, but all human-designed, engineered, and operated systems are prone to failures and accidents. In general, a slightly modified sequence of events occur: a spill or accident occurs, emergency response systems respond, and remediation (when possible) occurs. Responsible parties usually pay the incurred expenses, and appropriate fines if regulations have been broken.

These steps also outline our approach in this book. In this chapter, we will look at several historical hazardous waste release events, as well as recent ones, and describe types and sources of potential pollutant releases. In Chapters 2 and 3, we will look in-depth at the chemistry associated with fate and transport phenomena in environmental media. In Chapters 4–10, we will develop and learn to use pulse and step fate and transport models for rivers, lakes, groundwater, and the atmosphere. In Chapter 11, we will introduce basic chemical toxicology and use pollutant concentrations from the fate and transport modeling to perform basic risk assessment calculations to estimate risk to human health, look briefly at cost–benefit analysis, and the relatively new field of environmental life cycle assessment. In Chapters 12–14, we will look at the development and evolution of environmental laws in the United States and Europe. In Chapter 15, we will look at the history of several "world class" pollutants that are present at undesirable concentrations across the globe. In the last Chapter 16, laboratory experiments that support key chemical and modeling concepts will be presented, with actual student results.

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1.2 Need for Modeling of Pollutants in Environmental Media

Many pollutants have been found to be ubiquitous in nature; that is every environmental compartment that has been tested has shown some level of contamination. Note that presently ambient monitoring of water bodies and the atmosphere are both part of the missions of both state and federal government agencies. Historically, two of the chemicals that fall into this category and receiving much public attention are PCBs (polychlorinated biphenyls) and DDT (1,1′-(2,2,2-trichloroethylidene)bis[4-chloro-benzene]). These compounds accumulate especially well in the environment due to their refractory behavior (they are not easily chemically or biologically degraded). More importantly, their chemical and physical properties are such that they bioaccumulate in fatty tissue in many organisms. Modelers like to divide nature into more easily mathematically described boxes, such as the atmosphere, rivers, lakes, groundwater, and biota (living organisms). In this book, we simplify this further by only considering one section of a river, a small portion of a groundwater aquifer or a small portion of the atmosphere.

There are two basic goals in pollutant modeling: to explain how a pollutant arrived where it is (a form of thermodynamic equilibrium) and to predict how fast a pollutant will move through an environmental compartment in the future (a form of kinetics). Some engineers call this all-compassing field "chemodynamics" to reflect its transport, phase transfer, and equilibrium components. There are several excellent textbooks based on these principles (Thibodeauz 1996; Hemond and Fechner 2000). Later in this chapter, we will look at several examples of major pollutant release events; the approach taken to these reflects the first goal of modeling (an explanation of how a pollutant arrived where it is). Although this approach is very important to understand how pollutants move in the environment, a more common use of modeling today is to predict if and/or how fast a pollutant will move once it is accidentally released. In the United States, this is included in an EIS. Most Global North countries require a variety of industries to perform some type of environmental impact modeling in the unlikely and unfortunate event of an accidental pollutant release, which again is inevitable with most human-engineered systems. This book will concentrate on predictive modeling, but by understanding the processes involved in the predictive modeling approach, it is relatively easy to appreciate how the explanation type of modeling is completed.

In order to predict where a pollutant will go we use a set of fate equations that describe the chemical and physical processes occurring in the environmental compartment under evaluation, such as mixing, outflow through the effluent of the system, evaporation, volatilization, and chemical or biological degradation. Transport of chemicals is part of its fate. The same modeling equations and concepts are used for the explanation type of modeling (where pollution already exists) but a reverse process is used. In explanation modeling, the modeling equation is fit to pollutant concentration data from field measurements in order to obtain estimates of mixing and degradation rates in the specific system. Both modeling approaches will become clearer when we reach the modeling chapters in this text, especially beginning in Chapter 4.

1.3 Pollution versus Contamination; Pollutant versus Contaminant

Is there really a difference between the terms pollutant and contaminant? Some would argue no, while others will argue vehemently yes. In the United States, environmentalists and those working for US Environmental Protection Agency (US EPA) prefer the terms pollution and pollutant. But what makes a chemical a pollutant? Basically this distinction is determined by where the chemical is located and how much of the chemical is present. For example, a bottle of mercury chloride is typically not considered a pollutant when it is sitting on the shelf in a chemical storeroom. But pour that same chemical down the drain, and it immediately becomes a pollutant, even at extremely low concentrations. This is the logic behind usage preferred by other branches of the US government, such as the Department of Energy (DOE). The DOE prefers to use the terms contamination and contaminant. If a chemical is in its proper place it is not considered a problem and is thus not a contaminant. Likewise, if a chemical is present in an environmental media below the concentration deemed to be a problem (which is subject to a variety of views and laws), then the chemical is not a problem and contamination is not necessary present. Thus, the legal definition usually specifies two factors, where the pollutant is and its concentration. For example, the first author of this book (Dunnivant) worked on a project for the Idaho National Engineering and Environmental Laboratory (INEEL), one of many US DOE sites, in which we intentionally placed a rapidly degrading radioactive substance in a water-filled lagoon in order to characterize the movement of water and radionuclides in the subsurface media. As long as the chemicals stayed within the controlled boundaries of the lagoon (the approved experimental area) they were not considered a contaminant. But one day a violent storm blew a small amount of the water and sediment a few feet out of the lagoon. The DOE safety officials

overreacted and suspended all operations at the site for a time period that jeopardized a multimillion dollar field experiment! Although the vast majority (we would speculate over 99.99%) of the chemical was still present in the lagoon, the extremely small amount of chemical "released" (amounting to a few specks of dirt) was officially classified as a contamination event. Similarly, in the 1980s chlorinated dioxins and furans were attributed to wood pulp bleaching to achieve acceptable brightness attributes. In these cases, concentrations in the parts per trillion (10^{-12}) and parts per quadrillion (10^{-15}) were routinely part of the technical conversation, and they were termed "pollution" in most cases by technical and lay personnel (EPA 2017b). Today, wood pulp and paper processing plants have replace chlorine with peroxide to achieve the product with less pollution. So, when you use the terms pollution versus contaminant be aware who you talking to. In this book, we will use the more common terms pollutant and pollution.

1.4 Pollution Classifications

There are perhaps as many ways to categorize types of pollution as there are pollutants. One broad way to by physical phase: solid, liquid, or gaseous. This categorization is useful from a standpoint of treatment and disposal. Many treatment technologies are based on the physical phase of the pollutant, such as bag filtration houses for atmospheric particulates or filtration of particles in liquids. Another general but more chemical means of categorization is the inorganic, organic, and radioactive nature of the waste. Mixed waste, a very difficult, if not impossible waste to treat, usually refers to organic and radioactive waste being present in the same waste product. Inorganic waste can be further broken down into non-toxic and toxic metals, metalloids, and non-metals. Metal waste can be subdivided into heavy metals and transition metals. Toxic wastes can be grouped as carcinogens, teratogens, and mutagens (discussed in Chapters 11 and 12). Compounds that are subjects of heightened public awareness, such as PCBs, are divided out even further. Other wastes are listed as hazardous based solely on their origin from a specific industrial process (for example, metal plating wastes) or when a specific chemical is present in the waste stream (for example, the presence of PCBs). As you see there are many ways to categorize or list a waste and each country will have their own system for classifying pollutants. In the modern era, some compounds are known to accumulate in organism tissue with high lipid content that further increases the human health risk associated with their presence.

Another interesting way to categorize waste is by the risk it poses. For example, say you have a hazardous waste site that needs to be remediated and there are 20 pollutants of interest. But, from a risk standpoint, 5 of the 20 pose a significantly higher hazard based on risk assessment calculations (Chapter 11). In some countries, it is customary to focus the remediation effort on these 5 chemicals and disregard the other 15 "less hazardous pollutants." Such an approach is used by the US EPA to calculate health risk based on source and an overview of the approach is shown in Figure 1.1.

1.5 Sources of Pollution

As with types of waste, there are many ways of categorizing sources of waste (or potential pollutants). We will only mention a few of the more useful approaches and give examples of generated volumes from major industrialized countries. First, we will discuss point and nonpoint sources.

Sources of pollutants are commonly divided into one of two types, point or nonpoint sources. Point sources are well-defined sources, such as the end of a pipe, smoke stack, or drain. Nonpoint sources are less well defined, but contain all sources where you cannot directly pinpoint the emission. The distinction becomes a bit more vague depending on physical scale. For example, if you are studying a large watershed (the land surface that drains into a stream or lake), a cattle holding lot could be considered a point source. Obviously, the farm is the source of the cattle waste. But on a smaller scale, what is the point source? The answer is possibly each cow, or the entire holding lot, since the pollution will be spread over its entirety. But, in general the terms point and nonpoint are used to describe sources.

Table 1.1 lists sources of waste by 10 categories: agricultural, chemical industry, mining industry, energy industry, municipal and hazardous landfills, medical industry, food processing, domestic waste, municipal government, and federal government. General wastes for each source are also listed in the right-hand column. This list is certainly not complete, but contains the major sources of waste generated and provides a starting point for discussion of waste sources.

The terminology of wet and dry deposition applies to ambient air and the mode of transport in the atmosphere. Rain and snow can act to "scrub" some contaminants from the air and deposit them on trees, plants, and the soil where erosion and runoff infiltration further distribute them across the surface and subsurface environments.

