Pollution Prevention and Control: Part I

Human Health and Environmental Quality

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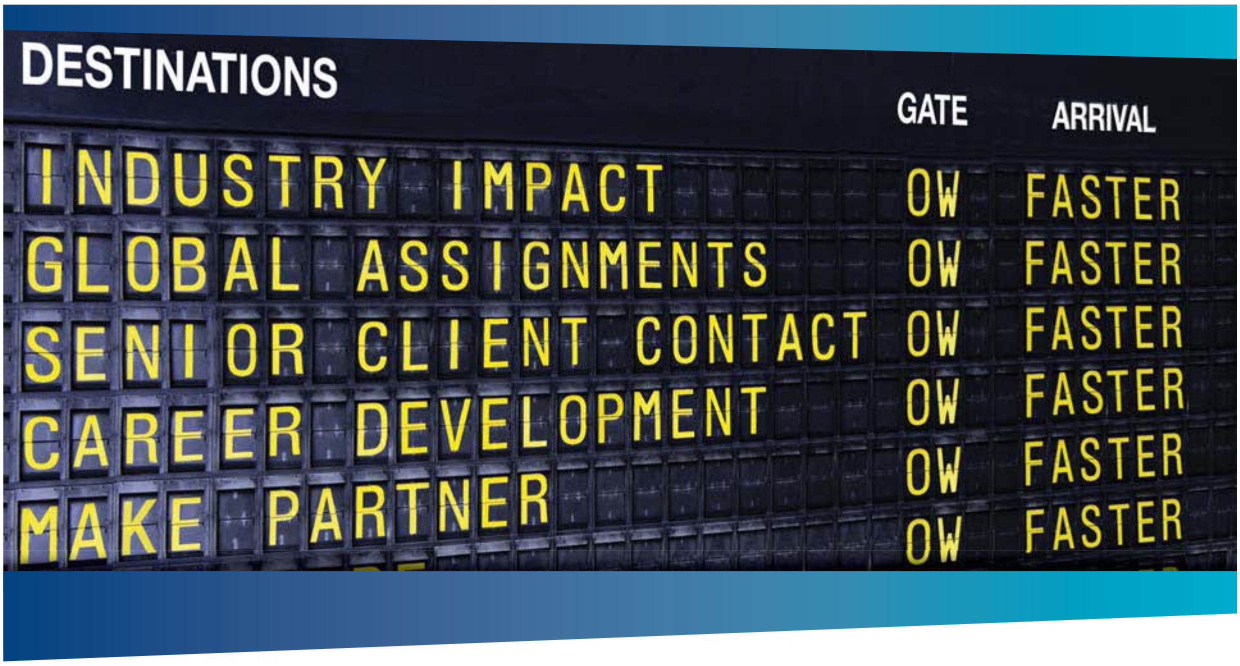
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Could you think of 101 new things
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Preface

This book introduces the general strategy of design, the natural environmental cycles and how human activities interrupt and control them, toxicity and risk assessment for the protection of human and environmental health, the fate of pollutants in the environment, and a review of U.S. and international laws and regulations. Understanding these broad environmental issues leads to better engineering.

Put in more simple terms, it is about a very simple idea from Tom Chapin's children's song, 'Someone's Gonna Use It After You', but the issue is not childish or trivial.

> When you stand at the sink, did you ever think
> About the water flowing down the drain?
> …
> Someone's gonna use it after you.…

This lyric wonderfully captures the essence of the environmental ethic. Our actions can protect or destroy.

We are reminded of it daily. In the past few days the New York Times has reported that the daily average atmospheric carbon dioxide exceeded 400 ppm for the first time, and the High Plains aquifer is so depleted by water mining that farmers in Kansas face water shortages. More tragic is the report that diarrhea kills an estimated 900, 000 children each year, mostly because of just four microorganisms that can easily be inactivated in drinking water.

These problems are not really 'news'. The warning signs have been evident for years. We know how to reduce carbon dioxide emissions. We know when aquifers are being over used. We know how to save lives by improving public health through clean water and better diet.

This book will be followed by four books about the design of pollution control processes and integrated systems that are widely used in water pollution control, air pollution control, and solid waste control.

Book 2 is about accounting for the flow of energy and material, both polluting and innocuous, through manufacturing and waste treatment systems.

Book 3 is about using chemical and biological reactions to destroy and transform pollutants to facilitate the separation of different materials, or to make substances safe for discharge to water, air or soil.

Book 4 is about the many ways to separate solids from liquids, solids from gases, solids from solids, and so on in all combinations. The solution of a problem is never stymied by lack of separation technology, but it may be weakened by failure to organize them into efficient processing systems, or to overlook an innovative combinations of transformation and separation.

Book 5 is about minimizing costs and comparing alternate designs. Engineering projects almost always have more than one feasible solution, and often there are several that are attractive. The options must be measured and compared by using an objective criteria like construction cost, lifetime cost, mass of pollutant discharged. Also discussed are methods for evaluating non-monetary aspects of projects.

The goal of the series is to build problem-solving strategies and skills that are widely useful in water pollution control, air pollution control, and solid waste control. We want to stimulate innovation in pollution control systems design and pollution prevention.

Pollution control engineers support the people who decide how public and private funds will be used to solve problems. They bring logic and order and solid quantitative information to the discussion so better decisions will be made. They design the machinery and structures and systems that are needed to make things better. And, they make sure the price will be right.

The ultimate goal of environmental engineering, and the part of it that we call pollution control engineering, is to increase the level of health and happiness in the world. We hope this series of books will help to do that.

Finally, we wish to thank Dale Rudd for many good ideas over many years, Erhard Joeres for his review of the book and A. 'Sam' James for help on water quality modeling.

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1 The Strategy of Pollution Control Engineering

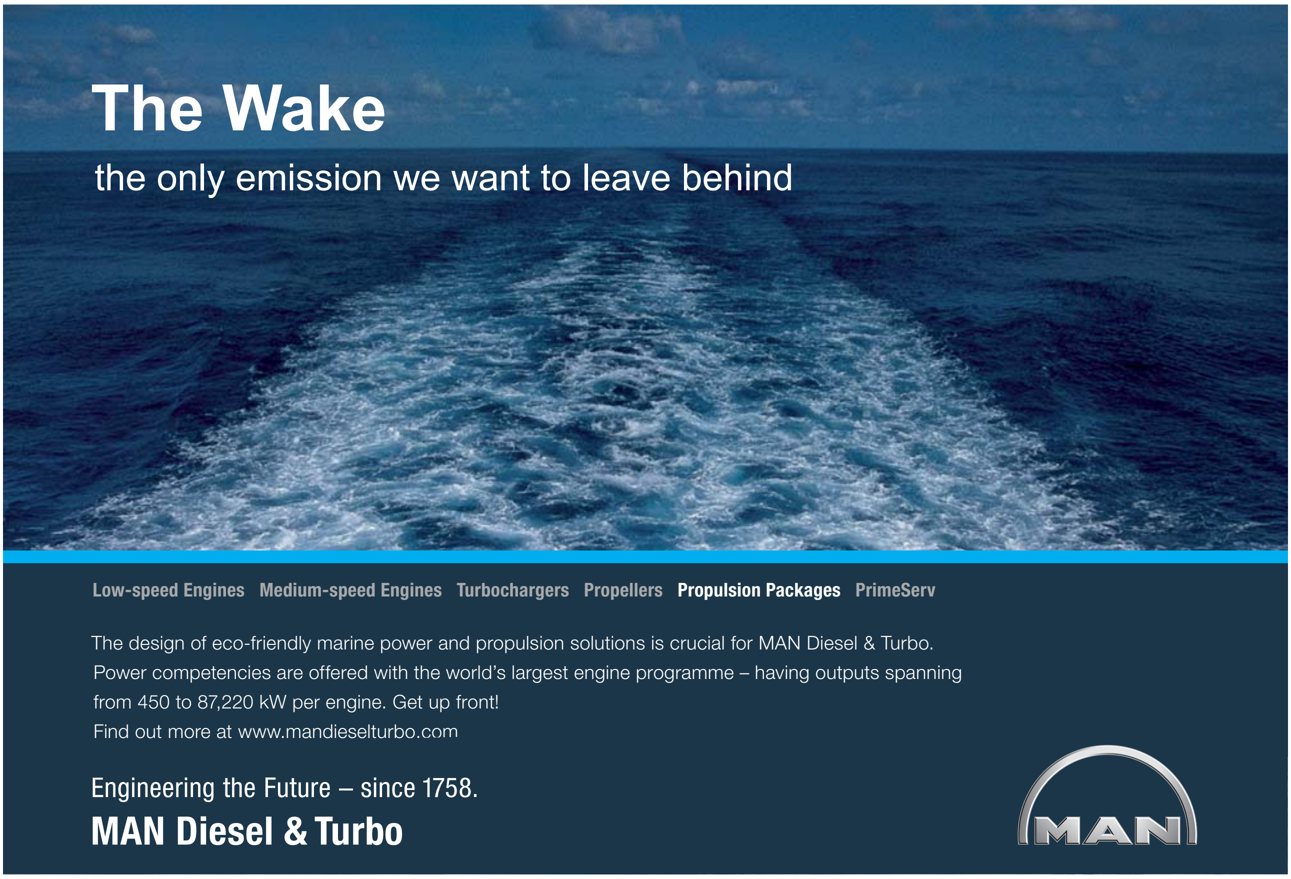
1.1 Our Round River

Albert Einstein said that the environment was 'everything that is not me'.

For 'me' to be healthy and happy, everything that is 'not me' must be healthy and happy. That includes an environment that is in a healthy balance between the demands of 7 billion people and the natural cycles of essential nutrients, and one that is safe from hazardous substances.

Aldo Leopold (1949, 1993) viewed our activities in terms of Paul Bunyan's Round River, which is part of the folklore of the early logging days. Paul discovered in Northern Wisconsin a river that flowed into itself, with no source and no mouth, a round river.

The earth is our round river, and we ride on the logs that float down it. The technique of birling is called economics, remembering old routes is called history, the selection of new routes is statesmanship, and the conversation about oncoming rapids and riffles is called politics.



The study of the soils, flora, and fauna that comprise the channels of the river is biology, and their origin through time is called geology and evolution, and the techniques of using them are called agriculture and engineering. Ecology is the lore of the round river, the study of biotic navigation.

We must disturb the environment as we draw from it food, water, shelter, clothing, energy, and all of our material needs, and as we dispose into it our wastes. Our disturbances must be planned carefully to avoid unnecessary damage.

This book is concerned with understanding the interactions of man and the environment and with maintaining balance in the natural systems that buffer those interactions. The goal is to promote health and happiness. The difficulty for engineers, who like to measure and quantify outputs, is that there is no metric for measuring happiness, and not very precise ones for measuring healthiness. The things we can count and measure are at the bottom of the hierarchy of goals shown in Figure 1.1.

This book, more specifically, is about the right-hand column of Figure 1.1. We know that clean air and clear water are essential for good health. We know that, at times, having excellent air and water quality may seem to be in conflict with having a high level of agricultural and industrial outputs. It is not necessary for one to give way to the other, but careful quantitative analysis is needed or there will be mistakes and inefficiencies. This book is about scientific and engineering methods that inform and support good policy and wise investment.

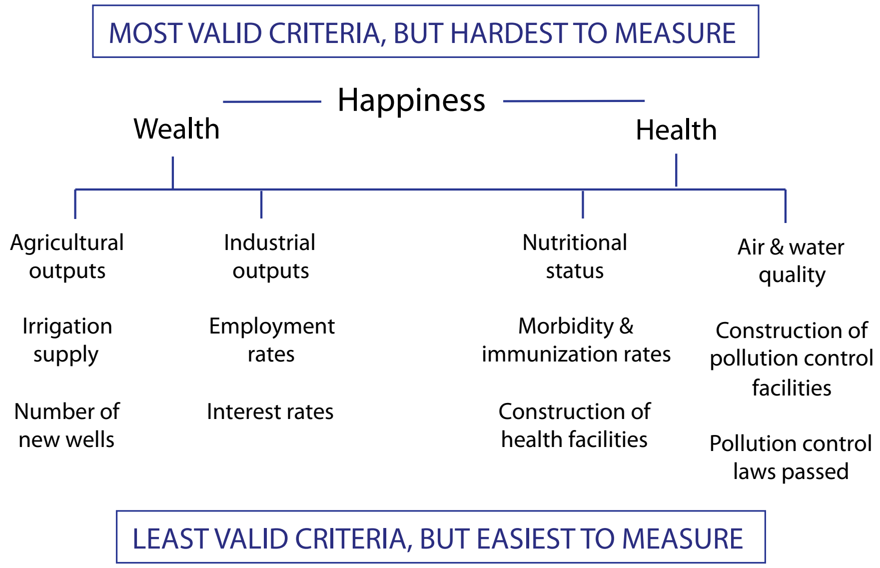


Figure 1.1 The hierarchy of goals for environmental and human health.

1.2 A Preview of This Book

Chapter 2 is an introduction to pollution prevention and control engineering. The subjects introduced there will be developed in detail in subsequent books. The immediate goal is to explain the scope of pollution prevention and control engineering.

Chapter 3 describes the intricate natural cycles that move the stuff of life (water, carbon, oxygen, nitrogen, phosphorus, and sulfur) between air, water, and soil, and between plants and animals, and between creation and death. These essential elements are linked by the water cycle, so water resources also must be protected and maintained in balance. These essential elements may themselves become pollutants, as when phosphorus fertilizer is carried into a lake where it stimulates a massive bloom of algae.

Toxicology and risk assessment are discussed in Chapters 4, 5 and 6. Toxic and otherwise harmful substances must be identified and criteria for emissions and effluents must be established that incorporate all that is known about their toxic effects.

The emission and effluent limits should take into account the fate of pollutants. Some are highly toxic even in minute amounts; some are ugly but not dangerous. Some persist for long periods of time; some rapidly dissipate. Will they accumulate in soil or in animal tissue? Do toxic chemicals degrade into forms that are innocuous? These issues are discussed in Chapter 7, 8 and 9.

Chapter 10 is about international and U.S. laws and regulations. The laws, rules and regulations must be fair and consistent. They must set forth clearly what is expected and what is acceptable, and also what are the penalties if expectations and requirements are not fulfilled. They should derive from the most complete possible understanding of the natural cycles, toxicology, and the fate of pollutants. Risk assessment should be part of the process. Economic considerations are not involved in most laws.

This is the first of five books about pollution prevention and control. This first, as should be evident from the description above, is mostly about goals and requirements. Creating engineering designs to accomplish those goals is the subject of the subsequent books. These are described starting in Section 1.4, after a brief discussion of some fundamental ideas about pollution control.

1.3 The Fallacy of Zero Emissions

Why not require every industry to emit nothing other than the goods it manufactures? This would protect the environment and public health would be guaranteed.

Zero emissions from a human would mean that we could not expire carbon dioxide from the lungs, rid ourselves of salts, or excrete food residues. The result would be death. Likewise, an industry or a community has certain needs for economic health and growth and cannot survive on a zero emission policy.

Figure 1.2 shows the daily metabolism of a hypothetical city with a population of 1,000,000 in 1965. This comes from the classic work of Abel Wolman (1965), an old but interesting reference because it was the first to recognize of the metabolism of a city, a concept that today is relevant to the concept of sustainability.