Since this book deals mostly with the transport of toxins, we will be especially concerned with hazardous

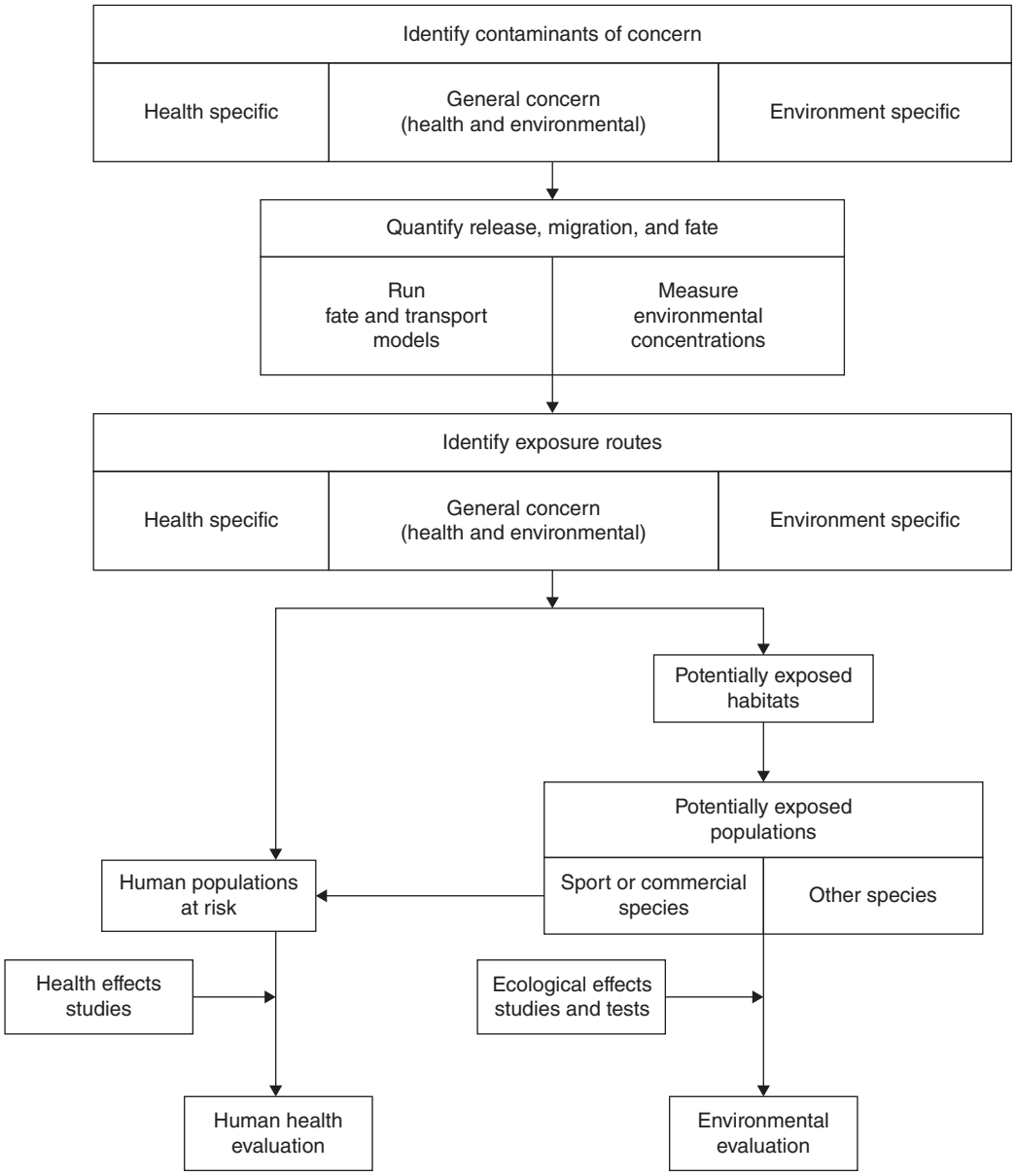


Figure 1.1 An overview of the approach to access human risk used in the United States. Source: DOE.

waste. A summary of the amounts of hazardous waste generated by country members of the Basel Convention (an international treaty regulating the reporting, disposal, and transport of hazardous waste) is given in Table 1.2 for the year 2000. Unfortunately this dataset is no longer available on the Internet, nor is updated total generation data available since data are now reported on an import–export basis. One would only speculate that the magnitudes of these values have increased and, in general, the more developed the country, still the more hazardous waste it generates. This correlation of waste to economical level is a homework exercise that you should conduct and, by the way, it would make an excellent examination question. You will undoubtedly note the lack of data on two highly industrialized countries: Japan and Germany. Even without these two countries the total amount of hazardous waste annually generated is an obscene 93 992 999 metric tons in year 2000. Another country you will note absence from the list is the United States, since it has not signed the Basel Convention (UN 2000). For comparison purposes, the United States generated 40 821 481 tons in the year 2001 (EPA 2001),

Table 1.1 Potential sources of chemical emissions (point and nonpoint sources).

Source	General waste (representative but not exhaustive)
Agricultural	Field and chemical wastes
	Nutrients (fertilizers)
	Pesticides/herbicides
	Petroleum fuels
	Feedlot waste
	Dairy waste
Chemical industry	Metal products
	Metal sludges
	Non-metal waste
	Electrical equipment waste
	Detergents/soaps/cleaners
	Petroleum-related waste
	Metal plating
	Cooling-tower additives
	Film-processing waste
	Solvents
	Wastewaters and off-specification wastes
	Pesticides
	Insecticides
	Chlorinated hydrocarbons
	Organophosphates
	Carbamates
	Microbial insecticides
	Pyrethroids
	Rodenticides
	Herbicides
	Petroleum oils
	Carbamates
	Triazines
	Phenoxy herbicides
	Amide herbicides
	Fungicides
	Precursors to smog (NO_x, hydrocarbons)
Mining industry	Mine tailings
	Mineral leaching (cyanide)
	Acid mine drainage
	Coal
	Smelting waste
	Atmospheric particulates
Energy industry	Petroleum-based waste
	Solvents
	Gas and vapor emissions
	Coal tars
	Boiler waste
	Nuclear waste
	Petroleum stored in underground storage tanks (gasoline stations)
	Precursors to acid rain and smog
Municipal and hazardous landfills	All chemicals disposed in the landfill
Incinerators	Incomplete combustion of feedstocks
	Combustion by-products
	Metals
	Particulates
Medical industry	Biodegradable waste (biohazards)
	Pharmaceutical waste
	Solvents
Food processing	Waste food products
	Rinsing waste
	Slaughter house waste
Domestic waste	Detergents/cleaners
	Pesticides, etc.
	Fertilizers
	Compose materials
	Paints/solvents
	Gasoline
Municipal governments	Chemicals associated with water and wastewater treatment
	Sewage (biochemical oxygen demand)
Federal governments	Weapons-related waste (conventional and nuclear)
	Nuclear waste
	Petroleum-based waste

which is 43.4% of the world total shown in Table 1.2. The US data delineated by geography and industry are reported under TSCA (EPA 2017c) and reported in public Internet sites. More recently, data for year 2011 show that the United States generated 28 million tons of RCRA (landfill and nonliquid) defined waste (US EPA 2017b). A summary of hazardous waste generated in 2015 for the United States is given in Table 1.3 by state and territory

Table 1.2 Total hazardous waste generated in year 2000 by the Parties to the Basel Convention.

Country	Total hazardous waste generated (metric tons)
Austria	980 558
Bulgaria	755 677
Canada	No data
China	8 300 000
Croatia	25 999
Cuba	1 023 638
Czech Republic	2 603 337
Denmark	287 491
Ecuador	85 859
Egypt	170 000
Estonia	5 965 750
Finland	1 203 000
France	9 150 000
Georgia	93 000
Germany	No data
Hungary	3 392 628
Iceland	12 550
Israel	279 987
Italy	No data
Japan	No data
Jordan	17 390
Kyrgyzstan	6 087 869
Luxembourg	96 526
Malaysia	344 550
Morocco	987 000
Netherlands	2 722 828
New Zealand	No data
Norway	650 000
Oman	242 098
Poland	1 627 143
Portugal	194 724
Qatar	280
Republic of Korea	2 756 984
Republic of Moldova	7 122
Romania	860 892
Russian Federation	12 800 000
Singapore	121 500
Slovakia	1 600 000
Slovenia	128 395
Spain	3 293 705
Sri Lanka	40 617
Sweden	1 100 000
Ukraine	2 613 400
United Kingdom	6 296 043
Uzbekistan	15 074 459
Total	93 992 999

Source: www.basel.int/natreporting/index.html (accessed 8 December 2003).

Table 1.3 Number of hazardous waste generators and amount of waste produced by the States of the United States.

Location name	Number of generators	Waste generated (tons)
National	Total	
	26 794	33 646 771
Alabama	432	709 666
Alaska	45	3 965
American Samoa	0	0
Arizona	320	38 696
Arkansas	109	338 703
California	3 395	309 109
Colorado	209	40 440
Connecticut	458	35 939
Delaware	101	12 577
District of Columbia	74	1 078
Florida	520	90 847
Georgia	821	172 752
Guam	19	140
Hawaii	100	484 603
Idaho	72	7 049
Illinois	1 083	601 542
Indiana	822	930 379
Iowa	209	56 946
Kansas	257	1 280 076
Kentucky	326	135 106
Louisiana	508	5 010 182
Maine	138	2 606
Maryland	342	125 807
Massachusetts	813	39 108
Michigan	535	407 754
Minnesota	362	120 862
Mississippi	147	1 946 349
Missouri	482	291 067
Montana	72	6 773
Navajo Nation	1	45
Nebraska	104	26 839
Nevada	141	13 141
New Hampshire	232	3 714
New Jersey	948	333 804
NEW MEXICO	89	5 631
New York	3 636	281 259
North Carolina	611	81 153
North Dakota	35	265 051
Northern Marianas	1	2
Ohio	1 324	1 711 110
Oklahoma	242	105 306
Oregon	252	52 830
Pennsylvania	1 422	293 947
Puerto Rico	97	20 312
Rhode Island	184	7 252

Table 1.3 (Continued)

Location name	Number of generators	Waste generated (tons)
South Carolina	519	154 595
South Dakota	43	1 917
Tennessee	290	47 756
Texas	1 686	16 288 728
Trust Territories	1	0
Utah	167	33 927
Vermont	62	288 019
Virgin Islands	5	299
Virginia	567	62 418
Washington	512	135 461
West Virginia	259	52 168
Wisconsin	559	172 716
Wyoming	34	7 250

Source: EPA (2015).

(EPA 2015a), and in Table 1.4 by type of industry (EPA 2015b). An excellent annual source of information is available from the US EPA's Toxic Release Inventory website at https://www.epa.gov/trinationalanalysis (EPA 2017c) but this will be used as a homework exercise.

From the standpoint of modeling, the main subject of this text, we would like to be able to express our waste emission or "sources" in mathematical terms. Two mathematical source terms we will use throughout this text will be the "pulse" and the "step" inputs of pollutant. The pulse and step inputs represent both extremes of the duration of pollutant inputs to a system. You should familiarize yourself with these terms. These two terms can be slightly confusing, mostly because of the use of multiple names for them. A pulse release, also commonly referred to as an instantaneous release, is one that occurs over a small time scale (an instant in time, hence instantaneous), but may contain large or small amounts of pollutant. Examples of pulse releases would be the immediate release of 1 gallon of acetone or antifreeze into a river, or the same into a groundwater well, or the flushing of one toilet of human waste into a stream. We use the terms pulse and instantaneous to stress that the release occurs immediately, travels through the system as a pulse of pollution (a narrow band of high pollutant concentration), and is not a prolonged release. Some prefer to characterize environmental releases as buoyant or nonbuoyant plumes. A plume is characterized by a conical release emanating from a discharge pipe or stack. An air emission appears white or gray when condensing moisture is present in the cooling discharge. The emission appears to spread because it is entrains (draws in) ambient air or water. Picture an aquarium tank with

Table 1.4 Top hazardous waste generators in the United States (greater than 10 000 tons).

Description	Generated (tons)
Basic chemical manufacturing	19 725 340
Petroleum and coal products manufacturing	4 827 640
Waste treatment and disposal	3 183 389
Iron and steel mills and ferroalloy manufacturing	1 333 956
Nonferrous metal (except aluminum) production and processing	914 990
Semiconductor and other electronic component manufacturing	429 610
Pharmaceutical and medicine manufacturing	268 950
Pesticide, fertilizer, and other agricultural chemical manufacturing	262 367
Coating, engraving, heat treating, and allied activities	246 545
Resin, synthetic rubber, and artificial synthetic fibers and filaments manufacturing	234 919
Remediation and other waste management services	212 438
Warehousing and storage	162 140
Waste collection	150 780
Other chemical product and preparation manufacturing	121 401
Other electrical equipment and component manufacturing	115 746
Paint, coating, and adhesive manufacturing	104 333
Alumina and aluminum production and processing	103 599
Administration of economic program	91 224
Steel product manufacturing from purchased steel	70 711
Motor vehicle parts manufacturing	58 445
Plastics product manufacturing	56 018
Electric power generation, transmission and distribution	55 986
Highway, street, and bridge construction	49 015
Cement and concrete product manufacturing	45 180
Aerospace product and parts manufacturing	43 889
Forging and stamping	43 651
National security and international affairs	43 326
Architectural and structural metals manufacturing	34 093
Miscellaneous durable goods merchant wholesalers	31 094
Motor vehicle manufacturing	29 908
Other fabricated metal product manufacturing	28 192
Foundries	27 672
Printing and related support activities	19 806

Table 1.4 (Continued)

Description	Generated (tons)
Soap, cleaning compound, and toilet preparation manufacturing	19 610
Glass and glass product manufacturing	19 079
Agriculture, construction, and mining machinery manufacturing	16 725
Chemical and allied products merchant wholesalers	16 292
Other personal services	15 726
Medical equipment and supplies manufacturing	14 860
Scientific research and development services	14 170
Administration of environmental quality programs	14 048
Furniture stores	12 663
Support activities for water transportation	12 534
Lessors of real estate	12 267
Sawmills and wood preservation	12 188
Household and institutional furniture and kitchen cabinet manufacturing	11 930
Beverage manufacturing	11 671
Other miscellaneous manufacturing	10 865
Rubber product manufacturing	10 507
Electrical and electronic goods merchant wholesalers	10 453
Colleges, universities, and professional schools	10 300
Residential building construction	10 179

Source: EPA (2015b).

a diffuser–aerator that appears to widen or spread as the bubbles rise. We also call a subsurface discharge a plume but clearly not visible but its transport has this plume characteristic as the leak moves by potential energy–driven diffusion from higher to lower concentration. We often call this motion one characterized by Fick's law of diffusion (Fick's law 2017) and is a useful process mathematical model in nature.

In contrast, a step or continuous release occurs over longer periods of time. For modeling purposes, we like to assume that the release occurs indefinitely. Examples of step releases would be the constant release of a pollutant from an industry at "acceptable" or "non-acceptable" levels, the continuous release of leachate from a landfill into the groundwater system, and the 24-hour outflow from a sewage treatment plant. Pollutant release concentrations can be high or low, but as long as they are constant, we can model them using relatively simple transport equations. When a discharge or release occurs at a constant rate, engineers and scientists refer to steady-state flow and its rate of change with time is zero and is a convenient mathematical assumption one makes to avoid complexity.

Many pollutant sources fit into these two simple categories, but you might think of them as end-members of a continuum because there are also other pollutant sources that do not fit neatly into these categories. For example, suppose an industry legally emits a pollutant for five years into a lake, but installs better waste treatment technology or shuts down the process completely. How could we treat this? One approximation would be to use a step model for the first five years and then switch to a pulse model. To be more accurate, we would derive a specific model to fit the exact emission scenario. As noted earlier, the pulse and step inputs are very common, and since this is an introductory text on pollutant fate and transport we will only use models based on these two types of pollutant inputs. As long as there is an equation describing the pollution input, mathematicians can modify the final fate and transport equation to model the pollution as it moves through an environmental compartment.

1.6 Historic Examples of Where Fate and Transport Modeling Are Useful

There is no lack of unfortunate and disastrous pollution events that fate and transport models have been applied to in an effort to better understand and be able to predict pollutant movement in the environment. These are divided into surface water, groundwater, and atmospheric events. You may recall many of the events, discussed below, from news reports or case studies that you have covered in other classes.

Surface water: Both the Great Lakes and Chesapeake Bay in the United States were subjected to extensive modeling in the later decades of the twentieth century and became by default the field laboratories of present-day state of the art for eutrophication and toxic fate modeling practice.

The Water Quality Analysis Simulation Program (WASP 1983 discussed in Chapter 10) was first used on the Great Lakes and the detail in benthos nutrient-water column exchange and kinetics evolved from Chesapeake Bay research. Further, load allocations based on water quality models, many of which resembled the classic Streeter–Phelps analysis for the Ohio River after World War I, were responsible for the attainment of water quality standards for dissolved oxygen (DO) in thousands of stream and river miles. This maturation of modeling science for water quality control is still evolving for nutrient-rich areas and further water quality improvements are very likely using tools in EPA's model toolbox.

Groundwater: The tragedy of Love Canal that arose during the late 1970s resulted in the statute we now call Superfund and resulted in the migration of toxic chemicals into a residential neighborhood causing disease, birth, and early childhood development defects. The EPA LUST (leaking underground storage tank) program and Resource Conservation and Recovery Act (RCRA) and Superfund Corrective Action decrees have hundreds of similar episodes, albeit with less tragic results. Detection of leaks from industrial landfills are monitored very closely with detection wells and modeled as an aid to corrective actions. Models are used to delineate source water drinking water protection.

Atmospheric events: The national ambient air quality standards (NAAQSs) were established early by the Clean Air Act to address deteriorating and unhealthy air throughout the country. State implementation programs (SIPs) were established in hundreds of areas, where these standards for CO, HCl, SO_x, NO_x, ozone (O_3), and particulates were not achieved. State SIPs were created to tell EPA and the public in turn how attainment would be achieved to the extent possible. Near-field and long-range dispersion models was part of these assessments.

1.6.1 Preenvironmental Movement and Legislation

Prior to the 1960s environmental movement and the 1970s rush of environmental legislation, environmental disasters were common place. As we have seen, regulations do not prevent disastrous environmental events from occurring; think Three-Mile Island, Deepwater Horizon, and Bhopal India. Probably, the first environmental concern was the same as today in many Global South (undeveloped) countries, mammalian waste and associated diseases. Since the evolution of mammals, animals have excreted their waste into waterways that resulted in highly degradable organic waste and microbial contamination. Although the concentrations were minor, disease vectors such as *Giardia lamblia* and *Escherichia coli* were common in many species. As humans evolved and populations concentrated into sedentary civilizations, management of human waste became a problem. This problem has only been addressed in recent centuries, but traced their origins to Ancient Rome and China. One of the most profound events shaping environmental movements in the United States was the open fires of the Cuyahoga River in 1969. This is less than 100-mi river flows from Akron to Cleveland, Ohio, into Lake Erie, and at the time one of the most polluted rivers and lakes in the United States. To attribute to the historic level of pollution, 13 fires were recorded between 1868 and 1969. The 1969 fire (from surficial oil slicks) certainly spurred the US environmental movement. But environmental disasters did not end after the passage of comprehensive legislation. Superfund sites were located, requiring extensive remediation that continues today, and accidents continue to happen. As noted several times in this book, human-engineered and human-maintained systems are prone to accidents or misguided national policy.

The release of biochemical oxygen demand (BOD) waste to streams; timeline – since the dawn of civilization up until today: One of society's greatest accomplishments, and possibly most extensive over time, has been the treatment and disposal of our sewage waste. However, you may be shocked to learn that as late as the 1980s, several major coastal (East and West) cites in the United States only partially treated their sewage before dumping it into estuaries, bays and oceans. Many major cities across the world are still modernizing their treatment facilities, and huge strides have been made in this effort. Since the installation of sewage treatment plants, then Global North has eradicated many diseases associated with human waste. But from the standpoint of nature, human pathogens are of little concern and the main problem is the large amount of biodegradable organic waste, known as BOD, that is released into natural systems. As we will discuss in detail in Chapter 7, water contains relatively small amounts of DO and when untreated sewage is released into a stream, the oxygen needed to oxidize these organic wastes far exceeds the oxygen present in the stream water. This causes the stream to become anaerobic (devoid of DO) and the biological organisms dependent on this DO quickly die. In addition, the stream smells like an open sewer, which is essentially what it is.

The modeling of the consumption of DO by organisms oxidizing BOD is relatively simple. The governing equation, known as the Streeter–Phelps equation, will be discussed in Chapter 7. For now, we will only concern ourselves with a plot of DO downstream from a sewage treatment plant. Figure 1.2 shows the DO profile of a stream starting at the input of untreated sewage and downstream from the inlet point. Note how the DO immediately plummets as waste enters the stream and microbes consume the organic matter. In fact, the stream modeled here becomes anaerobic from 180 to 430 km downstream from the waste input (an incredibly long distance) and only slowly recovers as the stream undergoes natural reaeration and as the BOD is oxidized by microorganisms.

Now note the effect of adding a sewage treatment plant to the system where sewage waste is treated prior to release to the stream (Figure 1.3). In this modeling effort, we assume that 95% of the BOD is removed,

$$DO = \frac{\%\ \text{Saturation}}{100} * \text{Saturation concentration} - \left(\frac{k'\ BOD_L}{k_2' - k'} (e^{k'(x/v)} - e^{k_2'(x/v)}) + D_0 * e^{k_2'(x/v)} \right)$$

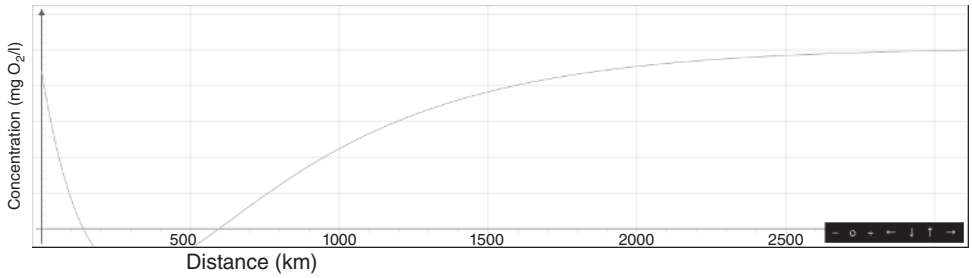


Figure 1.2 The dissolved oxygen concentration profile of a stream receiving untreated sewage waste (Results from Fate® 2018).

$$DO = \frac{\%\ \text{Saturation}}{100} * \text{Saturation concentration} - \left(\frac{k'\ BOD_L}{k_2' - k'} (e^{k'(x/v)} - e^{k_2'(x/v)}) + D_0 * e^{k_2'(x/v)} \right)$$

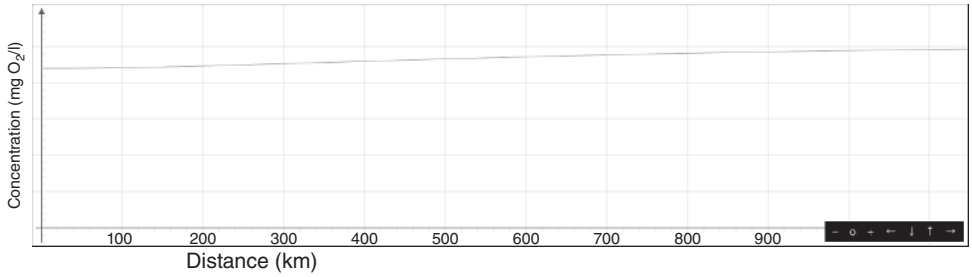


Figure 1.3 The dissolved oxygen concentration profile of a stream receiving 95% treated sewage waste (Results from Fate® 2018).

which is easily achievable in modern treatment facilities. The DO of the stream and its associated wildlife are not noticeably affected by the oxidized organic matter (treated waste). Thus, we can not only predict the effects of adding sewage to a stream but also evaluate the effects on the stream by adding treatment systems.