It is interesting, as well, because the world population today is more than double the population in 1965 when Wolman published his book, about 3.3 billion in 1965 and 7.0 billion in 2012. The 1965 population of the U.S. was 194.3 million; today it is 349 million. Worldwide, there are 476 city areas with more than 1,000,000 people, 63 with more than 5,000,000, and 26 with a population more than 10,000,000.

Figure 1.2 The daily metabolism of a city of 1,000,000 people (Wolman 1965). Not all inputs and outputs are listed. (Photo credit: pixabay)

Figure 1.3 Metabolism of an industry. Materials that are not converted into products or useful byproducts become wastes or emissions that are contaminated by reactants, impurities in reactants, useless byproducts, solvents, catalysts, and lost products. (Photo credit: freedigitalphotos / supakitmod)

The only way the chemical industry shown in Figure 1.3 could avoid creating waste would be if the raw material inputs were free of impurities, the synthesis chemistry required no excess reactant to drive the reaction and produced no unwanted by-products, and the process operated at ambient conditions of temperature and pressure. In some amount, materials other than product, pure water, and pure air must leave the system. The choice is not whether to discharge waste, but what form and volume shall be discharged and at what pollutant concentrations. Some industries do have a goal of zero discharge of toxic substances.

The following practical definitions of 'zero discharge' accept that zero mass of all liquid, gaseous, and solid outputs emissions is impossible.

- Eliminate priority pollutants or toxic substances from the wastewater effluent. Eliminate toxic air pollutants from gaseous emissions. Eliminate recyclable and hazardous materials from solid waste landfills.
- Discharge no water effluent stream from the processing site. All wastewater, after treatment, is recycled and reused.
- Discharge no material that will do harm in the receiving environment.
- Minimize the volume of slurries and sludges.

Asking questions such as these stimulates useful design questions:

- What raw materials are brought into the waste generating system?
- How much of each raw material leaves in useful products and how much is lost as waste?
- What are the waste streams?
- Where are the wastes generated?
- Which wastes are hazardous and which are not?
- Are potentially reusable materials being contaminated and degraded?
- Can the process be changed to eliminate a troublesome material?
- Can material be handled differently to reduce losses?
- Can the material be handled at a temperature more conducive to fume or dust suppression?
- Can process efficiency be improved with better instrumentation or control strategies?
- Can housekeeping practices be modified to limit waste production?

Recycling, like all other pollution control processes, operates under the fallacy of zero emissions. Collecting the discarded material and transporting it to a recycling center generates air pollutants. Recycled paper must be cleaned to remove ink, paper clips, staples, stamps, and other materials. The cleaning consumes fuel, chemicals, and water and creates waste. A paper recycling process reclaims only two-thirds of the fiber input. A three-ton input yields two tons of reclaimed fiber and two-tons of sludge. The sludge is the one-ton of lost fiber plus one ton of water. The result is one ton of sludge waste for each ton of reclaimed fiber.

Waste treatment itself produces emissions. Burning an unwanted by-product to produce energy creates exhaust gas that contains air pollutants. Capturing dust from the exhaust gas will produce a solid waste; absorbing gaseous pollutants into a liquid creates a new stream of wastewater. Achieving zero discharge of water-born pollutants will leave some pollutants to be discharged as a gas, sludge, or solid.

1.4 The Integration of Pollution Control

There are a few basic engineering principles that apply to all pollutant materials, whether the origin is municipal, industrial, or natural; whether the form is a liquid, gas, or solid; whether the discharge contains a single pollutant or a mixture, and also whether the material is toxic, non-toxic, reactive, or non-reactive. These principles can be used to solve problems with air pollution, municipal and industrial water pollution, soil pollution, groundwater pollution, and so on.

The goal of this series of books is to apply these principles to all sorts of pollutants and pollution control problems. We believe this will develop problem-solving skills better than the traditional course that compartmentalizes air pollution, water pollution, and solid wastes. Seeing problems this way is essential because real problems very often co-mingle issues with air, water and solids and cross boundaries between categories.

Dealing with polluted water may create gaseous emissions or solid residues that are part of the same problem. Contaminated groundwater can be pumped and cleaned of a solvent without making it safe for discharge to a stream, and the solvent will still exist in some form, perhaps as a gas or adsorbed onto a solid. A solid waste disposal problem, even one that is relatively straightforward like putting municipal refuse into a sanitary landfill, will produce a strong leachate and gas, both of which need to be collected and subjected to further management.

The strategy of pollution control is about engineering concepts that are widely useful in water pollution control, air pollution control, and solid waste management. It is about separating, transforming, and destroying molecules and compounds, and about the catalog of process technology that can be organized into systems that will convert a worthless mixture of materials into something of value (clean water, reusable aluminum, etc.) Selecting the processing technology and organizing it into feasible processing systems requires some engineering design strategy.

This will be done in a collection of five books. This one, the first, deals with how pollutants are regulated, which specific chemicals and compounds are restricted and why, how the natural system responds to pollutants, and the analysis of risk to organisms presented by toxic chemicals. This information is useful because many projects are driven by government rules and regulations. This information, however, is not essential to understanding the more technical material in the subsequent volumes.

Book 2 is about the two most important engineering design tools – the material balance and the energy balance. These are the basis for all process invention and design. This is how we account for what is known and estimate what is unknown. This is how we understand existing systems and how we analyze systems that exist only in our imagination. Figure 1.4 shows an accounting for a simple system.

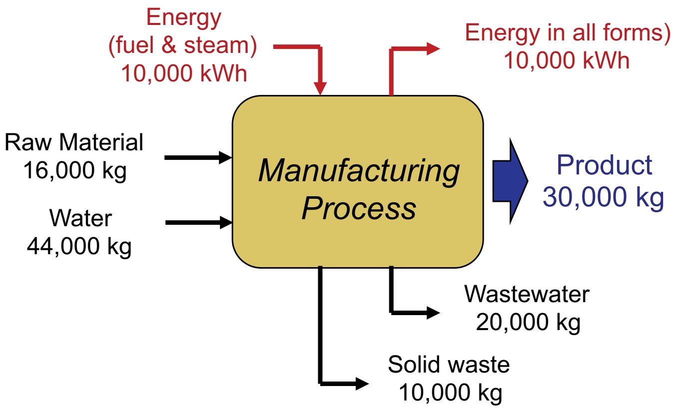


Figure 1.4 Understanding the flow of material and energy is fundamental to understanding and solving pollution control problems. All mass and energy entering the system must be accounted for in the system outputs.

Book 3 is about chemical and biological transformations that convert harmful substances into innocuous substances, useless materials to useful ones, make low value materials valuable, and make substances easier to remove from a gaseous or liquid stream. A second aspect is to make manufacturing more environmentally friendly. Most reactions yield a mixture of materials that that must be concentrated or separated and this means that the reactors must be integrated with separation technology.

Book 4 is about separation technology. Especially important separations are those that can separate harmful from harmless substances, and useless from useful materials. The design of separation systems is a playground for inventive engineers.

Separating materials is possible whenever they differ in size, density, ionic charge, solubility, or some other property. Each separation stage divides the feed stream into two output streams, one that is enriched with respect to a resource or a pollutant, and one that is depleted. Either of these outputs may need further processing before it is suitable for discharge to the environment, or it becomes a useful product. Figure 1.5 shows a generic separation of a solid from air. There are many ways to do this, as shown in Table 1.1, which is a catalog of methods for separating solids from liquids, solids from gases, gases from gases, liquids from liquids, and solids from solids.

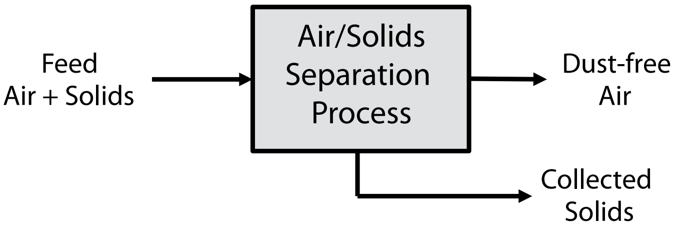


Figure 1.5 A separation process splits a feed stream into two output streams.

Separate a → from a ↓	Solid	Dissolved Substance	Gas or Vapor	Liquid
Liquid	Settling Flotation Filtration Microfiltration Centrifugation Hydrocyclone Foam fractionation Magnetic separation	Reverse osmosis Ultrafiltration Electrodialysis Ion exchange Distillation Freezing Crystallization Adsorption	Aeration Stripping Steam stripping	Extraction Distillation Settling
Gas	Filtration Electrostatic ppt. Cyclone Scrubbing	(not applicable)	Pervaporation Adsorption Absorption Condensation	Demister
Solid	Magnetic separation Inertial separation Air classification Optical sorting	Leaching/washing	Aeration Vapor extraction	Drying Settling Filtration Centrifugation Hydroclone

Table 1.1 Separation processes can be combined into hundreds of different pollution control systems and manufacturing processes.

Book 5 is about special tools for evaluating and comparing alternative solutions. Real problems have more than one possible solution. Identifying the solution to implement is another kind of separation problem – a separation of alternatives based on differences in some measure of their effectiveness, such as construction cost, lifetime cost, mass of pollutant discharged, labor requirements, amount of pollutant destroyed or recovered, chemical used, or energy consumption.

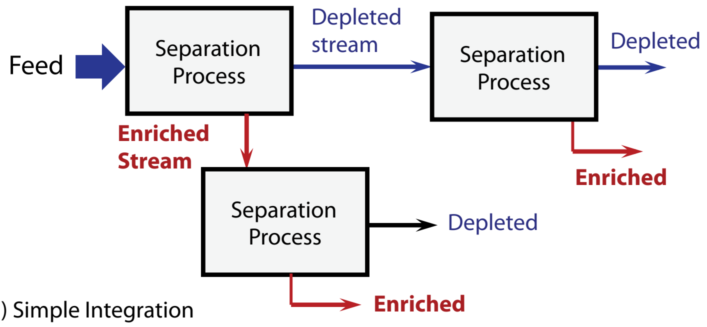
Often an evaluation scheme is needed that includes intangible and incommensurate factors such as improvement in public health, nuisance to neighboring properties, public acceptance, physical attractiveness, and so on. There is usually not one alternate that dominates in terms of all of these so some weighting of relative importance may be needed. This is cost-effectiveness analysis.

1.5 An Integrated Approach to Design

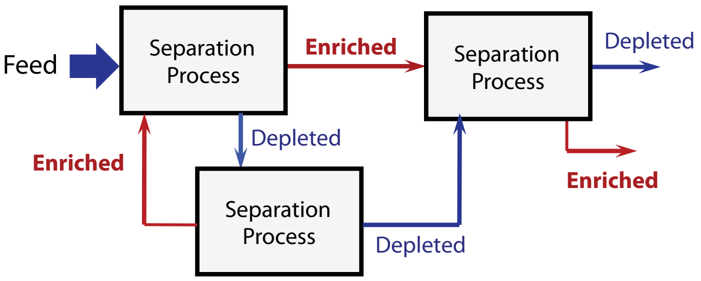
The big problem – the real problem – comprises a variety of sub-problems. The design of a car wheel means that someone must design a hydraulic brake line, a brake shoe, a tire and a valve stem, a rim and lug nuts, a wheel cover, a shock absorber, and so on. Each sub-problem must be solved correctly, and not all the sub-problems are easy to solve. And the parts must be integrated into a reliable working unit.

A pollution control system is designed by solving a sequence of sub-problems. Each chemical transformation and each separation is a sub-problem and within each of these problems are others like heating the process, supplying it with air, controlling the pH, removing solids that have been collected from air or water, and so on.

All of this is done with the understanding that everything entering the system must leave, in one form or another. The same is true for everything entering a single process. It will leave to the environment (air, water, or land) if it has been made safe and innocuous. Or it will go into another processing step to make it more suitable for release. This linking of process to process, and system to environment, is process integration.



(a) Simple Integration



(b) Recycle Integration

Figure 1.6 Process are linked, or integrated, as required to produce enriched and depleted outputs that can be released to the environment or transferred to a point of reuse.

Figure 1.6a shows a simple integration of three separation processes. The processes work together, but they are linked in the simplest way possible, without recycle or cross-connection.

Each process divides one input stream into two output streams, one that is enriched with respect to the input and one that is depleted. The designer must dispose of both output streams. If one output (or both) needs more processing it can be economical to recycle instead of increasing the number of processes in series, as in Figure 1.6b.

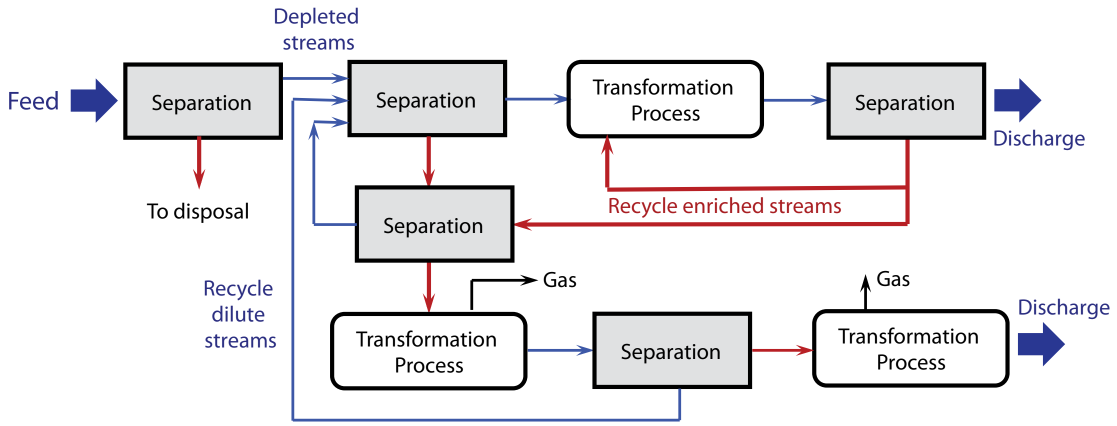
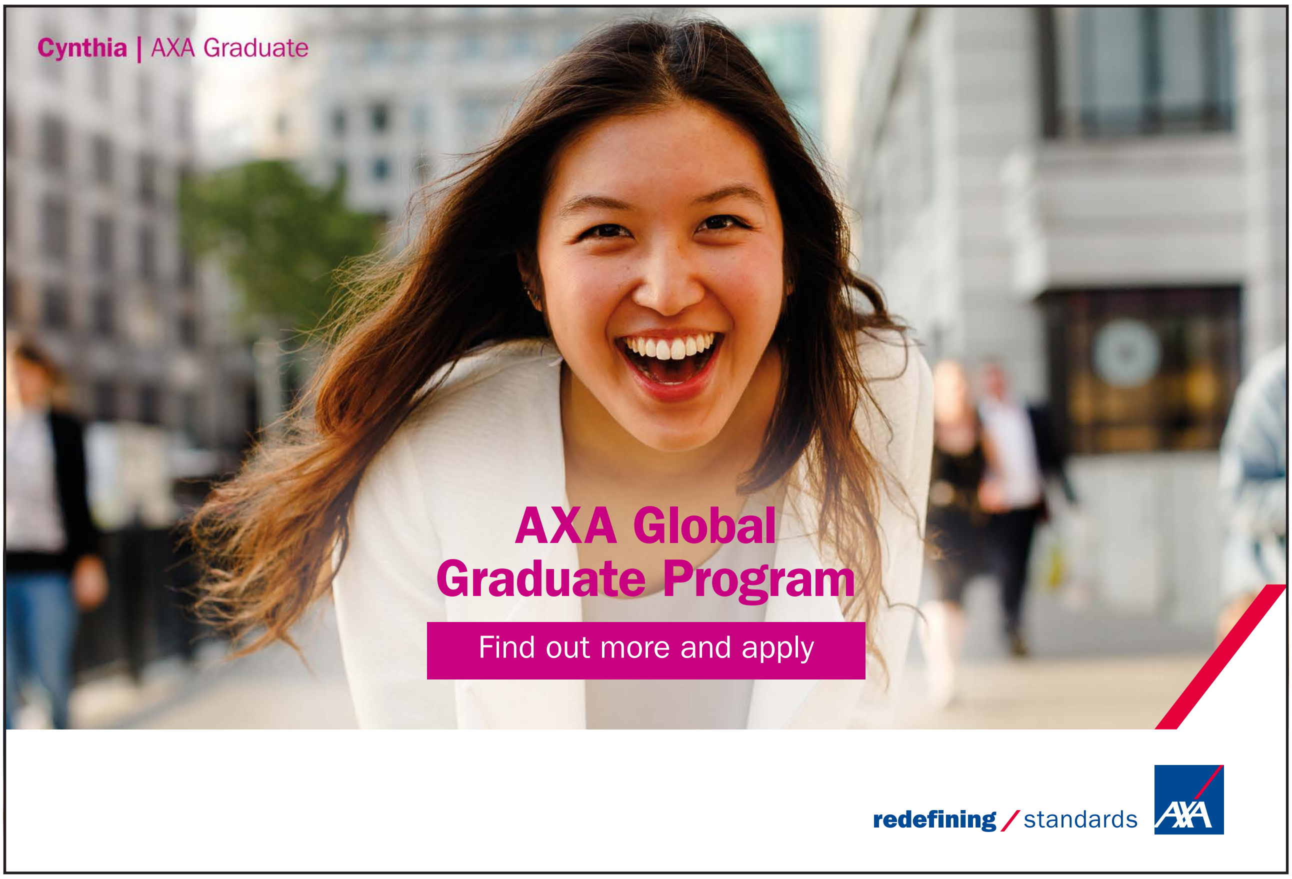