1.6.2 Legacy Waste Sites

Many legacy future Superfund sites existed across the United States (and world-equivalent sites) prior to the US and Europe environmental movements of the 1960s and prior to the series of environmental laws passed in the 1980s. Of course, industry was responsible for many of these environmental disasters such as the Love Canal site and others, but a surprising number of the most egregious acts were conducted by each country's governments prior to, during, and after the Cold War in the name of self-preservation (nuclear weapon programs). Examples of such sites in the United States are the Hanford site in Washington State, the Savanna River site in South Carolina, the Oak Ridge National Laboratory in Tennessee, and Idaho National laboratories site in Idaho, with each location having multiple Superfund designations. As an example, we will look at one of the Superfund sites at the INEEL. Then, a similar pre-World War II (WWII) site in Europe.

1.6.2.1 INEEL Test Area North Deep Well Injection; Timeline – Pre- and During World War II

The deep well injection project that the authors are most familiar with was located on the INEEL at the Test Area North (TAN) site (Dunnivant et al. 1994). This US government owned and operated hazardous waste site was placed on the US EPA's National Priorities List (NPL) on 21 November 1989. Injection well TAN-05 was drilled in 1953 to a depth of 93 m (305 ft) with a diameter of 30.5 cm (12 in). The groundwater surface at the site is approximately 63 m (206 ft) below the land surface. During its years of operation, the well received approximately 133 000 l (35 000 gallons; 193 000 kg) of liquid and dissolved trichloroethylene (TCE), organic sludges, treated sanitary sewage, metal filing process waters, and low-level radioactive waste streams. Basically, the well was the means of disposal for any liquid or semiliquid waste (domestic and hazardous) produced at the site. Although several pollutants of concern were disposed of and detected in the groundwater at TAN, we will only

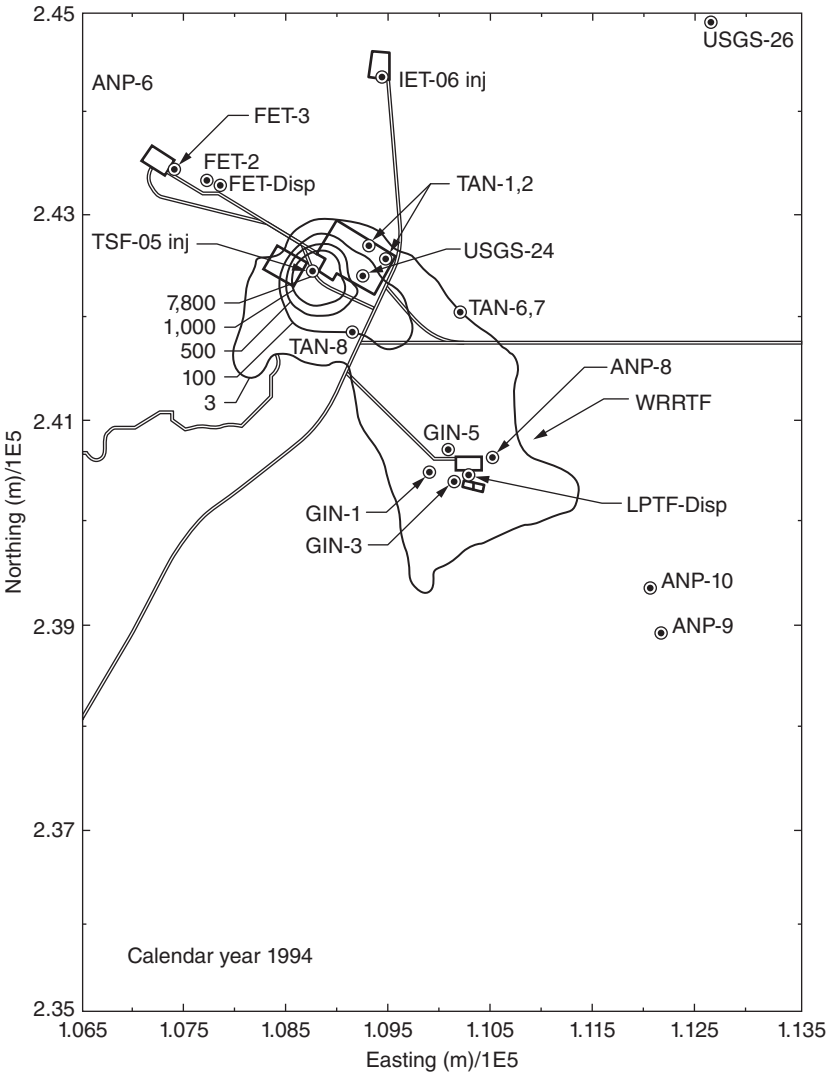


Figure 1.4 Predicted isoconcentration lines for TCE at the INEEL Tan injection site for the year 1994. Source: INEEL, Department of Energy, Dunnivant et al. (1994), and public domain.

show the results for TCE. It should be noted that the site is located in the mostly uninhabitable region of the Snake River Plain.

Figure 1.4 shows isoconcentration circles (isopleths; lines of equal TCE concentration) for the TAN that were obtained by fitting a step model to field measurements of TCE concentrations in the groundwater (explanatory modeling). Since TCE is suspected of being present in the aquifer as a dense nonaqueous phase liquid (DNAPL), it solubilizes slowly and the input of TCE can be considered a continuous source (step input over an extended period of time). You will note that near TSN-05 injection well, the isopleth is for 1000 parts per billion (ppb) while the lowest concentration shown in this figure is 3 ppb (the maximum allowed drinking water concentration). If no remedial action was to be taken in 1994 (the proposed year of remediation if any was to be attempted) and the DNAPL continued to release TCE to the groundwater, another step model predicted that the TCE plume would expand to the one shown in Figure 1.5 for the year 2044 if no remediation was taken.

So, how do we decide what is to be attempted in the way of remediation? Pollutant fate and transport modeling can be one of many tools to evaluate this question. For example, what if, through extensive and expensive remediation of the site, the source of TCE could be removed. How would this affect the TCE concentrations for year 2044 (a date selected by DOE and EPA)? These results are shown in Figure 1.6. As you can see, there is significant improvement in the groundwater quality. In this scenario, the source of the contamination has been removed and the plume of contamination has migrated down gradient and been significantly diluted. Still, pollutant fate and transport modeling cannot be the only tool in the decision process. Other factors, such as the cost of this magical cleanup and the associated health

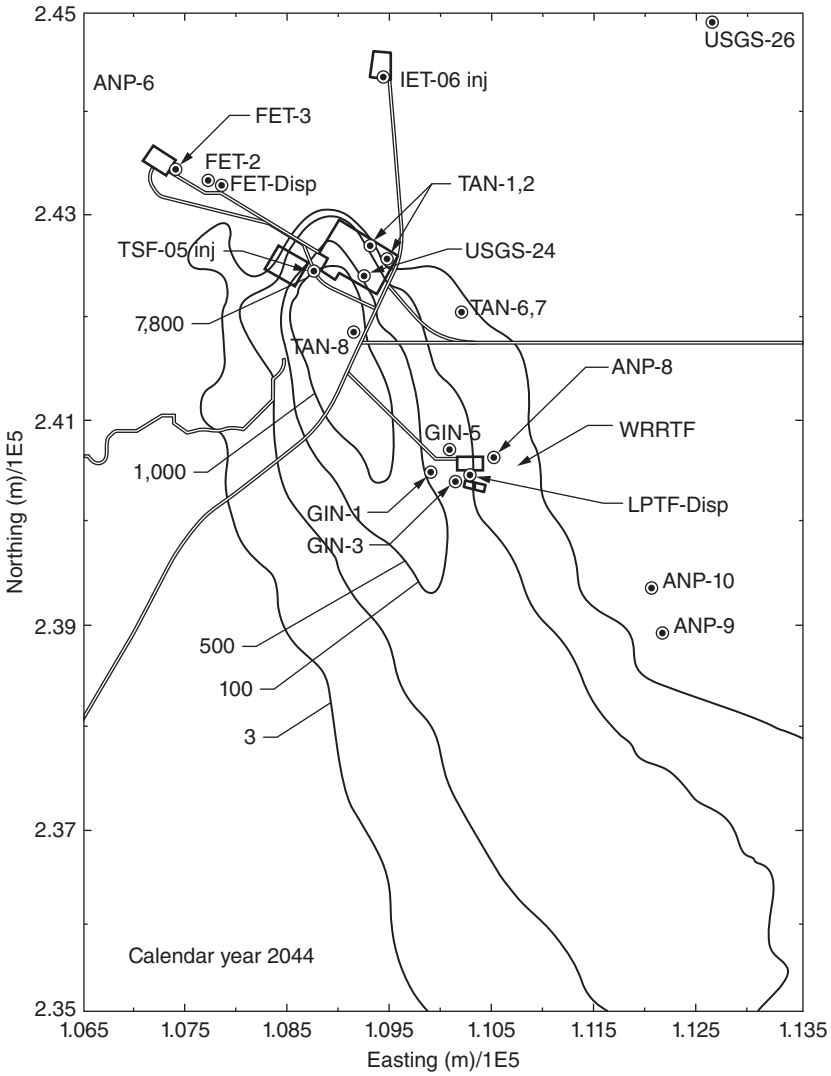


Figure 1.5 Predicted isoconcentration lines for TCE at the INEEL Tan injection site for the year 2044 without remediation. Source: INEEL, Department of Energy, Dunnivant et al. (1994), and public domain.

risk of drinking the contaminated groundwater and of remediation practices must also be considered. And note again, the contaminated groundwater is inaccessible to any human through restrictions on the installation of groundwater wells.

1.6.2.2 The Release of Nitrobenzene-Based Solvents at the Sondermulldeponie Landfill in Kolliken, Switzerland; Timeline – Pre- and During World War II

This pre-WWII, Superfund-type site is a bit more complicated since it involves a lot of chemistry to understand the pollution scenario. Around 1978, Sondermull disposed of nitroaromatic liquid wastes in metal drums in a shallow pit (Dunnivant et al. 1992; Schwarzenbach et al. 1990; Colombi 1986). The disposal pit was lined with sawdust in the event that the drums would someday leak. Due to flooding from changes in the groundwater table, the metal drums rusted and eventually leaked their contents. In 1985, groundwater wells located downgradient ("downhill" in a groundwater system) from the disposal area were found to contain reduced aromatics, such as chloroanilines, but no nitrobenzene compounds. Anyone who knows the Swiss knows that they are meticulous recordkeepers and always have been. The company that disposed of the waste produced records showing that they had not disposed of any aniline compounds, and thus asserted they were not the ones responsible for the contamination. So, an investigation was conducted to attempt to explain this dilemma.

Groundwater modeling could have easily been conducted using a step model if you were only modeling the transport of nitrobenzene compounds. But this was not the issue since the monitoring well downgradient from the point source (the landfill) only contained anilines. Thus, the importance of considering the chemistry occurring in the landfill and groundwater became apparent. Schwarzenbach et al. (1990) proposed that as the water table changed it could have allowed water

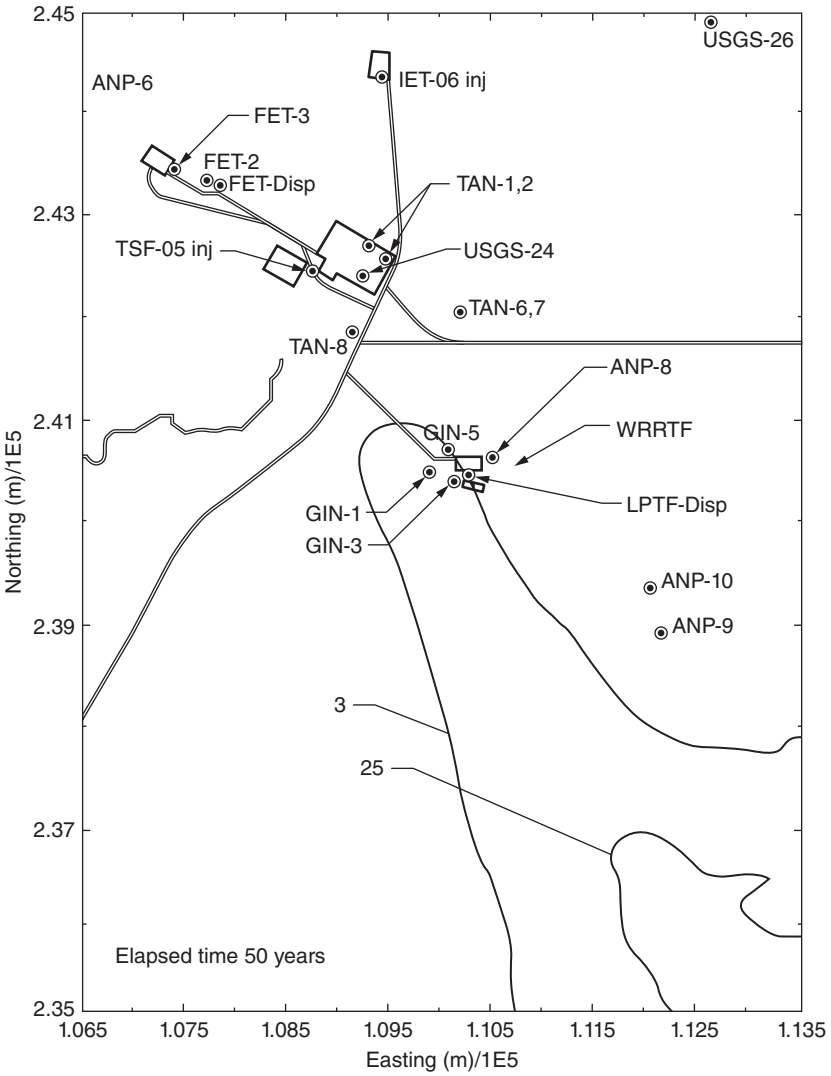


Figure 1.6 Predicted isoconcentration lines for TCE at the INEEL Tan injection site for the year 2044 after remediation of the immediate area around the injection well. Source: INEEL, Department of Energy, Dunnivant et al. (1994), and public domain.

to enter the landfill and allowed oxidation of the metal drums. After the drums ruptured, the leaking nitrobenzene compounds were subjected to reducing conditions from the presence of reduced humic acid (degraded and dissolved sawdust), and the nitrobenzene compounds were reduced to their respective anilines. This case demonstrates the importance of recordkeeping, and the integration of chemistry and modeling in assessing the history of and in predicting the effects of a pollution event. This is why we will be discussing the role of chemistry as part of the modeling approaches in this book.

1.6.3 Postenvironmental Movement Era Accidents

Even with extensive environmental regulations, accidents still continue to happen around the world. These are expected in countries with poor or no environmental regulations or enforcement, but citizens of the Global North are shocked with these disasters happen in their country. The following examples are in chronological order and result from a variety of causes from lax maintenance, poor inspections, to simply no fault accidents.

1.6.3.1 Methyl Isocyanate Release in Bhopal, India; Timeline 1984

In the early hours of 23 December 1984, a pesticide manufacturing plant in Bhopal, India, accidentally released methyl isocyanate (MIC). The event was a pulse release (short term) resulting in estimated concentrations that range from 13 (Dave 1985) to 100 ppm (Varma 1986). Death estimates range from 2000 (Dave 1985) to 10 000 (Shrivastava 1987) while approximately 300 000 injuries were reported (Shrivastava 1987). Although records indicate that concerns were raised before the accident, pollutant fate and transport modeling, as well as risk assessments should have been conducted before the

plant was even built. If the citizens of Bhopal had known of such modeling results, they may have been willing to surrender the small economic benefits from the factory in order to avoid the deaths and injuries caused by the accident. We will look at the Bhopal accident in more detail at the beginning of Chapter 9.

1.6.3.2 Accident at the Nuclear Power Plant at Chernobyl, Ukraine (Chernobyl Accident 2003; Chernobyl Disaster 1986); Timeline 1986

A number of radioactive releases have occurred since our development of nuclear power plants. England experienced a major release at the Windscale site as early as 1957 (Bailey et al. 2002), and the United States' nuclear industry suffered the accident at Three Mile Island, Pennsylvania, in March 1979. The world was shaken by the serious accident at the Chernobyl Unit 4 in the Soviet Union (present day Ukraine) in 1986. Radionuclides were spread across both Eastern and Western Europe contaminating dairies in Austria, Hungary, Poland, and Sweden, not to mention the hazards posed by eating fresh fruit and fish from the immediate area. Released radionuclides were subsequently detected in the atmosphere over Canada, Japan, and the United States (Bailey et al. 2002). Thirty workers at the plant were directly killed from accident (20 from radiation exposure), another 209 were treated for acute radiation poisoning, and countless others were exposed to lower doses of radiation with unknown effects (Chernobyl Accident 2017). In the end, 210 000 people had to be resettled. Modeling of such a large, widespread area, such as that affected by the Chernobyl accident is also possible but less accurate given the scale of the system and dynamic nature of weather systems. Still, you can rest assure that worst-case scenarios have now been modeled by governing agencies of nuclear power plants in the Global North.

1.6.3.3 A Chemical Spill on the Rhine River (Capel et al. 1988); Timeline 1986

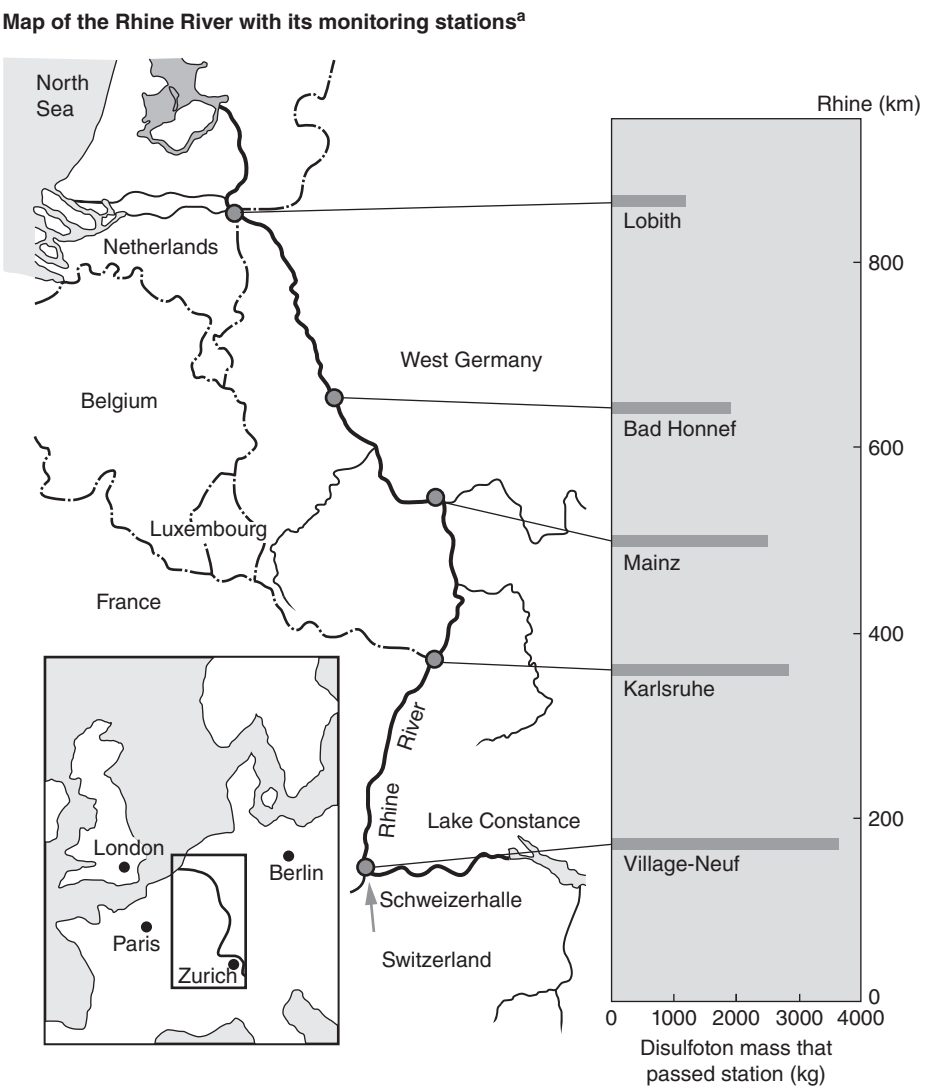
The Rhine River system in Western Europe is lined with chemical and pharmaceutical plants. It should come as no surprise that there are occasional chemical spills into this aquatic system. A major release occurred on 1 November 1986, when a storehouse owned by Sandoz Ltd. near Basel, Switzerland, caught fire and released pesticides, solvents, dyes, and various raw and intermediate chemicals (Capel et al. 1988). Figure 1.7 shows a map of the route that the Rhine River takes through this part of Europe. This release has been referred to as "one of the worst chemical spills ever" (Anonymous 1987). For modeling purposes, this was treated as a pulse (instantaneous, short duration) release. Environmental and academic groups rapidly formed monitoring points for the various chemicals at the stations labeled in Figure 1.8 (Capel et al. 1988). One of the most abundant pesticides released was disulfoton, a thiophosphoric acid ester insecticide. Figure 1.8 shows the movement and flushing of disulfoton through the Rhine (Capel et al. 1988). Note the bell or Gaussian shape of the concentration profile, which is characteristic of a pulse release. As the pulse of disulfoton moved downstream, it was diluted and degraded as indicated by the broader peaks and lower concentrations shown in Figure 1.8. This is a case where the model can be fit to the data to better understand how pollutants move through the system and thus can be used to predict downstream concentrations of future releases of pollutants. Of course, this does not help the wildlife affected by a disaster, but it can help to minimize the impact on drinking water systems that can be shut down as the peak concentrations of pollution pass. As we will see in Chapter 6, most rivers have a built-in cleansing system – flow downstream – eventually into a lake or the ocean. We will discuss this further in Chapter 6.