Figure 1.7 A generic integrated system that includes transformations and separations.



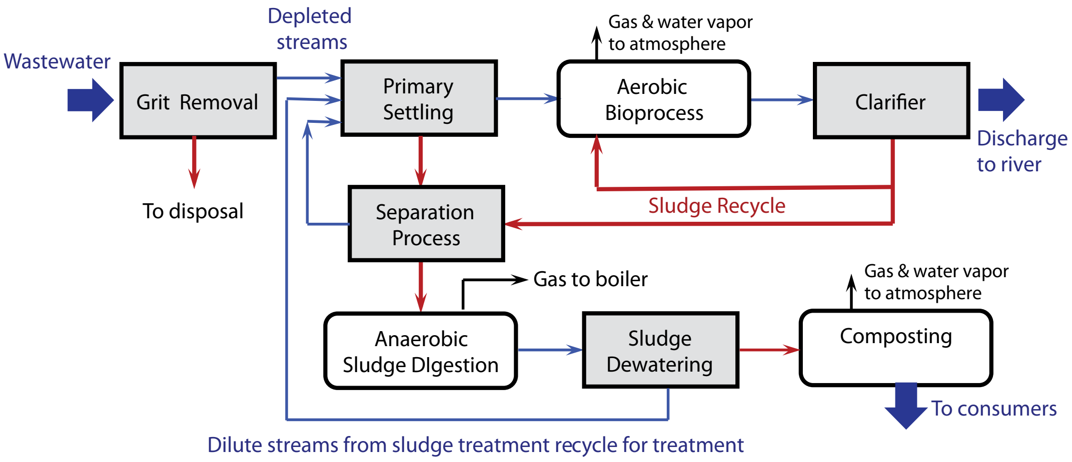


Figure 1.8 The arrangement of processes is identical to Figure 1.7, but naming the processes reveals a commonly used scheme for treating municipal wastewater. The three transformations are all done biologically. The boxes all represent physical separations of solids and water. Separations of gases from liquid are shown with arrows.

The most common integration is separations with chemical or biological transformation. Figure 1.7 shows a generic integrated system and Figure 1.8 shows the same system with the names of the treatment processes in a conventional municipal wastewater treatment plant.

1.6 The Integrated Approach to Learning Pollution Control Engineering

Many textbooks compartmentalize pollution control according to air pollution, municipal wastewater, industrial wastewater, solid wastes, hazardous wastes, etc. Air pollution control is considered as somehow separate from water pollution control and from solid waste control. This may happen in part because the laws are compartmentalized and regulatory agencies tend to be as well.

An integrated approach to air pollution control, for example, considers the interaction of efforts applied to treat and dispose of solid wastes and polluted water and gaseous emissions. The treatment and management of gaseous, liquid, and solid materials must be coordinated so problems are not shifted from one environmental sector (air, land, water) to another.

This integration and coordination leads to the effective use of both proactive and reactive pollution control measures. Proactive measures include source reduction, recycling, and the other strategies of pollution prevention. Reactive measures are traditional practices of collection and treatment at the end-of-pipe, stack, or landfill.

Real problems are multi-pollutant and multi-faceted. Good engineers know that holding a narrow view of problems or prescriptions of solutions is anathema to creative design. Creative design is better and it is more fun.

2 The Engineering Design Process

2.1 Defining the Design Problem

The systematic solution of an engineering problem follows a logical process that is not a bit different from that which everyone should follow in conscious everyday reasoning. It does differ, however, from making a casual judgment that lacks a thorough and impartial pursuit of fact and data. Casual decisions are distinguished from engineering decisions largely by the clarity with which hypotheses and assumptions are stated, by the careful collection and use of factual information, and by adherence to the implications of the conclusions that have been critically tested.

A problem is a difficulty that needs to be resolved. It is an opportunity in work clothes. It is an opportunity to make someone happier, healthier, wealthier, or wiser. New, better, more efficient, and less expensive systems come from recognizing a need or opportunity to make the current situation better.

A clear definition of the problem is essential. What exactly is the problem? Is more effort required, or just more resources? What are the best sources of information about the problem, and about possible solutions? What are the strengths and weaknesses of the available information (statistics, case studies, and anecdotes)? These questions are how we start to identify better ways of doing design and management.

Here is a hypothetical conversation between a plant manager (M) and a pollution control engineer (E) when a printing plant receives notice from the State EPA that Volatile Organic Compounds (VOCs) emissions exceed the allowable limits.

M We are emitting more volatile organic compounds (VOCs) than allowed by the Clean Air Act. If we are not in compliance in 90 days our company will be hit with huge fines and unfavorable publicity. We want to be in compliance. If the cost is reasonable, we prefer to be well under the statutory limits for emissions.

E A variety of technology exists to solve the problem. There will be several workable technical solutions. The net cost will depend upon the kind and quantity of the solvents being emitted and whether they can be recovered and reused as solvents or as fuel.

M A variety of solvents are used, but the largest volume is toluene. We can tell you the total losses of each solvent that is used in the plant. We can tell you which printing processes, and which cleanup operations use the chemicals. We can tell you which printing presses emit which solvent, and when they have been operated. Is that the information you need?

E It is. That will give us estimates of the average and maximum emissions for each solvent type and how much of each must be removed to meet the new standards. Next we identify useful technologies and make some preliminary cost estimates. And a very interesting part is when we look at the cost of solvents lost and the value that might be recovered. With some luck – or should I say good engineering – the project will save you money after the first year or two.

M I understand how that could happen. We use a lot of solvent, and lose a lot, and the price per kilogram is quite high. The net effect of solvent recovery is like using less and losing less.

E Many companies have done so. If the polluted air stream contains a single solvent, we may be able to capture it, concentrate it, and recycle it to the printing process. We can do this with adsorption, onto resins or activated carbon. Or, we can do it with a membrane process, for example, pervaporation.

M What if the emissions cannot be adsorbed? Or if they are a mixture of solvents, which would make recycle and reuse problematic?

E If the exhaust air contains a mixture of solvents, we might separate them at the source. If the concentrations are too low for economic separation and recovery, we may be able to use incineration and recover heat instead of solvent.

M The technology – adsorption, membranes, and incineration – must be expensive.

E The pollution control equipment may cost a lot of money. Whatever it costs, non-compliance with the Clean Air Act will cost more. Non-compliance is not an option.

M True. It’s necessary, but still, it will be expensive.

E ‘Expensive’ is a pseudo-technical word that carries a lot of emotion. The person who says “expensive” and the person who hears “expensive” may have quite different ideas. We will have alternate technical solutions. Some will cost more than others to build, and the same is true for operating costs. Let’s get the costs. What is the net annual cost? What is the net cash flow, year by year? What is the payback period?

M I agree. That’s how we evaluate the manufacturing operations. If say, ’We had a good day.’ my boss will want to know what ‘good’ means in terms of product shipped, project rejected, materials used, manpower, and quality control data. Let’s get the data and solve this problem.

They set to work accounting for all material used in the plant. The first steps produced the material flow diagram shown Figure 2.1. This is preliminary. Some inputs and outputs may be missing and the quantities will be revised as more details are added and preliminary design progresses.

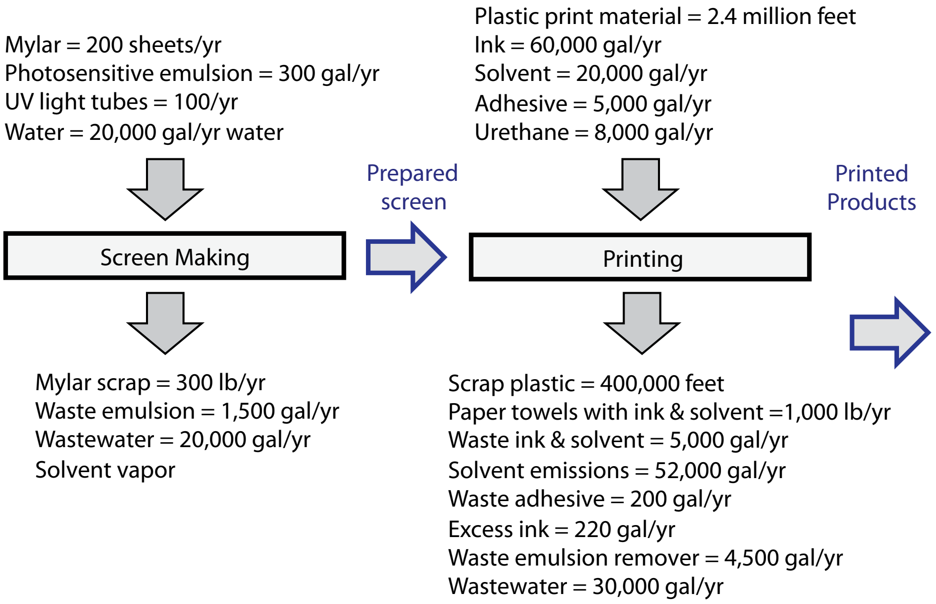
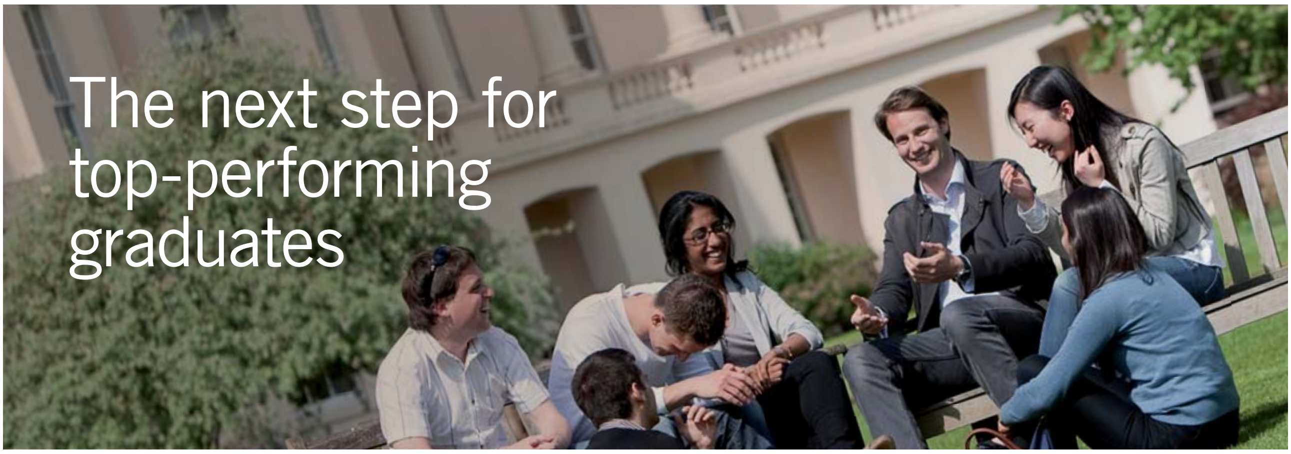


Figure 2.1 A preliminary schematic for the screen-printing operation. More details will be needed on the solvent composition, point of use, and point of ventilation or emission. Quantities will be revised.



Alternate ways of meeting the emission standards by making process modifications and installing new pollution control equipment were worked out. The capital cost, operating cost, and net life-cycle cost of the alternate solutions were compared.

Our hypothetical design engineer might have submitted a memo that said something like: One alternative is to install a still to recover the waste solvent. The still bottoms will be a hazardous waste and there will be a cost for disposal. The payback period is 2 to 3 years. Option 2 is to burn the solvents and recover heat energy, which is needed in winter but not in summer. The payback period is 2 to 3 years.

Each possible solution will have pros and cons, and plant management will select one. They may prefer a solution with a high operating cost and a low construction cost over one that costs more to build and less to operate. These are financial decisions, and they depend on interest rates, company debt, and competition for money among possible company investments.

The severity of a problem is not by itself sufficient reason to give it high priority. We also need to be convinced that it can be solved. Distinguish between problems that are insuperable given current resources, technologies, and knowledge; and those that are capable of solution if approached in the correct way. Reserve the word ‘problem’ for those conditions that have a detrimental effect on quality of life, but which are believed capable of being modified in beneficial ways.

Good problem formulation is the key to success. It is to a large degree an art that is learned through practice and study of successful applications. Beware of problems that are stated in pseudo-technical language, for example “use the smallest number of units that is feasible.” Small and feasible convey no precise information. They may start a useful conversation, but a more precise definition will be needed to avoid confusion and misunderstanding.

A solution is a prescribed intervention that will: (1) produce better information, (2) apply better physical technology, (3) improve analytical techniques, (4) modify management styles, (5) reduce the cost, or (6) accomplish more than one of these objectives. In most problems a set of possible prescriptions is written and the designer endeavors to select the best.