1.6.3.4 A Chemical Spill into the Tisza River Bordering Hungary and Romania (UNEP 2002); Timeline 2000

On 30 January 2000 a mine tailing dam, owned by the Aurul SA Baia Mare Company, broke and released a cyanide-rich waste into the Săsar River, an already highly contaminated river, which subsequently drained into the Tisza and Danube before entering the Black Sea (UNEP 2002). It has been estimated that nearly 50 000 and 100 000 m^3 of aqueous and suspended cyanide and heavy metals were released that resulted in the death of 500 tons of fish. This pollution event, like the one of the Rhine discussed above, illustrates the international effort needed in controlling release events and the politics of such a release. While the company in Switzerland bore the full responsibility (liability) for the Rhine incident, Romania took the stand that they had no international treaties with Hungary, thus, they were not responsible for damages to the fishing industry (Schaefer 2000). Liable or not, if an environmental impact study (utilizing fate and transport modeling) had been conducted showing the possible extent of damage to the affected rivers, more stringent safety measures would certainly have been in place.

1.6.3.5 The Kingston Fossil Plant Incident (Coal Ash Spill, Tennessee 2008; Dewan 2008; EPA 2017d; Kingston Fossil Plant Coal Fly Ash Slurry Spill 2008; Lisenby 2014; Sludge Graphic 2008; Southeast Coal Ash site 2017), Tennessee (USA); Timeline 2008

On 22 December 2008, an ash dike ruptured at an 84-acre (19.4 ha) solid waste containment area at the Kingston Fossil Plant in Roane County, Tennessee. The plant



[a]The dashed lines are international borders. The graph on the right side shows the mass of disulfoton that passed the five monitoring stations.

Figure 1.7 The route of the Rhine River in Western Europe. Source: Capel et al. (1988). Reprinted with permission of American Chemical Society.

released over 2.2 million pounds of coal fly ash slurry into a holding pond. The slurry then traveled across the Emory River and its Swan Pond embayment onto the opposite shore, covering about 300 acres (121 ha) of surrounding land. The incident damaged homes and polluted the water systems nearby (the Emory River and Clinch River).

According to one source (Kingston Fossil Plant 2017), the spill dumped around 45 000 lb of arsenic, 49 000 lb of lead, 1.4 million pounds of barium, 91 000 lb of chromium, and 140 000 lb of manganese. As a result, a lot of fish were killed and a test on the river water was taken on 1 January 2009 which indicated that there were significantly elevated levels of toxic metals (including arsenic, copper, barium, cadmium, chromium, lead, mercury, nickel, and thallium). These pollutants are well known to be factors in causing cancer, liver damage and other neurological problems. The type of release was a pulse release that continues to affect the water systems as pollutants become more available depending on environmental conditions.

1.6.3.6 Lead in the Domestic Drinking Water of Flint River, Michigan (Flint Water Crisis 2014); Timeline 2014

The City of Flint Michigan normally received its drinking water from Lake Huron, but in an effort to decrease operating cost, switched sources to the Flint River, a river known for its exceptionally polluted water. The Flint River is polluted from a couple of main sources before processing, in the form of natural biological waster, as well as treated and untreated human and industrial waste. This leads to a higher level of bacteria

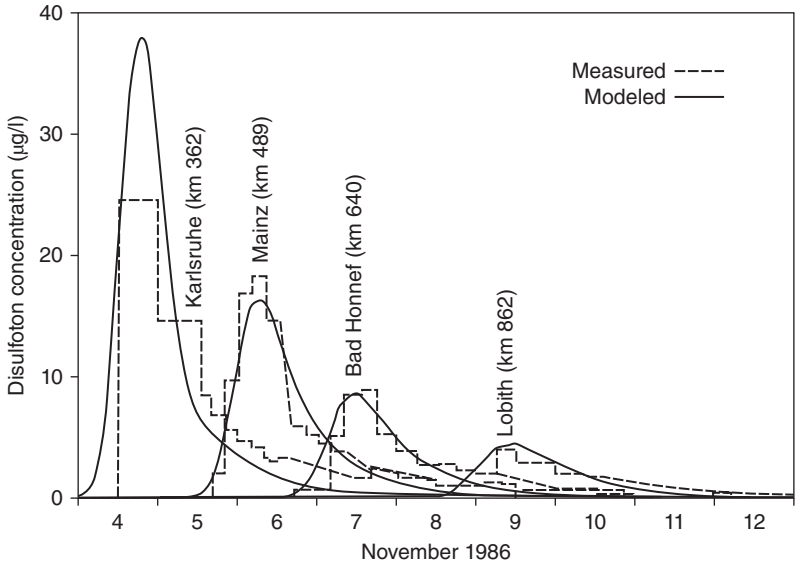


Figure 1.8 The concentration of disulfoton at each monitoring station on the Rhine river. Source: Capel et al. (1988). Reprinted with permission of American Chemical Society.

and organics as well as potential inorganic contaminants. Most importantly, corrosion inhibitors were not added to the treated water prior to distribution. The corrosion and lower pH of the water resulted in the release to lead (Pb) from the piping system and also damaged the distribution piping network. As a result, 6000–12 000 children were exposed to elevated lead concentrations in their drinking. Several hundreds of millions of government dollars have been spent to address the problem, yet the initial saving from switching water sources has been estimated to be between a few tens of thousands of dollars to 1 million dollars. Governmental officials were blamed for the oversight and several have resigned due to this likely avoidable event. As of 2017, residents continue to drink bottled water and will do so until a permanent remediation is expected in 2020. The different chemistry of the source waters was the main cause of the problem, and while this problematic chemistry was noted by some, others choose to ignore it. Chemical speciation of pollutants will be covered in Chapters 3 and 4. One problematic result of the Flint crisis is the current lack of trust of domestic water treatment plants that is woefully misguided. Treatment plants in the Global North are routinely tested and shown to be perfectly safe; piping in residential homes on the other hand can still be a source of toxic lead (Pb) and are not the fault of the city's treatment system.

1.6.3.7 Ajka Alumina Plant Accident (Hungary) (Ajka alumina plant accident 2010); Timeline 2010

On 4 October 2010, the dam of a reservoir collapsed containing 1 million m^3 of caustic waste from an alumina plant in Ajka, Veszprem County, in western Hungary. The red mud spill flooded the town of Devecser and eventually reached the Danube River. The red mud primarily contained transition metal oxides (i.e. Fe_2O_3, Al_2O_3) but also contained 660 mg/kg (parts per million) chromium, 110 mg/kg arsenic, and 1.2 mg/kg mercury. Ten people died and 150 were injured. The liquid–solid waste killed all life in the Marcal river, and finally reached the Danube on 7 October. Cities and countries downriver developed emergency plans for their drinking water as the pollutant plume flowed downgradient. Initial estimate placed the cleanup timeframe and costs to be at least a year and tens of millions of dollars. The plant was found guilty of several violations and a second dam was installed to prevent another disaster. As the modeling standpoint, the release could be treated as a pulse input into a river and the soluble pollutants were relatively quickly washed downstream. Toxic metals adsorbed to oxide particles sank to the river bottom and were more slowly released.

1.6.3.8 Talvivaara Mine Leak (Finland) (Talvivaara Mine Release 2012); Timeline: 2012. (Author: Aaron Lieberman Class Assignment, 2016)

The Talvivaara mine primarily mined nickel metal, but other toxic metals such as uranium were found. All the excess metals were dumped in the Gypsum Pond to be contained in a single source. In November 2012, the pond leaked ~250 000 m^3 of contaminated liquid as a pulse release. The leak was quickly capped, but later the following year in April 2013 the pond began to release wastewater 7000 m^3 an hour. This step release caused ~250 000 m^3 wastewater to be released into the

environment. The major environmental issues that were brought up were that the pollutant was a mixture of both metal–inorganic compounds as well as radioactive waste caused by the uranium. This caused fish downstream to be affected with abnormally high cadmium, aluminum, and nickel. The overall fate of the compounds would eventually end up in human consuming the fish, but the government made fishing in the nearby river systems illegal. Furthermore, nothing has been done by the company to attempt to fix the large amount of contamination in the local rivers, as evident by the nearby River Lumijoki turning red and orange from contamination. These two contamination events allow both a pulse and step model to be used.

1.6.3.9 Huangpu River (China) (Shanghai River's Dead Pig Total Approaches 15,000 2013; Rivers of Blood 2013); Timeline: 2013. (Author: Teddy Pierce, Class Assignment, 2016)

In March 2013, more than 16 000 young pigs were fished out of the Huangpu River and its tributaries in China. The river is the major source of tap water for Shanghai. The pigs were dumped into the river by pig farmers up river in the Zhejiang province. Some analysis on the pigs showed that they were infected with porcine circovirus, which is not known to infect humans. The waters of the river were described as "inky black, covered in a slick of lime green algae, and it smells like a blocked drain." This incident is believed to be a sign of the collapse of the pig farming industry that boomed in the region starting in the 1980s.

This unique, but specific release of thousands of pigs was a pulse release. This release was likely caused by farmers going out of business or suffering an outbreak of disease disposing of their pigs in the cheapest way possible, tossing them in the river. The high amount of organic matter being added to the river likely resulted in an anaerobic aquatic system since thousands of rotting carcasses would further increase the BOD to the point that the river DO levels could not be restored, killing of fish and other life forms.

Fishermen along the river have been affected by these lower-level step releases and this pulse release because they are finding it harder and harder to make a living fishing on the river as animal life in the river is choked out due to high BOD and nitrogen levels. Many of these fishermen, including the ones in the village of Xinfeng, make most of their money being paid by the government to help clean the river.

The water was reported to meet national standards by Shanghai's municipal water department but no test results were released. This opacity combined with the whole situation caused demonstrations for reform in Shanghai that were quickly shut down by police. Fortunately for the people who live along the river and depend on it for water, this specific event had a relatively short effect. A real cleanup effort would need to monitor and control and/or treat the amount of sewage and manure being added to the river by the pig farms. The river recovered rapidly as it flushed excess organic matter out and the DO increased to healthier levels.

1.6.3.10 Tianjin Chemical Plant Explosion (China) (Tianjin Explosions 2015); Timeline: 2015. (Author: Adrian Morton, Class Assignment, 2016)

The 2015 Tianjin explosions were a series of explosions from chemical containers in the port of Tianjin, China. Because this explosion occurred at a transit facility, the chemicals actually involved in the explosion were difficult to distinguish. The people storing these chemicals were less practiced at their safekeeping, recordkeeping because these chemicals were spotty at best, and the amount being stored was beyond legal limitations. This hindered the ability to deal with these disasters after they had occurred and also made it extremely difficult to assess the amount of risk the public was at to contamination and harm.

The first explosion was caused by an overheated container of nitrocellulose (also known as flash paper), which created a large fire. A smaller fire was the most likely cause of this overheating, but once this initial explosion occurs, the situation turned much more serious. A second explosion occurred within 30 seconds of the first and was much larger. This explosion involved the detonation of over 800 tons of ammonium nitrate. This was the largest and most damaging explosion of the event, but fires continued throughout the week, setting off a series of other explosions in the facility. These explosions included calcium carbide being heated and mixed with water to create acetylene gas. The most harmful species involved in this disaster was sodium cyanide. Seven hundred tons were stored at this facility, much of which was dispersed around the surrounding area of Tianjin and its port waters through the explosions.

This disaster was a series of pulse releases of various pollutants into the environment. The main pollutant, sodium cyanide dust, was sprinkled around the area as well as in the water and atmosphere. This cyanide salt has severe effects on humans and animals. When the first rains came after the event, the streets foamed white, and people who came in contact with the rain complained of chemical burns and rashes on their skin. Sodium cyanide is very mobile because it is rather soluble in water, and because it was turned to dust and thrown into the atmosphere, it has plenty of time to react with rain and become the much more harmful gaseous form of cyanide. Cyanide reacts under acidic conditions to form

hydrogen cyanide gas, which is extremely harmful to most organisms including humans. Carbon dioxide in the air is acidic enough to complete this transition, and since the rainwater was more acidic than usual in this area, this transformation to hydrogen cyanide gas was further assisted.

Thousands of dead stickleback fish washed up on shore soon after this event. The Chinese government attempted to calm fears by blaming these fish deaths on lowered oxygen levels in the water due to a large chemical oxygen demand created by new pollutants in the water. While anoxic waters are preferable to large amounts of cyanide, other types of pollutants likely occurred as sodium cyanide was detected in the water around the explosion site. The main factors affecting the fate and transport of sodium cyanide in this case is the pH of the water, affecting its reaction into hydrogen cyanide, and the solubility of the species allowing it to be easily incorporated into rainwater and the surrounding bay. The reduction potential, E_H, is also related to the chemical oxygen demand and its effect, and in this case the E_H became very low (reducing conditions) as a result of the pollution from this event.

1.6.3.11 Animas River Mine Tailing Spill (Animas River Spill 2015; Brumfield 2015; Schlanger 2015); Timeline 2015 (Author: Dylan Price, Class Project, 2016)

The Animas River in Colorado (USA) is surrounded by abandoned gold mines, some dating back to the late nineteenth century and have been closed for years while others that have only been closed for only 10 years. These gold mines, especially the old ones, often contain large tailings ponds ridden with heavy metals. Ironically, a team of EPA workers were sent to one of these mines to reinforce the walls of a tailings pond and add a tap that would clean and slowly release the tailings over time and ended up breaching the tailings and causing a massive release of toxic mine waste into Cement Creek, a tributary to the Animas river. An estimated 3 million gallons (11 400 m^3) were released over about a week starting on 5 August, while efforts were taken to stop the spill. The waste drained into the Animas and quickly made its way to the San Juan River by 10 August. The San Juan river flows into the Colorado and then into Lake Powell on 14 August – at which point the waste was diluted to a point where it was no longer dangerous according to the fate and transport model constructed for the disaster.

The main toxins of concern in the spill were lead, iron, cadmium, and arsenic. Measurements were taken 15 mi upstream from Durango (CO) and lead was found in levels 100 times larger than the limit. Iron was found to be 326 times the limit. Local residents, relying on water from wells fed by the Animas, were told not to drink well water and that it had to be analyzed for purity. The river was also closed from recreation for weeks. The upper Animas River was devoid of fish prior to this spill – from previous mine leakage in the area. Had there been fish to kill this spill certainly would have.

This release was treated a step pollutant release at a well-defined point source, containing inorganic heavy metals. The heavy metals were both suspended and aqueous. There was not a prolonged release of tailings at this rate and the spill was controlled with emergency tailings ponds. The sediment in the river is expected to dilute the released heavy metals to acceptable levels.

The spill required Superfund money that had, again ironically, been offered to this site years earlier and declined due to expected decrease in tourism with the major cleanup operation. The US EPA did not notify locals until almost 24 hours after the spill, and overlooked warning New Mexico of this spill for even longer. The governor of New Mexico sought legal action against the EPA and the governor of Colorado declared the spill an official disaster. This spill is a prime example of the politics associated with major pollution and the importance of fate and transport modeling.

1.6.3.12 Duke Power Coal Ash Spill; Timeline 2016 (Author: Ellie Finnegan, Class Project, 2016)

Coal ash is found in multiple forms. Produced from coal burning factories and power plants, coal combustion residuals (CCRs) range anywhere from small fly ash particles to boiler slag glassy pellets (EPA 2017e); Southeast Coal Ash site 2017. Plants that generate coal are required under regulations such as water discharge permits to properly treat and manage coal ash waste; however, sometimes regulations of these standards are not kept. In early February 2014, 39 000 tons of coal ash and 24 million gallons of wastewater were released as a pulse into the Dan River of North Carolina near the town of Eden. Duke Energy and the state agency responsible for protecting North Carolina waters were held responsible for the disaster.

Duke Energy, and other coal-fired power plants, primarily stores coal ash waste in unlined lagoons that are notoriously difficult to manage. This mechanism of storage is typically considered a poor choice because heavy metals are still able to leach into the soil and thus groundwater. In the scenario of the Duke Energy spill, the infrastructure was dated. Despite multiple voices of concern from Duke employees, and at least two requests from Duke engineers for funding to better monitor the lagoons, the company headquarters chose not update the outmoded waste treatment system. Finally, drainage pipes collapsed under the lagoons and caused the major spill in 2014 contaminating the Dan River with 70 mi of sludge.

Coal ash is considered a hazardous waste when not treated properly because it holds contaminants such as mercury, cadmium, and arsenic. Pollutants such as these can leach into groundwater systems and, as seen in the Duke Energy spill, contaminate downriver ecosystems. Because toxicity of heavy metals is concentration dependent, the spill caused the most harm at the point source. Though over time the Dan River diluted the system as the pollutant traveled downstream, heavy metal transport can rely on the mass of contaminant and the conditions of the river water system. If the metal-associated sediment is heavy, it may sink to the bottom of the river and thus take more time to be "flushed out" through resuspension events. If the river has high levels of dissolved organic matter, the metal ion may attach to the chemical sites on the soluble and mobile organic molecules thus increasing mobility. The oxygen levels of the water system also may play a large role in the fate and transport of associated metal pollutants. Generally, a metal in oxygenated water (metal oxide) will stay in its precipitated form thus decreasing the solubility and potential toxicity. If, however, the Dan River had low oxygen levels at the time of the spill, some metals would be reduced and may have become more soluble, traveled further, and created more damage. Heavy metal ions are more mobile under acidic conditions and/or anoxic conditions. This is the type of chemistry that will be discussed in Chapters 3 and 4.

In May 2015, Duke Energy was sued under the Clean Water Act for 64 million dollars in fines and 36 million dollars to go toward environmental projects and land conservation of rivers and wetlands in North Carolina and Virginia. During prosecution, Duke Energy pleaded guilty for a step pollution release of coal ash wastewater into the Dan River dating back to 2010.

The events above are only the major terrestrial disasters, and not ocean shipping accidents or the Fukushima nuclear plant disaster which are beyond the scale of any modeling scenario. It is likely that hundreds to thousands of accidents have happened since the year 2000 but were not reportable news events. Again, pollution events will continue to happen but strict enforcement of environmental regulations will deter these from becoming common place.

The news savy reader will note the absence of several large-scale estuary and oceanic incidents, such as the Deepwater Horizon disaster that released tons of dispersed petroleum in the Caribbean, the mercury contamination in Minamata Japan (Minamata Disease 1956), the many zones of hypoxia across the globe (USGS 2017; discussed at the end of Chapter 7), and the piles of plastics accumulating in our oceans, with microspheres documented at every beach in the world. These events are beyond the modeling scale of this text but are still noteworthy human-caused disasters.

1.7 Environmental Laws

Each country has developed a set of environmental laws governing the adequate premanufacture testing, use, and appropriate disposal or treatment of hazardous chemicals. Some countries have extensive rules, while others are still in the process of writing enforceable laws as their chemical industry develops. Environmental movements and the major environmental laws for the United States, Europe, and China will be discussed, in detail, in Chapters 12, 13, and 14, respectively. If the reader is from a different country, you may wish to research the laws for your country and compare them to those for the United States, Europe, and China. The main point here is most countries have environmental laws in place but compliance with these laws varies from the national, to state, to local level. In many countries, the creation of jobs overrides enforcement of laws, both environmental and safety.

Internationally, we are all affected by a process known as "Environmental Colonialism" in which developed countries prey on less-developed nations for disposal of hazardous wastes. This egregious act that exports hazardous chemical risks to unknowing nations for badly needed cash was addressed by the United Nations in its Basel Convention of 1989.

In the United States, the Environmental Protection Agency, along with other agencies, has made great strides since the 1970s to improve environmental compliance. Our rivers and lakes are not no longer open sewers, nor do they catch on fire any longer, but closer to the swimmable–fishable vision of the pre-1960s. The leakage of underground storage tanks has mostly been solved. And our metropolitan areas are much cleaner. Hazardous waste are strictly controlled and disposed. Recent revisions in the Toxic Substances Control Act (TSCA 2017) corrected long overdue expansion of Federal authority regarding toxic chemical management. But we do still have accidents, some that could have been prevented and others that are a result of inevitably flawed human-engineered and political systems. Several good sources of this good news is available including Protecting the Environment: A Half Century of Progress from EPA (http://www.epaalumni.org/hcp/Overview.pdf), Success Stories in Human Health (https://www.cdc.gov/features/sharingsuccessstories/index.html), the recognition of Seven Spectacular Places Saved by the Environmental Movement (http://www.slate.com/articles/health_and_science/science/2013/04/environmental_success_stories_on_earth_day_visit_places_saved_by_conservationists.html), and the popular science book entitled *Environmental Success Stories* by Frank Dunnivant (2017). Our successes are remarkable and will only continue to progress as we educate our citizens.