We strive to formulate alternative solutions and judge them with respect to some measure of system performance. There is considerable choice in defining such a criterion: total capital cost, annual cost, annual net profit, return on investment, cost-benefit ratio, or net present worth. Or, the measure might be stated in terms of technological factors, like minimum production time, maximum production rate, minimum energy utilization, minimum weight, and so on. In practical situations it may be desirable to find a solution that is good with respect to more than one criterion (for example, a design that simultaneously minimizes cost while also increasing reliability and reducing energy use). Evaluating multiple competing objectives is possible when judgment and experience complement mathematical solutions.

2.2 Identifying the Alternatives

Identifying alternatives combines imagination with engineering savvy. If ideas are constrained there is a risk of prematurely rejecting promising solutions. Constraints imposed at the formative stage too often are imaginary. Avoid judgments like “it is too expensive” or “it is too complex” and let subsequent analysis select the alternatives that need to be studied in more detail.

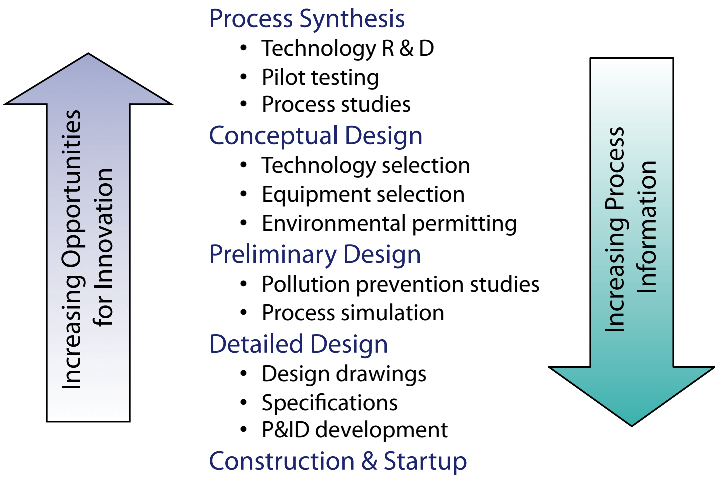


Figure 2.2 Design proceeds in stages, from preliminary concepts to final design. The early stages offer the greatest opportunity for innovation.

The first stages hold the greatest possibility for a brilliant large step, but also the greatest danger of failing to see a profitable direction. Figure 2.2 shows that the greatest opportunities for innovation are early in a project. We would like to be aware of all alternatives at the beginning. If one is overlooked we must turn back and improve the analysis.

Detailed design – the closing gambit – takes into account operational characteristics, process stability, and other detail.

2.3 Voluntary Pollution Prevention by Industry

Pollution Prevention, Clean Manufacturing, Green Manufacturing, Waste Minimization, Design for Environment, are popular terms in recent years. Whatever name is used, the goal is to simplify and reduce the cost of compliance with environmental regulations.

The names are new, but the ideas are not. As far back as the 1940s, energy conservation, water conservation, water reuse, material substitution, reclamation and recycling were practiced, mainly for economic reasons. The motivation to implement these ideas has increased as environmental regulations become more strict and the costs of water, fuel and electricity increase.

Clean manufacturing is based on the idea that an unsafe material cannot be accidentally released if it was never created. You cannot emit or spill what you never had. It is better not to create a pollutant than to capture and treat one. The principle applies equally to gaseous, liquid, and solid waste materials.

An impressive voluntary initiative to reduce pollution in the U.S. was the 33/50 program that targeted the toxic chemicals listed in Figure 2.3. The goal was a 33% reduction in releases and transfer of these chemicals by 1992 and a 50% reduction by 1995, as measured against a 1988 baseline.

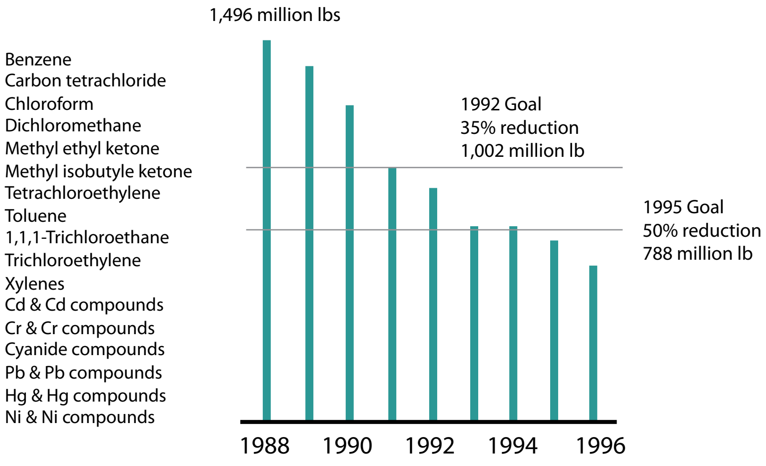


Figure 2.3 Industrial reductions in 17 targeted toxic chemicals under the voluntary 33/50 program (USEPA 1999).

2.4 Designing for Pollution Prevention

The conceptual design phase is when creativity and technical analysis can come together to conserve energy and water, to reduce and eliminate waste, and be most effective in pollution prevention. The yin and yang – the complementary parts that comprise this philosophy – are:

Waste is eliminated at the drawing board.
Waste is generated at the drawing board.

The Product Stewardship Code of the Chemical Manufacturing Association says that a goal is '…to make health, safety and environmental protection an integral part of designing, manufacturing, marketing, and distributing, using, recycling and disposing of [chemical] products.' Figure 2.4 shows the life cycle of a manufactured product. There are opportunities for waste minimization and energy conservation at each stage, including final disposition. This philosophy extends to manufacturing products that are easy to dismantle at the end of their useful life so parts and materials can be recycled.

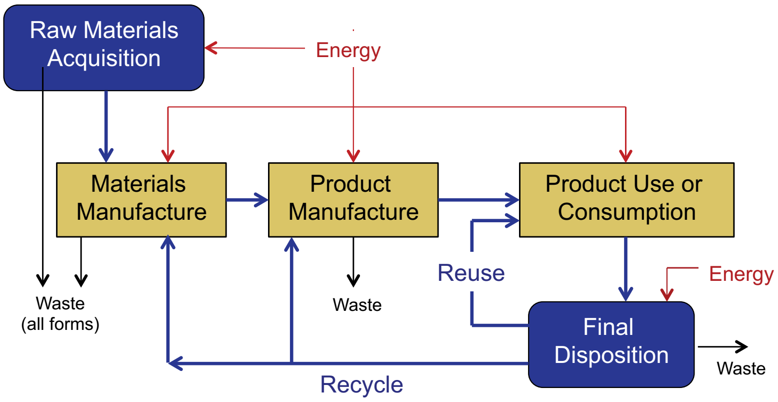


Figure 2.4 Cradle-to-grave analysis of a manufactured product. Energy is consumed and waste is generated in each phase of the life cycle.

Pollution prevention will

- Reduce waste monitoring, treatment, and disposal costs.
- Reduce regulatory compliance cost.
- Reduce insurance costs and future liability associated with toxic wastes.
- Improve worker safety associated with less exposure to hazardous materials.
- Reduce raw material usage and manufacturing costs.
- Increase process efficiency.
- Improve product quality and purity and reduce off-specification product.
- Improve public image and employee morale.

Useful steps are to

- Eliminate the source. Don't build a pollutant-generating factory. Shut down the offending process.
- Modify the source so that released materials are less in quantity and of a less harmful nature.
- Capture emitted materials for recycle, secondary use, or sale.

Figure 2.5 shows some waste minimization strategies. Raw material substitution, product reformulation, process modification, improved housekeeping, and on-site recycling are intimately linked to the manufacturing process and making changes may not be easy even if good ideas seem plentiful.

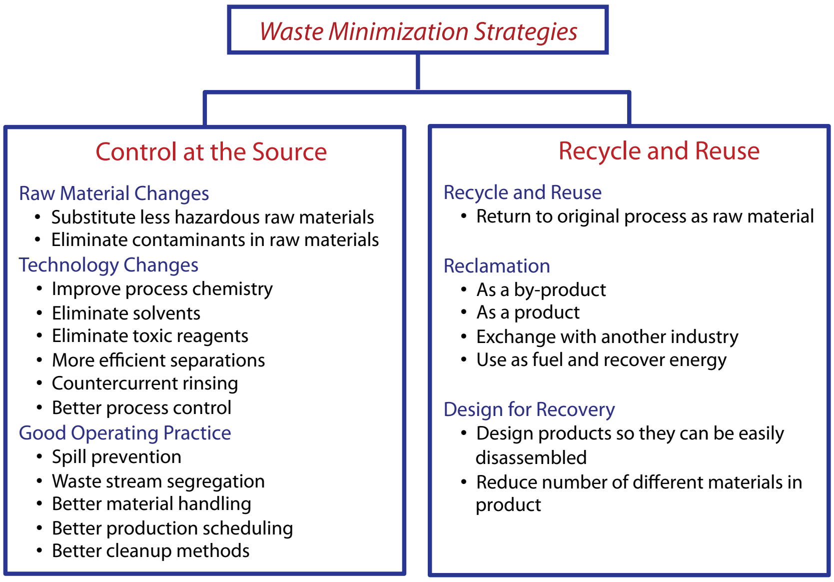


Figure 2.5 Waste minimization methods.

2.5 Green Chemistry

Figure 2.6 shows why pollution prevention might be needed in a chemical manufacturing process. An ideal chemical process would fully incorporate the reactants into to product. There is no waste. This is a 'clean' or 'green' reaction. This is the goal of Green Chemistry.

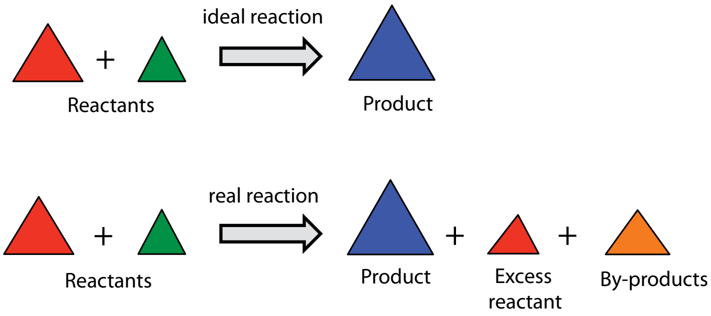


Figure 2.6 An ideal reaction produces no waste. Real reactions yield a mixture of product and other materials. A separation process is needed to support the chemical transformation.

Real reactions produce a mixture of product, excess reactant, impurities in the reactants, and by-products. Additional processing must be added to separate the product from the impurity and the by-product. Solvents, chemicals and energy may be needed to drive the separation. The separated materials may be voluminous, difficult to handle, or toxic. Clearly it is best to avoid separations when possible.

2.6 Savings from Pollution Prevention

Many kinds of equipment, treatment processes, and entire treatment systems have cost functions of the form

$$C = KQ^M$$

where C is the cost, Q is the design capacity, K the cost when $Q = 1$, and M is an exponent that indicates the economy-of-scale. Typical values are $M = 0.5\text{-}0.9$, with values of 0.6-0.7 being common.

If the cost exponent is less than 1.0 there is an economy of scale. This means that doubling the capacity does not double the cost. For $M = 0.7$, doubling the capacity increases the construction cost by 62%. This also means that halving the design capacity will reduce the cost by 38%.

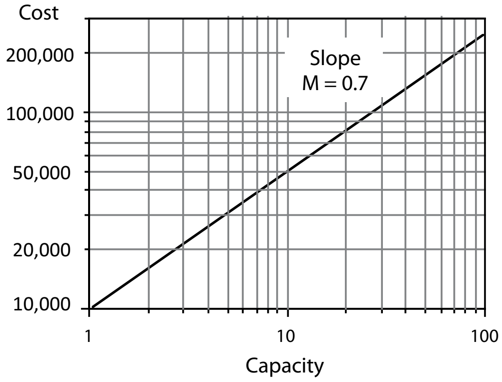


Figure 2.7 Economy-of-scale cost function used for making preliminary cost estimates. This curve is for a hypothetical machine that is used for pollution control. $C = \$10{,}000Q^{0.7}$ where Q = design capacity (volume, area, flow rate, etc.)

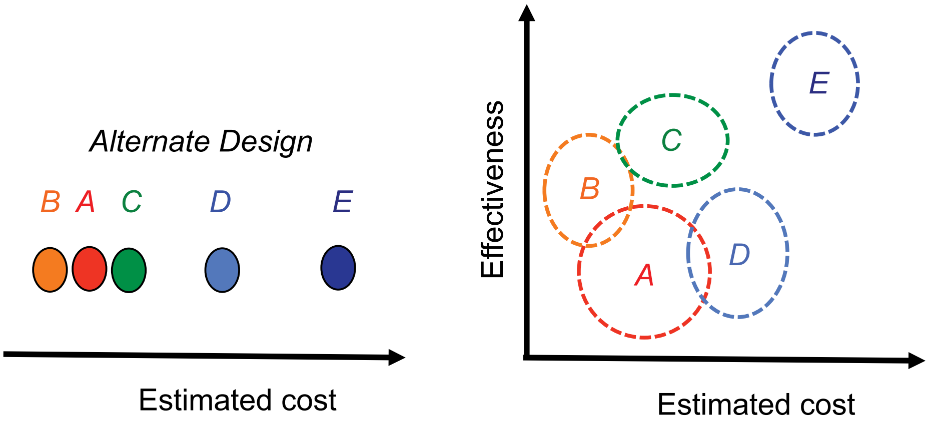
Here is a simple example of how pollution prevention could reduce the cost of a project. The purchase price shown in Figure 2.7 is $C = 10{,}000Q^{0.7}$. The installed cost of the equipment will be approximately 4 times the purchase price.

Suppose the original design capacity was 4 units of flow at a cost of \$91,000, but some clever design at the source could reduce the flow to 3 units. This would reduce the equipment cost from \$91,000 to \$74,500, a savings of \$16,500. (The costs are rounded because estimates of this kind have an error of 10% to 30%.) Reducing the flow from 4 units to 1 unit would save \$56,500, or 65%. The installation cost is also reduced, so is the cost of operating and maintaining the smaller equipment.

2.7 Selecting the Best Design

Real problems have more than one feasible solution. They will differ in construction cost, operating cost, ease of maintenance, flexibility of operation, robustness to shifts in ambient conditions, changes in loading rates, the amount of chemicals used, and amount of solid waste and sludge that must be hauled away. No single alternate will be the most desirable with respect all these factors.

Cost effectiveness analysis tries to consider more than just cost. Figure 2.8 shows the essence of the analysis. Alternate E can be dropped as a serious contender. Alternate B has the lowest cost and is more effective than A, but less effective than C. There is some overlap, at least in the preliminary design analysis, and more work needs to be done.



(a) Preliminary cost estimate

(b) Uncertainty in both estimated cost and project effectiveness

Figure 2.8 Alternate designs may be compared on the basis of cost, either the first cost of construction or the lifetime cost, but they differ in many characteristics and effectiveness should be considered as well.

2.8 Conclusion

Design is not just the preparation of detailed drawings and specifications. Important design decisions are made long before these documents are prepared.

In some projects there are no drawings at all. The design may be a better way of financing bonds, a new way of scheduling waste hauling, or improved maintenance of a pump.

Project design is a series of activities in which the amount of information about the process grows and more details become fixed. The early design stages involve broad concepts; the last stages involve thousands of intricate details. The early stages offer the greatest opportunity for pollution prevention – Waste is eliminated at the drawing board. Once detailed design begins it is virtually impossible to go back and make major changes in the processing concept.

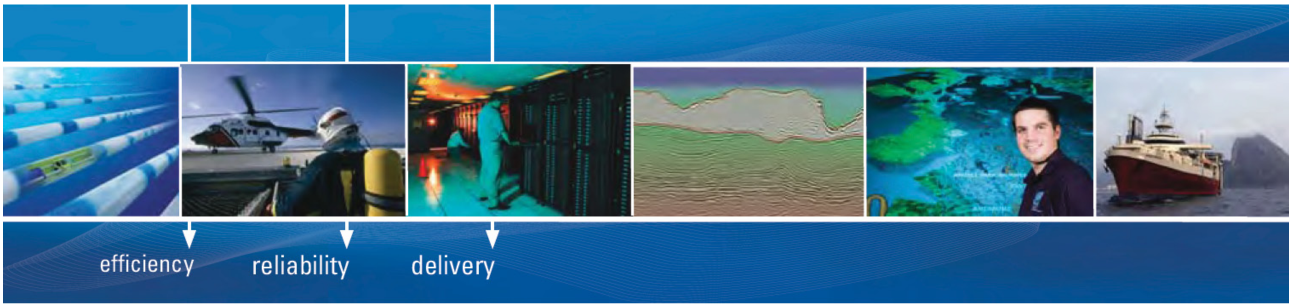
3 The Environmental System

3.1 Environmental Cycles and Environmental Stability

The environment operates in a state of dynamic equilibrium. Water evaporates from the surface of the earth and the oceans, leaving behind salts and silt. Precipitation renews the fresh water reservoirs. The essential compounds of life contain carbon, nitrogen, hydrogen and oxygen that cycle between organic and inorganic forms. Some of these compounds are water-soluble and travel with streams or groundwater; some are volatile and move into the atmosphere to be returned to earth by precipitation, photosynthesis, or nitrogen fixation. When these pathways and cycles are disturbed, life patterns are interrupted.

Many problems arise from the exceptional reactivity of the six elements that are the stuff of life: hydrogen (H), carbon (C), oxygen (O), nitrogen (N), phosphorus (P), and sulfur (S). These are the building blocks of proteins, carbohydrates, and fats.

Carbon, nitrogen, oxygen, hydrogen, sulfur, and water can exist as soluble and as volatile forms, and have a full cycle of movement between the atmosphere, the water, and the land. Phosphorus is soluble, but lacks a volatile form, so it moves between the land and water.



So long as these cycles are stable, environmental conditions are stable, but they can be interrupted or overloaded by the activities that keep 7,000,000,000 people alive on this small planet. Burning coal and oil overloads the carbon dioxide reservoir in the atmosphere. The heavy use of phosphate and animal wastes as fertilizer overloads the phosphorus balance in lakes, reservoirs, and rivers and causes excessive growth of algae and aquatic plants. The instability can be magnified because the cycles are linked. The carbon, oxygen, nitrogen, phosphorus, and sulfur cycles are linked to the oxygen cycle, and all are linked to via the water cycle.

3.2 The Water Cycle

The water cycle, driven by the sun's energy, provides continual regeneration of fresh water by evaporation from land and sea. Snow and rain condense from this evaporated water. Figure 3.1 shows the major movements of water through the natural environment. Preserving the integrity of this hydrologic cycle is a central problem in environmental protection.

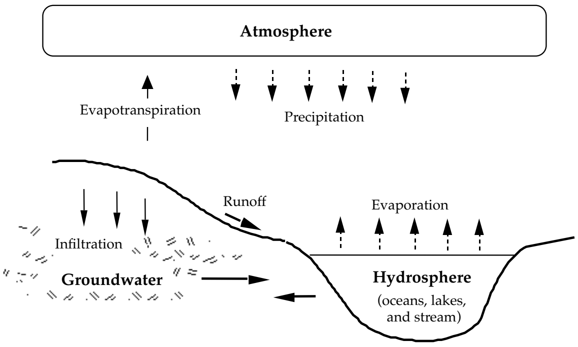


Figure 3.1 The water cycle, or hydrologic cycle.

Figure 3.2 shows that 99% of all water on earth is not directly available for human use. About 97% of the total is saline (oceans). Almost 68.7% of the fresh water on earth exists as ice in glaciers and icecaps and 30.1% is groundwater. That leaves 0.9% of the total as surface water. Of this small fraction, only 2% is in rivers, 87% is in lakes, and 11% is in swamps. Almost one-quarter of the world's population, 1.7 billion people, lives in regions where groundwater is being used up faster than it can be replenished (Gleeson 2012, Pearce 2006).

In the United States, 0.6 percent of the annual rainfall is withdrawn for use in municipal water supplies, and only five percent of that is used for drinking or in the preparation of food. Within the household, about 35% of water is used for showers and baths, 30% for toilet flushing, 20% for laundry, 10% for kitchen and drinking, and 5% for cleaning.

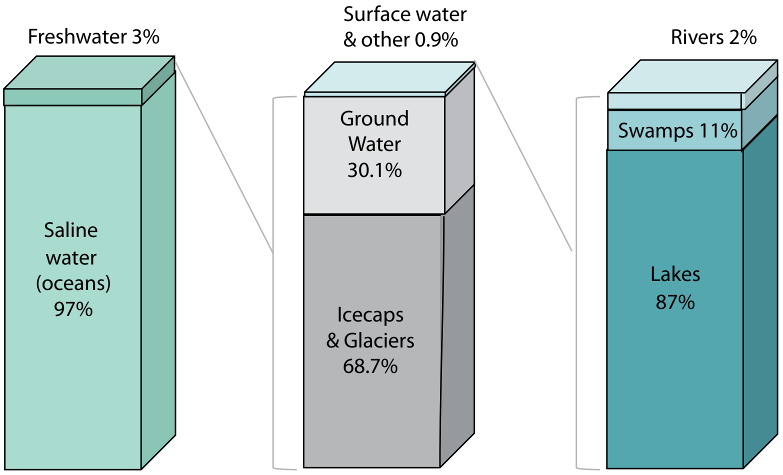


Figure 3.2 Distribution of the earth's water (adapted from U.S Geological Society).

Water consumption in some developing countries may average as little as 15 L/d per capita. The world average is estimated to be 60 L/d per capita. The average in the U.S. is 360 L/d per capita (100 gal/cap-d) for household use. Overall, including commercial and industrial uses, the average is about 680 L/cap-d (180 gal/cap-d).

The design of a municipal wastewater treatment plant in the U.S. is typically based on an average daily base flow of 270 to 380 L/day per capita (70–100 gal/day per capita) plus the flow from industry and other non-residential sources, plus stormwater that may enter the wastewater collection system. A multiplier of 2.0 to 2.5 is used to estimate the peak flow. These design flows are applied to an estimated population 20 years in the future (Vesilind 1998).

The industrial water cycle, shown by Figures 3.3 and 3.4, takes in clean water, uses and reuses it, and discharges wastewater. Water from a river, lake, or well usually must be treated before use in boilers, condensers, manufactured product formulation, or washing. Wastewater is treated for reuse or discharge.

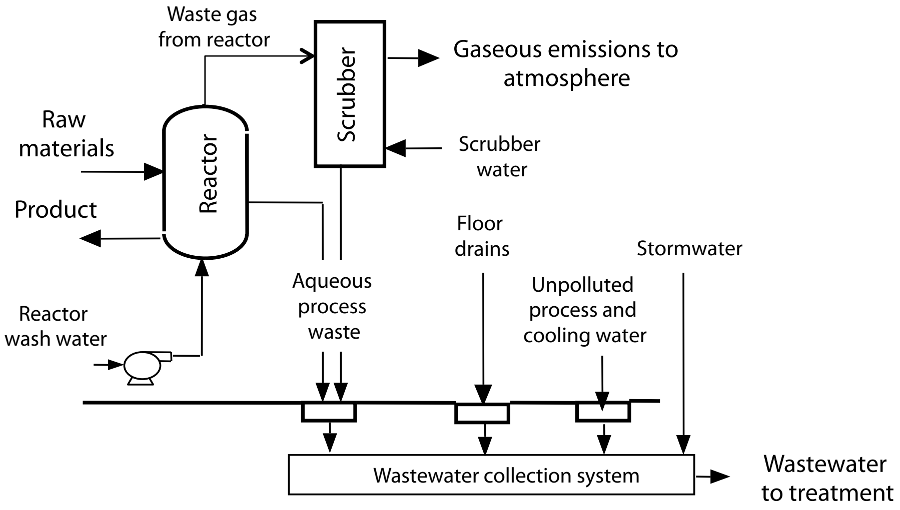


Figure 3.3 Water use in the manufacturing process. Wastewater consists of process waste, water used for cleanup and for air pollution control, drainage from floors, as well as unpolluted process and cooling water and stormwater. This diagram, for simplicity, shows all wastewater going into a common drain. Better practice is to segregate (i.e. collect separately) different kinds of wastewater. For example, do not mix unpolluted water with polluted water.

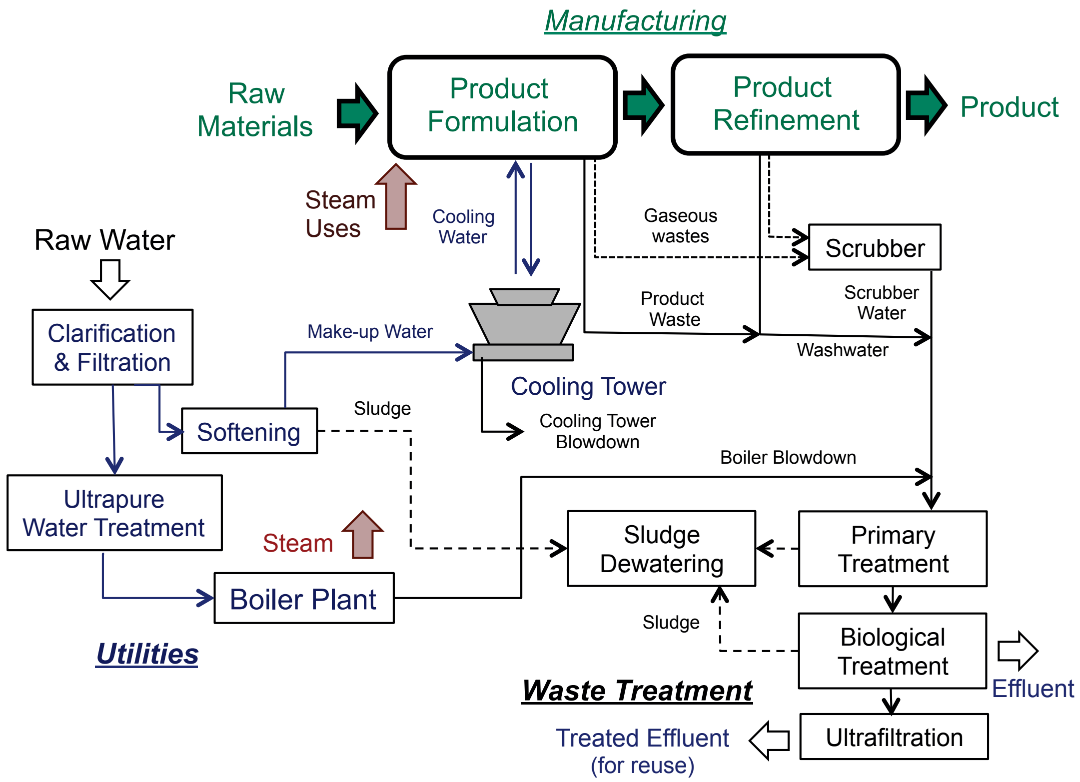


Figure 3.4 The Industrial Water Cycle. Industries run on water and energy as much as on raw materials used in the actual manufacturing. Water for the formulation and refinement of the product is supplied from plant utilities, which also supplies boilers and cooling towers. Wastewater streams include blowdown from boilers and cooling towers, scrubbers, and waste from manufacturing, including washwater. Water treatment and wastewater treatment produce sludge. There may also be solid wastes (not shown) from manufacturing. Waste treatment may be done off-site at a municipal treatment plant, but on-site treatment will offer more opportunities to recycle water.

An important use of water in industry is cooling. Cooling water may be used once and discharged, but recirculation and reuse is more common. Figure 3.5 shows a recirculating cooling water system. The cooling is caused by evaporation of a small amount (1–2%) of the circulating water.

One hundred percent closed-loop recirculation is not possible even in a system as simple as a cooling water loop. The water contains natural dissolved minerals and more chemicals are added to prevent scaling and corrosion in the cooling system. The salt concentration increases as water evaporates and this limits the number of times the water can be recycled. Removing some of the saline water and replacing it with fresh water controls the salt concentration. The freshwater addition is called make-up water. The water that is removed, called blowdown, must be discharged to a sewer or treated before discharge.

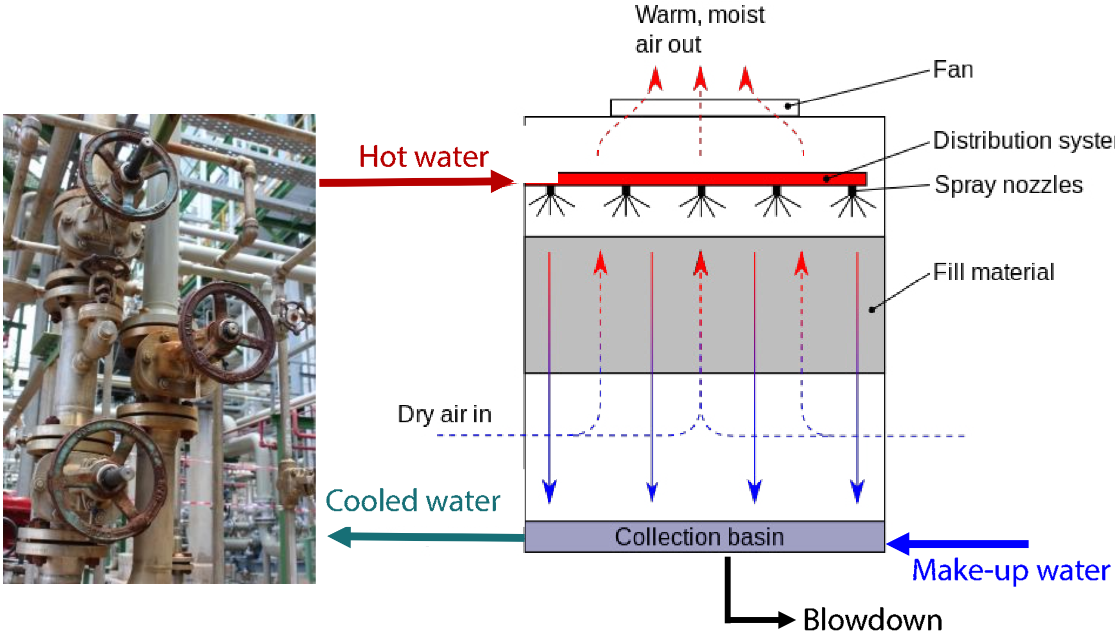


Figure 3.5 Cooling water loop showing make-up water being added and blowdown being removed. (Photo credit: freedigitalphotos, supakitmod)

3.3 The Natural Carbon Cycle

Living organisms synthesize carbon, hydrogen, oxygen and nitrogen into carbohydrates, fats and proteins. Some organisms consume oxygen to do this, and some function without oxygen (O_2). Green plants consume carbon dioxide (CO_2) and produce oxygen. When living organisms die, cellular components are decomposed by microorganisms into smaller and simpler compounds. The decomposed compounds may be mineralized to carbon dioxide and water, or to organic compounds such as methane or acetic acid.