Concepts

1.1 What is the difference between explanatory and predictive modeling?

1.2 Explain the difference between a pollutant and pollution.

1.3 What is meant by chemodynamics in the concept of this course?

1.4 Define and give three examples of nonpoint source pollution from the Internet.

1.5 Define and give three examples of point source pollution from the Internet.

1.6 Define and give three examples of a step pollution event.

1.7 Define and give three examples of a pulse pollution event.

1.8 What does steady-state imply regarding environmental discharges or emissions?

1.9 Give three examples of environmental plumes, and why are they significant?

1.10 Using the Internet provide two examples of why the UN created the Basel Convention in 1989. Why do you think the United States did not sign this Treaty?

Exercises

1.1 Outline one of the pollution events given in Section 1.6.2 and include date, location, and main pollutant.

1.2 The US government, as with most Cold War governments around the globe, is the most serious of polluters. For your country (in the United States, this will be current DOE and DOD installations), research your weapon programs sites and write a two-page summary for one Superfund-type site.

1.3 Research a pollution event on the Internet. Write a one- to two-page summary including as many of the following as possible: the location, the company responsible for the site, the pollutants, the concentration of pollutants, the extent (surface area or volume) of pollution, the health effects of the pollutants, and the planned remediation. Include any retrospective (what did we learn and/or what's different because of the incident?)

1.4 Become socially active and research one of the chemical companies given in Table 1.4 using the Internet or by telephone or email. What chemicals do they use? What are their wastes? How do they dispose or destroy their wastes? How has their reported hazardous waste amounts changed in recent years?

1.5 Research the term "Pollution Prevention" on the Internet and for three industries. How has pollution prevention affected these manufacturing processes?

1.6 Become socially active and research one of the chemical companies in your home state using the Internet or by telephone or email. What chemicals do they use? What are their wastes? How do they dispose or destroy their wastes?

1.7 Visit the US EPA's Toxic Release Inventory website at https://www.epa.gov/trinationalanalysis and research a topic of your choice based on your zip code.

Bibliography

Ajka alumina plant accident (2010). https://en.wikipedia.org/wiki/Ajka_alumina_plant_accident (accessed 21 September 2017).

Animas River Spill (2015). Department of public health and environment. https://www.colorado.gov/pacific/cdphe/animas-river-spill (accessed 21 September 2017).

Anonymous (1987). *Environ. Sci. Technol.* **21** (March): 5.

Associated Press (AP) (2015). http://www.foxnews.com/us/2015/05/15/duke-energy-pleads-guilty-fined-102m-in-connection-with-2014-coal-ash-spill.html (accessed 21 September 2017).

Bailey, R.A., Clark, H.M., Ferris, J.P. et al. (2002). *Chemistry of the Environment*, 2e. New York: Academia Press (Chapter 14).

Basel Convention (1989). Table 1.2. www.basel.int/natreporting/index.html (accessed 8 December 2003)

Bioaccumulation (2017). Wikipedia. https://en.wikipedia.org/wiki/Bioaccumulation (accessed 3 October 2017).

Brumfield, B. (2015). Animas River spill: the massive toll by the numbers, CNN. http://www.cnn.com/2015/08/13/us/animas-river-spill-by-the-numbers/index.html (accessed 24 September 2017).

Capel, P.D., Giger, W., Reichert, R., and Warner, O. (1988). Accidental input of pesticides into the Rhine River. *Environ. Sci. Technol.* **22** (9): 992–997.

Coal Ash Spill, TN (2008). http://earthobservatory.nasa.gov/NaturalHazards/view.php?id=36352 (accessed 21 September 2017).

Chernobyl Accident (2003). http://www.basel.int/ (accessed 1 November 2003).

Chernobyl Disaster (1986). https://en.wikipedia.org/wiki/Chernobyl_disaster (accessed 25 September 2017).

Colombi, C. (1986). Sondermulldeponie Kolliken, wie weiter? *Phoenix Int.* **1**: 10–15.

Dave, J.M. (1985). The Bhopal methyl isocyanate (MIC) incident: an overview. In: *Proceedings of an International Symposium, Highly Toxic Chemicals: Detection and Protection Methods* (ed. H.D. Schiefer), 1–38. Saskatoon, Saskatchewan, Canada: Springer.

Dewan, S. (2008). At plant in coal ash spill, toxic deposits by the ton. http://www.nytimes.com/2008/12/30/us/30sludge.html (accessed 21 September 2017).

Dimdam, E. (2014). Discovery magazine. http://list25.com/25-biggest-man-made-environmental-disasters-in-history/ (accessed 3 October 2017).

Dunnivant, F.M. (2017). *Environmental Success Stories: Solving Major Ecological Problems and Confronting Climate Change*. Columbia University Press 9780231179195.

Dunnivant, F.M., Stromberg, G.J., Wiley, A.H. et al. (1994). Feasibility Study Report for Test Area North Groundwater Operable Unit 1-07B at the Idaho National Engineering Laboratory (INEEL), EFFF-ER-10802, January, 1994, Idaho Falls, Idaho, USA.

Dunnivant, F.M., Schwarzenbach, R.P., and Macalady, D.L. (1992). Reduction of substituted nitrobenzenes in aqueous solutions containing natural organic matter. *Environ. Sci. Technol.* **26** (11): 2133–2141.

EPA (1989). *Risk Assessment Guidance for Superfund Volume II, Environmental Evaluation Manual, Interim Final*, EPA/540/1-89/001, 4. Washington, DC: Office of Emergency and Remedial Response.

EPA (2001). National Analysis, The National Biennial RCRA Hazardous Waste Report (based on 2001 data). https://www.epa.gov/hwgenerators/biennial-hazardous-waste-report (accessed 14 December 2018).

EPA (2013). https://www.epa.gov/sites/production/files/2015-09/documents/rcras_critical_mission_and_the_path_forward.pdf (accessed 25 July 2018).

EPA (2015a). U.S. hazardous waste by state. https://rcrapublic.epa.gov/rcrainfoweb/action/modules/br/summary/view (accessed 25 September 2017).

EPA (2015b). U.S. type of waste by industry. https://rcrainfo.epa.gov/rcrainfoweb/action/modules/br/naics) (accessed 25 September 2017).

EPA (2016). https://blog.epa.gov/blog/2016/06/tsca-reform-a-bipartisan-milestone-to-protect-our-health-from-dangerous-chemicals/ (accessed 3 October 2017).

EPA (2017a). https://www.epa.gov/caa-permitting (accessed 3 October 2017).

EPA (2017b). http://www.ecologydictionary.org/EPA-Terms-of-Environment-Dictionary/Waste_Load_Allocation (accessed 3 October 2017).

EPA (2017c). https://www.epa.gov/toxics-release-inventory-tri-program (accessed 3 October 2017).

EPA (2017d). www.epa.gov/aboutepa/our-mission-and-what-we-do (accessed 3 October 2017).

EPA (2017e). www.epa.gov/coalash/coal-ash-basics (accessed 21 September 2017).

Schlanger, A. (2015). EPA Causes Massive Spill of Mining Waste Water in Colorado, Turns Animas River Bright Orange. Newsweek, 7 Aug., 2015. www.newsweek.com/epa-causes-massive-colorado-spill-1-million-gallons-mining-waste-turns-river-361019 (accessed 21 September 2017).

Fick's Law (2017). en.wikipedia.org/wiki/Fick%27s_laws_of_diffusion (accessed 3 October 2017).

Flint Water Crisis (2014). en.wikipedia.org/wiki/Flint_water_crisis (accessed 21 September 2017).

Hemond, H. and Fechner, E.J. (2000). *Chemical Fate and Transport in the Environment*. Amsterdam: Elsevier, Academic Press.

Kingston Fossil Plant (2017). https://www.tva.gov/Energy/Our-Power-System/Coal/Kingston-Fossil-Plant (accessed 22 September 2017).

Kingston Fossil Plant Coal Fly Ash Slurry Spill (2008). en.wikipedia.org/wiki/Kingston_Fossil_Plant_coal_fly_ash_slurry_spill (accessed 21 September 2017).

Lisenby, D. (2014). Duke energy coal ash spill pollutes river and threatens drinking water. ecowatch.com/2014/02/04/duke-energy-coal-ash-spill/ (accessed 21 September 2017).

Minamata Disease (1956). en.wikipedia.org/wiki/Minamata_disease (accessed 3 October 2017).

NPR (2015). What caused the warehouse explosions in Tianjin, China? Interview. www.npr.org/2015/08/14/432280627/what-caused-the-warehouse-explosions-in-tianjin-china (accessed 21 September 2017).

Rivers of Blood (2013). The dead pigs rotting in China's water supply. www.theguardian.com/world/2013/mar/29/dead-pigs-china-water-supply (accessed 21 September 2017).

Schaefer, A. (2000). Disastrous cyanide spill could spawn liability reforms. *Environ. Sci. Technol.* **34**: A-203.

Schwarzenbach, R.P., Stierli, R., Lanz, K., and Zeyer, J. (1990). Quinone and iron porphyrin mediated reduction

of nitroaromatic compounds in homogeneous aqueous solution. *Environ. Sci. Technol.* **24**: 1566–1574.

Shanghai River's Dead Pig Total Approaches 15,000 (2013). phys.org/news/2013-03-shanghai-river-dead-pig-total.html (accessed 21 September 2017).

Shrivastava, P. (1987). *Bhopal: Anatomy of a Crisis*. Cambridge, Massachusetts: Ballinger Publishing Company.

Sludge Graphic (2008). http://www.nytimes.com/imagepages/2008/12/25/us/20081225_SLUDGE_GRAPHIC.html (accessed 21 September 2017).

Southeast Coal Ash site (2017). http://www.southeastcoalash.org/ (accessed 21 September 2017).

Tianjin Explosions (2015). https://en.wikipedia.org/wiki/2015_Tianjin_explosions (accessed 21 September 2017).

Talvivaara Mine Release (2012). http://www.nuclear-heritage.net/index.php/Talvivaara_mine:_environmental_disaster_in_Finland (accessed 21 September 2017).

Thibodeauz, L.J. (1996). *Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil*, 2e. New York: Wiley.

TSCA (2017). https://en.wikipedia.org/wiki/Toxic_Substances_Control_Act_of_1976 (accessed 3 October 2017).

United Nations Environment Programme, UNEP (2002). Office for the co-ordination of Humanitarian Affairs, OCHA. *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare*. 23 February – 6 March 2000, Geneva, March.

United Nations (U.N.) (2000). Secretariat of the Basel Convention, United Nations Environment Programme, Country Fact Sheets. http://www.basel.int/natreporting/index.html (accessed 21 July 2018).

USGS (2017). https://toxics.usgs.gov/hypoxia/hypoxic_zone.html (accessed 3 October 2017).

Varma, D.R. (1986). Anatomy of the methyl isocyanate leak on Bhopal. In: *Hazard Assessment of Chemicals* (ed. J. Saxena), 233–299. Hemisphere Publishing Corp.: New York.

WASP (1983). Water quality analysis simulation program. https://www.epa.gov/exposure-assessment-models/water-quality-analysis-simulation-program-wasp (accessed 2 October 2017).