Oxygen and carbon are inextricably linked through the carbon cycle, as shown in Figure 3.6. Carbon, hydrogen and oxygen can exist as dissolved and gaseous compounds. Large quantities of carbon dioxide are held in the aquatic reservoir (mainly the ocean) and this CO_2 interacts and exchanges continually with the atmosphere.

The amount of carbon dioxide stored in the ocean is more than fifty times the amount stored in the atmosphere. Carbon is removed from the atmosphere by photosynthesis and returned by respiration, mainly by bacteria and fungi that decompose organic matter, and in lesser amounts are returned by the combustion of coal, wood, and petroleum. The respiration of plant and animal life releases much smaller amounts of carbon dioxide.

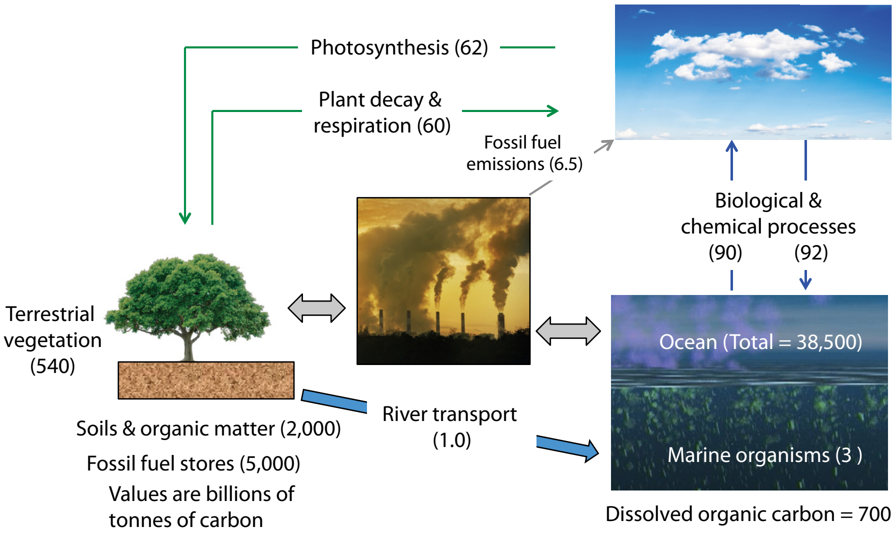


Figure 3.6 The natural carbon cycle is linked to the oxygen cycle. (Quantities are from NOAH Research 1996. Photo credits: freedigitalphotos)

One of the important reactions in the carbon cycle is a classical cause of water pollution. Lakes and rivers absorb oxygen from the atmosphere while microorganisms simultaneously consume dissolved oxygen and organic carbon from the water. When food (carbon) is plentiful, oxygen is consumed faster than it can be replaced from the atmosphere. This reduces the dissolved oxygen (DO) and can endanger fish and other desirable aquatic organisms.

Reducing organic carbon in wastewater effluents is a keystone of water pollution control. The same biological reactions that occur in a river are used to advantage when they are accelerated in a biological wastewater treatment process. George Box (2013), an eminent statistician and scientist, who worked as a chemist in a wastewater treatment plant when he was nineteen years old, described this process.

‘Clean water is essential to life, but there is only a certain amount of water in the world, and this must be used and reused. Nature has provided a means for this cleansing to be done. It is achieved by aerobic microorganisms that exist in every body of water that is exposed to air. About ten parts per million of oxygen can dissolve in perfectly clean water, and if you check, you’ll find that some quantity slightly less is to be found in streams, rivers, and oceans. Every natural body of water is to some extent slightly polluted. The pollutants provide aerobic organisms with nutrients, which they absorb at the expense of slightly lowering the level of dissolved oxygen. This sets up a tension, and as more oxygen is needed, more is dissolved, so that we have a permanent system for cleaning up the water supply on the planet. The aerobic organisms are quite remarkable; in a matter of a few hours, they can clean up even raw sewage in the activated sludge process, employed in almost every town throughout the industrial world (used with the kind permission of John Wiley & Sons).

3.4 The Industrial Carbon Cycle

The industrial counterpart of the decomposer cycle is the use of fossil fuels for heating, power generation, and in vehicles. The producer analogy is the use of oil and gas as raw materials in the chemical process industries. Many chemicals that consist only of carbon and hydrogen are manufactured in huge quantities. For example, in 2010 the U.S. produced about 6,000 metric tons of benzene (C_6H_6).

The carbon cycle is at the heart of discussions about the environment in the 21st century because of the increasing atmospheric concentration of carbon dioxide (CO_2). CO_2 is a green house gas. Scientists understood that carbon dioxide, as well as methane and a few other gases, act to retain heat within the earth’s atmosphere long before global warming became a critical issue.

Another fact is that the concentration of CO_2 in the atmosphere has been increasing. The level today has reached 400 parts per million by volume (ppmv) and is increasing by about 2.5 ppmv per year. (400 ppmv measured at the Mauna Loa Observatory in May 2013.) Antarctic ice core measurements indicate that atmospheric CO_2 levels were 260–280 ppmv in the 10,000 years before industrial emissions increased. This is shown in Figure 3.7.

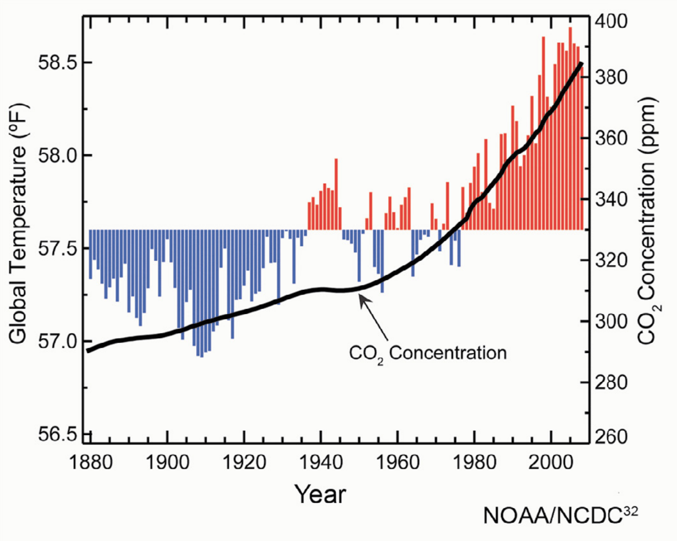


Figure 3.7 Global annual average temperature (as measured over land and oceans). The curve shows the historic levels of atmospheric carbon dioxide (CO_2), measured in ppmv. The horizontal line is the average temperature for the period 1901-2000. The bars indicate temperature deviations above and below the average temperature. The year-to-year fluctuations in temperature are due to natural processes, such as the effects of El Niños, La Niñas, and the eruption of large volcanoes. (Karl et al. 2011)

Burning coal, petroleum and natural gas emits roughly 7.5 billion metric tons of carbon per year. The U.S. emissions are 29 tons/person (in 2006), which adds up to about 22% of the world total emissions. This closely follows China, the current leader in CO_2 emissions (Wikipedia).

The magnitude and rate of future change, though not exactly known, are expected to increase on this worrisome trend. Managing greenhouse gas emissions is an important world issue that has, so far, been resisted by the United States government.

3.5 Essential Nutrients

Table 3.1 shows elements that are essential to life. The first six elements in the table, C, H, O, N, P, and S make up almost all the mass of living matter. The most important nutrients in environmental systems are nitrogen and phosphorus, and to a lesser extent sulfur. These exist as organic or inorganic chemicals.

A second group (iron through iodine) is essential for building and maintaining healthy bone, blood, and electrolytes.

The metals (silicon through zinc) have three functional levels. They are essential in low doses, but the amount can get below the level needed for healthy life, and at high doses they become toxic.

Element		Comments
Carbon	C	Required for organic compounds
Hydrogen	H	Required for water and organic compounds
Oxygen	O	Required for water and organic compounds; necessary for aerobic organisms
Nitrogen	N	Required for many organic compounds, especially amino acids and proteins.
Phosphorus	P	Essential for biochemical synthesis and energy transfer
Sulfur	S	Required for some proteins and other biological compounds
Iron	Fe	Essential for hemoglobin and many enzymes
Manganese	Mn	Required for activity of several enzymes
Fluoride	F	Growth factor in rats; constituent of teeth and bones
Potassium	K	Principal cellular cation
Sodium	Na	Principal extracellular cation
Calcium	Ca	Major component of bone; required for some enzymes
Magnesium	Mg	Required for activity of many enzymes; in chlorophyll
Chlorine	Cl	Principal cellular and extracellular anion
Iodine	I	Essential constituent in thyroid hormones.
Silicon	Si	Structural element in diatoms
Boron	B	Essential in some plants
Chromium	Cr	Essential in higher animals; related to action of insulin
Cobalt	Co	Required for activity of several enzymes; in vitamin B12
Copper	Cu	Essential in oxidative and other enzymes and hemocyanin
Selenium	Se	Essential for liver functions
Molybdenum	Mo	Required for activity of several enzymes
Vanadium	V	Essential in lower plants, certain marine animals and rats
Zinc	Zn	Required for activity of many enzymes

Table 3.1 Elements essential to life.

3.6 The Nitrogen Cycle

Figure 3.8 shows the Nitrogen Cycle. The organic forms of nitrogen are protein and urea. These decompose to ammonia (NH_3), which in turn can be converted to nitrite (NO_2^-) and to nitrate (NO_3^-). Nitrate can be converted to nitrogen gas (N_2) and returned to the atmosphere. Gaseous nitrogen can be used directly by legumes (e.g. soy beans) and certain algae. Commercial nitrogen fertilizer is made from gaseous nitrogen. Thus, nitrogen cycles between reservoirs in the atmosphere, living and decomposing biota, soil, and water.

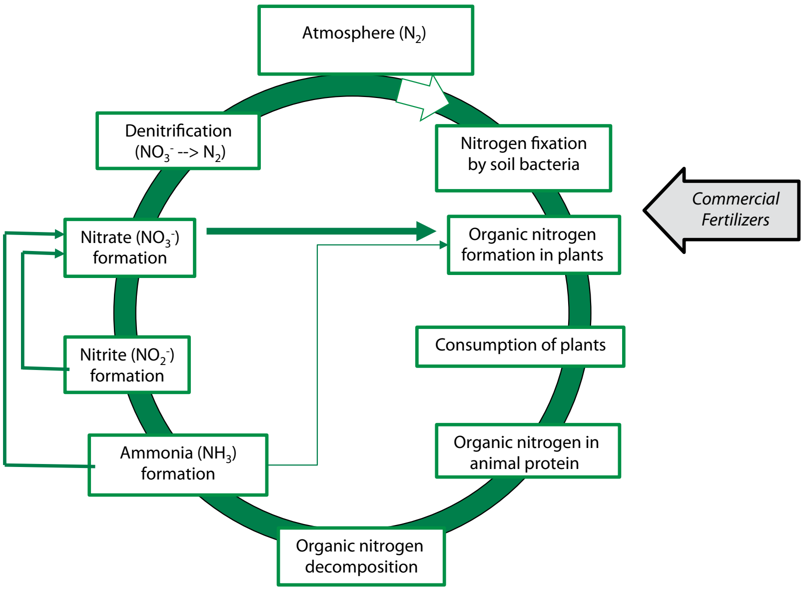
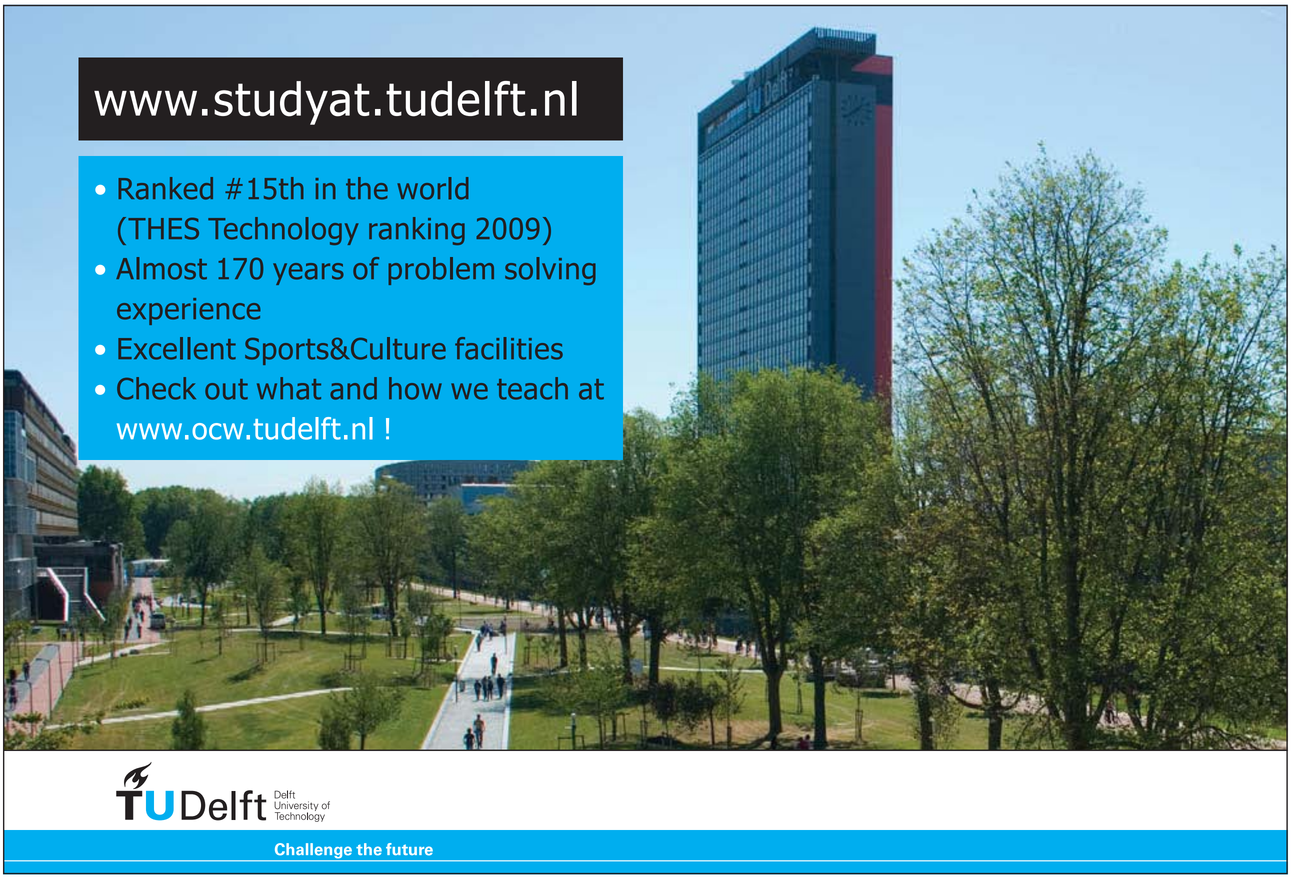


Figure 3.8 The Nitrogen Cycle. Nitrogen in the atmosphere can be fixed by industrial fertilizer production or by nitrogen-fixing plants (legumes). Organic N, mainly proteins, decomposes to yield ammonia, which is converted in the body to urea for excretion. In the presence of oxygen, nitrifying bacteria will convert ammonia to nitrite and to nitrate (NO_2^-) and then nitrate to nitrate (NO_3^-). Ammonia, nitrite and nitrate can be taken up by plants and, hence converted back to organic nitrogen. Nitrate can be converted, in a biological process to nitrogen gas.



Nitrogen in foods comes from amino acids in protein (and other nitrogen-based compounds); proteins are between13–19% nitrogen. The human body needs about 2 g of N per day, but most humans consume closer to 13 g/d, so 11 g/d will go into the waste stream. Before excretion, amino acids are broken down to form organic acids and ammonia. Ammonia would be fatal to humans if the liver were not able to quickly convert it, along with carbon dioxide, to less toxic urea, CH_4ON_2.

3.7 The Phosphorus Cycle

All plants and animals need phosphorus to grow so every food contains phosphorus. No phosphorus, no food! It is that simple.

The demands of modern life may interfere with the phosphorus cycle (Figure 3.9) more than any other, with the exception of the modern massive release of carbon dioxide. Phosphorus is mined to make fertilizer that is spread on farmland in generous quantities and carried into waterways by erosion and storm runoff. One consequence is over stimulation (eutrophication) of algal and weed growth in lakes, reservoirs, and estuaries.

Phosphorus makes up about 1% of human bodyweight and 85% of phosphorus in the body resides in bones and teeth. Dietary phosphorus is absorbed in the small intestine and excreted in urine. Children need 0.6 g P/day, and adults need 1.2 g P/day. We excrete about 3–4 g P/day. The phosphorus contained in urine and feces produced in urban settings is currently approximately 0.88 million metric tons

A typical living bacterial cell is about 3% P by weight. Phosphorus is a major component in adenosine triphosphate (ATP), an energy-rich molecule that is essential in the basic metabolism of all living organisms. When the organism needs energy, a molecule of phosphorus is removed from ATP and the ATP becomes adenosine diphosphate (ADP). When an organism has energy to store, ADP is converted back to the high-energy ATP form. This ongoing conversion of ATP to ADP to ATP is a biological dynamo that produces, and consumes, about 40 kg of ATP per day in a typical human.

Orthophosphate (PO_4^{3-}), a readily available nutrient, is soluble and will follow the water cycle to the sea. There is no gaseous form of phosphorus to move from water to land through the atmosphere. Phosphorus is carried by sea birds back to the land, or by human harvesting of fish or aquatic plants. Local airborne transport, via dust or sea spray, is not an important part of the cycle.

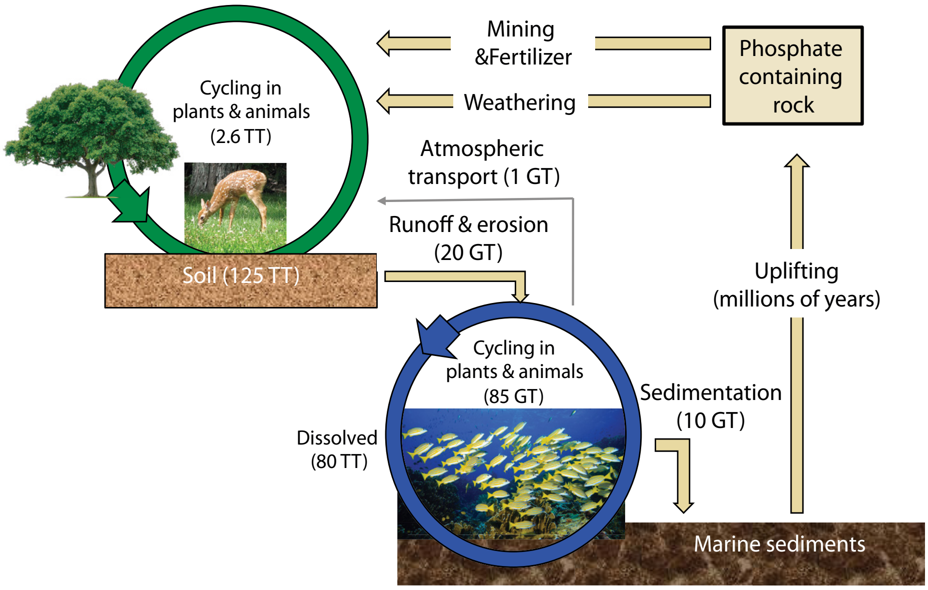


Figure 3.9 The natural cycle of Phosphorus (P) in water. Organic and inorganic P can exist as particulate or soluble materials. Transport of P to land by sea birds and by human harvesting of fish or aquatic plants is not shown. Atmospheric transport of sea spray is a minor mechanism. (Photo credit: pixabay)

Organic phosphorus from plant and animal cells is converted by decomposition to orthophosphate. Both organic and inorganic phosphorus exist in soluble and particulate forms. Algae are a particulate form. Inorganic phosphorus can form mineral precipitates, such as calcium phosphate.

An overload of nitrogen and phosphorus in a lake will cause eutrophication, a condition of excessive algae and weed growth and oxygen depletion by bacteria consuming the dead and dying algae. Phosphorus is usually the limiting factor in freshwater lakes. If it is reduced to sufficiently low levels the growth of algae will also be reduced. Even after this happens it takes a long time for the lake to clear itself of the accumulated load. The flushing time for the water in a lake may be 6 months to many years. The flushing time for sediments, which release phosphorus back to the water column, is tens of years.

Most of the phosphorus in lakes and streams comes from nonpoint sources (agricultural runoff, erosion, urban runoff, roadway and sidewalk deicing chemicals, and atmospheric deposition). The phosphorus from these sources is from 30% to 80% bio-available.

Residential wastewater (based on the input of individual homes to septic tanks) is 35–100 mg/L total N, including 6–18 mg ammonia/L and essentially zero nitrate and nitrite. The total phosphorus is 18–29 mg/L as P, including 6–24 mg/L phosphate (PO_4^{3-}-P). Toilet waste contains about 200 mg/L total N and 100 mg/L total P; kitchen waste (including garbage disposal) has 85 mg/L total N and 10 mg/L total P. The average amount of excrement that one person contributes to the waste stream is 120 g feces and 1.1 L urine. The feces contain 1.2 g N and 0.36 g PO_4^{3-}.The values for urine are 11 g N and 3.3 g PO_4^{3-}.

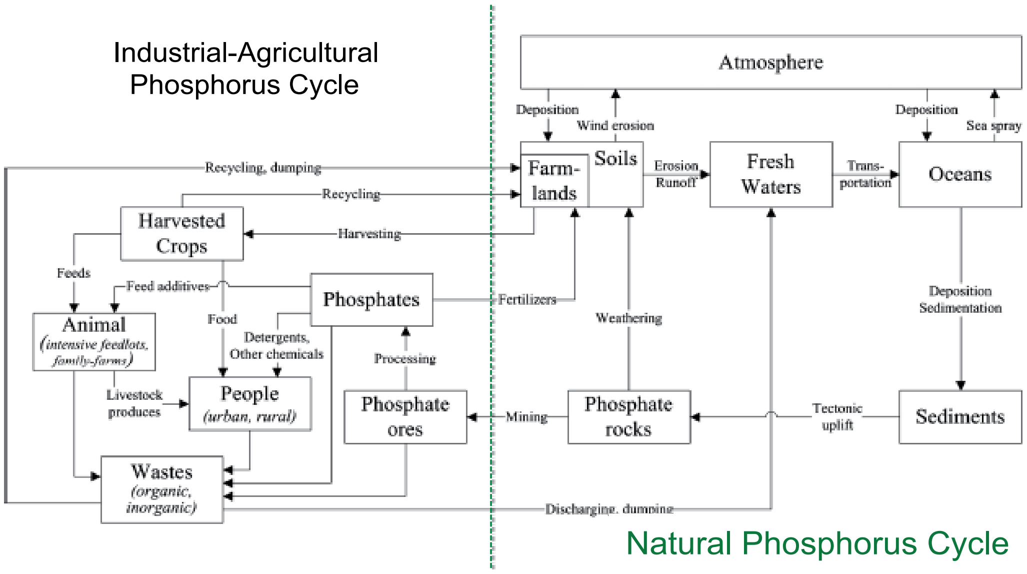


Figure 3.10 The natural and industrial cycles of phosphorus are linked by agriculture's huge appetite for fertilizer.

Wastewater treatment plants that discharge to lakes, including the Great Lakes, typically are required to reduce effluent phosphorus to 1 mg/L total P. The reason is to prevent excessive algae growth and eutrophication. Removal can be done by adding chemicals (iron or aluminum salts) or biologically.

The industrial phosphorus cycle, shown in Figure 3.10, is based on mining phosphate rock to make fertilizer. Florida, a major producer and exporter, accounts for about 20% of the world's phosphate fertilizer. A strip mine yields a mixture of pebble phosphate that is mixed with clay, sand and chemical impurities. The ore matrix is crushed, sifted and mixed with water to produce a granular rock that is shipped to processing plants. Converting this to fertilizer involves mixing the 'rock' with sulfuric acid or phosphoric acid. If ammonium phosphate fertilizer is produced, there will be a facility to manufacture ammonia.

Waste products are slimes and phosphogypsum. Slime is produced by the separation of clay and other fines from the phosphate rock. Gypsum (calcium sulfate) is produced in the reaction of sulfuric acid with the rock. Most of the gypsum is placed in settling ponds, often hundreds of acres in size, and in stacks up to 60 meters tall. A modest percentage (about 15%) is reused in agriculture and construction.

3.8 The Sulfur Cycle

The atmosphere is an important part of the sulfur cycle, shown in Figure 3.11. The major form of sulfur in the atmosphere is sulfur dioxide (SO_2), which can originate from natural causes (e.g. volcanoes), but mainly comes from the combustion of coal and petroleum products. Sulfur dioxide reacts with water vapor in the air to form sulfuric acid (H_2SO_4).

Sulfide readily forms hydrogen sulfide (H_2S), a smelly, toxic, and corrosive gas. It also oxidizes to form sulfite (SO_3^{2-}), or sulfate (SO_4^{2-}). These forms can be reduced back to sulfide. So, like carbon and nitrogen, sulfur can move freely between the air, biota, water, and soil.

The conditions that promote or inhibit these transformations are important in wastewater treatment plants and aquatic environments. The strongly odorous sulfides, mercaptans, and skatoles are the cause of most odor problems around wastewater treatment plants, landfills, pulp and paper mills, and certain other industries.

Acid rain became a concern in the 1960s when worldwide emissions from motor vehicles and power plants were virtually unregulated. The pH of pure distilled water is 7.0. Normal rain can be from pH 4.5 to pH 5.6, the lower pH value being caused by carbon dioxide (carbonic acid H_2CO_3) and organic acids that are dissolved in the rainwater. Sulfuric acid or nitric acid emissions made the rain more acidic.

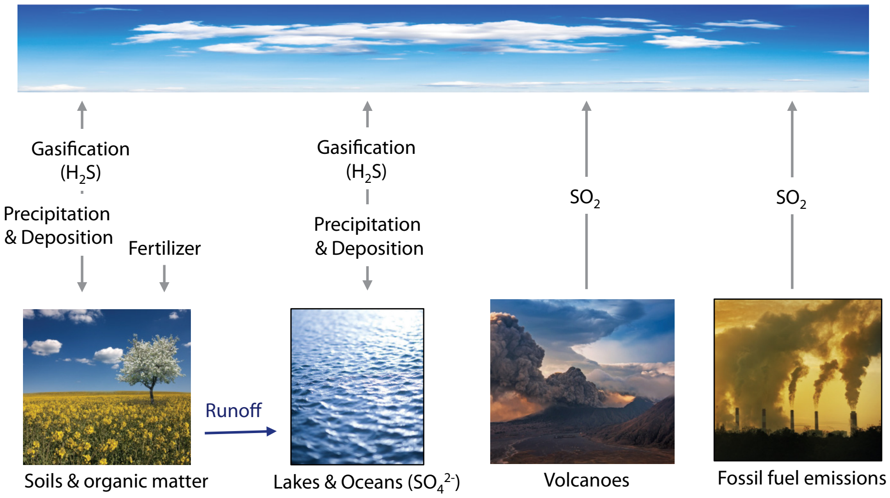


Figure 3.11 The Sulfur Cycle. (Photo credit: pixabay; freedigitalphotos, worradmu & prozac1)

3.9 Conclusion

The manufacture and use of chemicals in manufacturing is linked to the natural cycles of chemicals in the environment. Some of the important elements are the staples of life – carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur. If our activities upset, unbalance, or interrupt the natural cycles of these chemicals, we create local conditions that are unstable and unhealthy. There is no lack of technology to control these chemicals.

4 Toxicity and Aquatic Water Quality Criteria

4.1 Toxicity

Toxic chemicals are a challenge, but not because we lack the technology to remove or destroy them in liquid effluents and gaseous emissions. The technology exists. The challenge comes from the rich menu of potential chemical-related problems. Toxic compounds come in many forms and cause diverse harmful effects.

Another kind of challenge comes from the way toxic or hazardous chemicals are regulated. The five main U.S. laws regulate 1134 chemicals. Only 49 are common to all five laws. Of the 269 pollutants in the Clean Water Act and the Clean Air Act, only 68 are common to both laws.

A toxic chemical will cause harm only when an animal (fish, bird, crustacean, human) is exposed by being in the wrong place at the wrong time. Harm is done only at certain levels and durations of exposure. Chemicals that are poisons in high doses may be needed in small amounts for normal healthy life. Many potentially poisonous substances can be excreted or metabolized if the dose does not exceed some critical level. The dose makes the poison.

Table 4.1 uses everyday terms to relate acute toxicity values for oral, inhalation, and dermal exposure to probable lethal doses for humans.

Toxicity Rating	Commonly Used Term	Oral LD_{50} (single dose to rats) (mg/kg)	Inhalation LC_{50} (exposure of rats for 4 hrs) (ppm)	Dermal LD_{50} (one application to skin of rabbit) (mg/kg)	Probable Lethal Dose for Humans
1	Extremely Toxic	1 or less	10 or less	5 or less	1 grain (a taste, a drop)
2	Highly Toxic	1–50	10–100	5–43	4 ml (1 tsp)
3	Moderately Toxic	50–500	100–1,000	44–340	30 ml (1 fl. oz.)
4	Slightly Toxic	500–5,000	1,000–10,000	350–2,810	600 ml (1 pint)
5	Practically Non-toxic	5,000–15,000	10,000–100,000	2,820–22,600	1 liter (or 1 quart)
6	Relatively harmless	15,000 or more	100,000 or more	22,600 or more	More than1 liter (or 1 quart)

Notes: LC = Lethal Concentration. LC_{50} is the dose that is lethal to 50% of exposed rats in 4-hrs
LD = Lethal Dose. LD_{50} is the dose that is lethal to 50% of exposed animals.

Table 4.1 Scale of toxicity for three routes of administration. (Hodge and Sterner 1956)

4.2 Toxic Chemicals and Effects

4.2.1 Toxic Effects

Toxic substances cause: (1) cancer, tumors, or neoplastic changes, (2) permanent transmissible changes in offspring (mutations), (3) physical defects in the embryo, (4) asphyxiation, (5) irritation or sensitization, or (6) diminished mental alertness or altered behavior. Environmental regulations are supposed to prevent suffering due to these calamities. Table 4.2 lists some chemicals that are regulated by the USEPA. The purpose of the table is to show the variety of toxic chemicals and the range of toxic effects.

Inorganic Chemicals		Organic Chemicals	
Antimony	Alters cholesterol and glucose levels	Atrazine	Reproductive and cardiac effects
Arsenic	Dermal and nervous system affects	Benzene	Anemia, risk of cancer
Barium	Circulatory system effects, high blood pressure	Benzo(a)pyrene (PAHs)	Reproductive difficulties, risk of cancer
Beryllium	Cancer risk and damage to bones and lungs	Carbon tetrachloride	Liver problems, risk of cancer
Cadmium	Concentrates in liver, kidney, pancreas, thyroid	Chlordane	Cancer risk
Chromium	Skin sensitization, liver, and kidney effects	Chlorobenzene	Liver or kidney problems
Copper	Nervous system damage and kidney effects	Endrin	Liver problems
Cyanide (as free cyanide)	Spleen, liver and brain effects	Ethyldenzene	Liver or kidney problems
Fluoride	Skeletal damage	Heptachlor	Liver damage, cancer risk
Lead	Nervous system damage and kidney effects	Lindane	Liver and kidney problems
Mercury (inorganic)	Nervous system damage and kidney effects	Methoxychlor	Reproductive difficulties
Nitrate (as N)	Nervous system and skin sensitization	Polychlorinateed biphenyls (PCBs)	Skin changes, cancer risk
Nitrite (as N)	Methemoglobinemia	Pentachlorophenol	Liver and kidney problems, cancer risk
Selenium	Hair or fingernail loss, circulatory problems	Tetrachloroethylene	Liver problems, cancer risk
Thallium	Gastrointestinal effects	Toluene	Nervous system, kidney or liver problems
Radionuclides		Toxaphene	Liver and kidney problems, cancer risk
Gross alpha	Cancer risk	1,2,4-Trichlorobenzene	Changes in adrenal glands
Gross beta	Cancer risk	1,1,11-Trichloroethane	Liver problems, cancer risk
Radium 226 + Ra 228	Cancer risk	Trichloroethylene	Liver problems, cancer risk
Uranium	Cancer risk, kidney toxicity	Vinyl chloride	Increased risk of cancer
		Xylenes (total)	Nervous system damage

Table 4.2 Some toxic elements, chemicals, and radionuclides and their toxic effects.

4.2.2 Mercury (Hg)

Mercury is found in trace amounts in the atmosphere, soil, rock, water, and in the tissue of plants and animals. In soil, the concentration is normally measured in parts per billion. It may exist in the atmosphere as vapor or in particulate form at parts per billion levels and less. In water, the level is generally parts per trillion. The highest concentration to which a freshwater aquatic community can be exposed indefinitely without an unacceptable effect is 0.77 μg/L (0.77 ppb).

Mercury is a threat because it can be concentrated up to 120 ppb in fish. The mercury is sequestered in the fatty tissue of the fish. It does not harm the fish, but it is dangerous to animals, including people, who consume the fish.

The most dangerous are the organic forms, especially methyl and dimethyl mercury (CH_3Hg and C_2H_6Hg). These compounds have an affinity for attaching to proteins, chromosomes, and brain cells. The bonds are persistent and can remain destructive for months. Inorganic and phenyl mercurials (e.g. C_6H_5Hg) are also dangerous but the injuries they cause are nearly always reversible.

4.2.3 Benzene

Benzene is a human carcinogen for all routes of exposure, based on convincing human evidence and supporting evidence from animal studies. Inhalation of benzene (C_6H_6) can cause leukemia. The increased cancer risk to an individual who is exposed for a lifetime to air that contains 1.3–4.5 μg/m³ benzene is 1 in 100,000. The same risk results from lifetime exposure to drinking water that contains 10–100 μg/L benzene. (USEPA Integrated Risk Information System – IRIS)

4.2.4 DDT

Pesticides are designed to kill specific plants, insects or animals. The good ones are efficient in killing the target organism, harmless to other organisms, and biodegradable. Unfortunately, many are persistent, mobile, bioaccumulative, and dangerous to untargeted species. DDT, once regarded as the miracle chemical that would eradicate malaria, is one of these.

Bioaccumulation (bioconcentration) occurs because the food an organism consumes is divided between respiration for energy and synthesis of new tissue. A substance that is not involved in respiration and is not excreted efficiently may be concentrated in the tissue by a factor of ten-fold at each step in the food chain. The concentration can increase by 1000-fold from one end of the food chain to the other.

The solubility of DDT in water is about 1 μg/L (1 ppb). If water contains 1 ppb DDT, plankton living in the water may contain 0.4 ppm, minnows 12 ppm, and a carnivorous bird 75 ppm. The accumulation can devastate an animal population even when the accumulated chemical does not kill outright. DDT put eagles on the endangered species list by weakening eggshells so they broke before the chicks could hatch. The catastrophe was beautifully explained in *Silent Spring* (Carson 1962). When the use of DDT was restricted the eagle population recovered and flourished.

4.2.5 Radioactive Substances

Radioisotopes are metabolized in the same way as their stable isotopes. This means that most of them are not concentrated in the food chain. Strontium 90 is similar to calcium and it concentrates in bones. The route from atmospheric fallout to humans is fallout deposit on plants or incorporation into plants from the soil. Fortunately, since it lodges in the bones there is no transmission from one animal to another unless a predator eats the bones.

Cesium-137 behaves chemically like potassium. Potassium is an essential element for all cells, so cesium becomes widely distributed within the body after ingestion. Consequently, it can pass from predator to prey and accumulate at each step up the food chain.

Cesium-137, Cobalt-60, Iodine-129 & -131, Plutonium, Strontium-90, Thorium, and Uranium are the radioisotopes most commonly used for medical, military, or commercial purposes and most commonly found in Superfund Sites.

4.3 Aquatic Bioassays

4.3.1 Bioassays

A biological assay (bioassay) uses an organism as the reagent for measuring the amount of a toxic substance that can be tolerated. The result depends on the species of the test organism, organism age and size, diet, other factors, some of which may be unknown or unmeasured.

The critical difference between setting aquatic criteria and human health criteria is that aquatic bioassays provide direct evidence about the organisms of interest. We do not have to predict toxicity to fish from tests on rats. Fish, insect larvae and plankton, at any life stage, can be exposed to toxic materials and observed. The procedures and costs are reasonable.

Testing for human carcinogens and mutagens is an order of magnitude more difficult. We cannot do dangerous experiments with people as test subjects so we test rats and mice and other small animals. This raises the problem of translating those results into predictions about human health.

An aquatic bioassay uses several parallel aquaria that are populated with the same species, number, and size of test organisms (fish, macro-invertebrates, or algae). It is common in running bioassay tests to maintain all factors except the lethal factor at levels that should be healthful. Oxygen, pH, and temperature are important factors to maintain at healthful levels.

At least one aquarium is used as a control with clean water. The others are contaminated with the toxicant being studied. The toxicant concentration is constant in a single aquarium, but different across the parallel units. If fish are tested, a continuous flow of water would be maintained through the aquaria. For smaller animals this may not be required. The influent may be clean water that has been dosed with the toxicant, or it can be effluent that is diluted in different proportions.

4.3.2 Acute Toxicity Bioassays

The dose-response curve for an acute bioassay shows the percentage of organisms surviving (or dying) within a specified time of exposure, usually 48, 96, or 144 hours. The concentration that kills half the test organisms is called the LC_{50} (LC indicates Lethal Concentration). The LC_{50} is meaningless unless the time of exposure is stated. The result should be reported as the 144-hr LC_{50}, or the 96-hr LC_{50}.

Figure 4.1 shows that the survival of bluegills exposed to copper (Cu) decreases as exposure time increases. At 0.6 mg/L, the 96-hr $LC_{50,}$ 85% of organisms survive for 48 hours, 50% survive for 96 hours, and just over 10% survive for 144 hours. In this case the relation between exposure time and LC_{50} is almost linear and we find LC_{50}-144-hr = 0.40 mg/L, LC_{50}-96-hr = 0.60 mg/L, and LC_{50}-48-hr = 0.76 mg/L Cu.

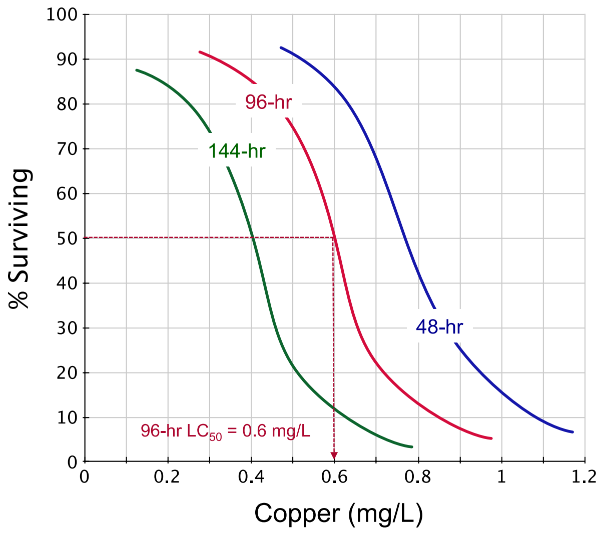


Figure 4.1 Acute toxic bioassay data for bluegill exposed to copper

4.3.3 Chronic Toxicity Bioassays

The response in a chronic bioassay can take many forms. Heart beat, gill movement, and breathing rate of fish can be measured continuously and used as a signal of stressful but non-lethal conditions. Growth rate and breeding efficiency of small aquatic animals are also used to assess chronic toxicity.

A special kind of chronic bioassay is effluent biomonitoring, which can be required in a wastewater discharge permit. A screening test exposes test organisms to a mixture of 50% effluent and 50% non-toxic dilution water. Responses that can be observed in each test are:

- Death – number of organisms killed by a test solution.
- Growth – increase in body weight or size of test organisms.
- Reproduction – offspring produced per female or increase in number of organisms.
- Terata – gross abnormalities shown in early life stages.

A toxic response in the screening test may lead to a definitive test to estimate the concentration or percentage of effluent at which a certain percentage or significant fraction of organisms exhibit a certain response. Organisms are exposed to a predetermined array of test solutions containing various proportions of effluent.

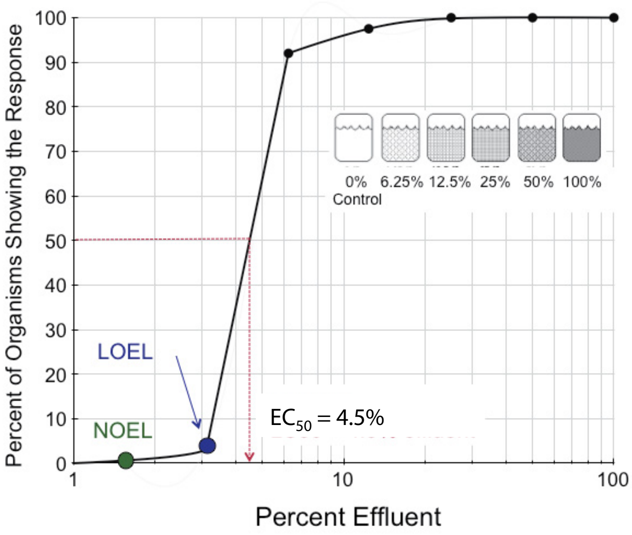


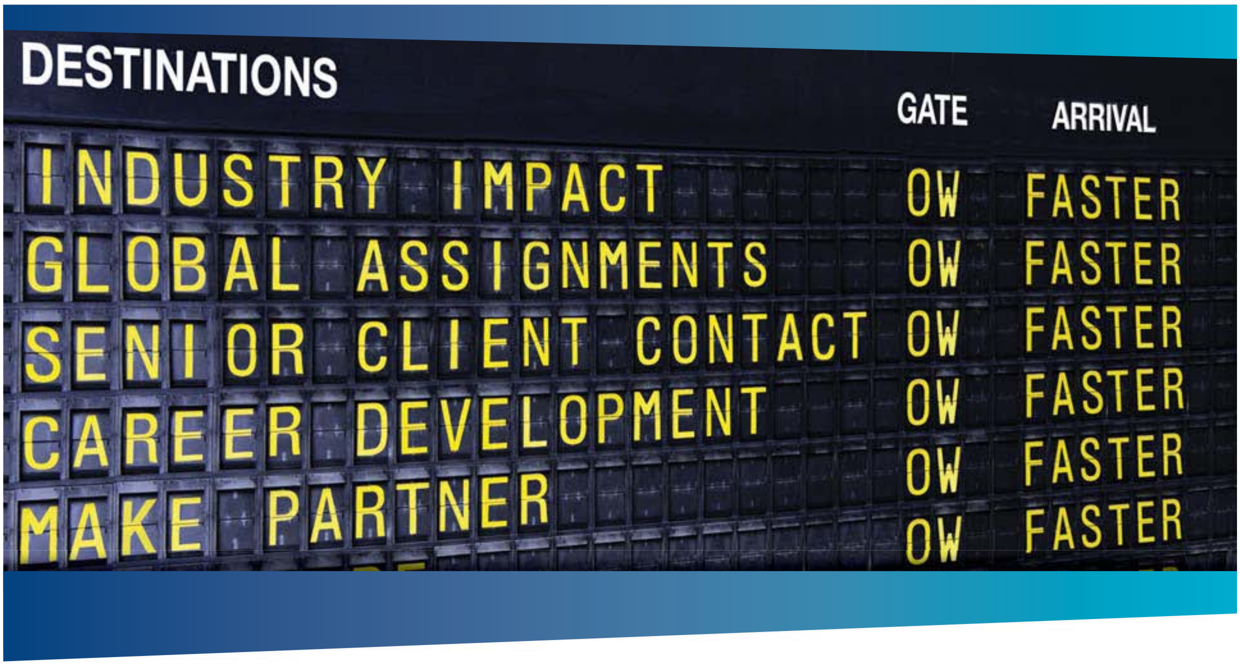
Figure 4.2 Typical effluent bioassay test showing the NOEL, LOEL, and EC_{50}. NOEL = No Observed Effect Level, the highest level at which the response is not significantly different statistically from controls. NOEL is normally only used in chronic toxicity tests. LOEL = Lowest Observed Effect Level, is the lowest dose at which the response can be statistically distinguished from the control group. The NOEL is the next lowest dose below the LOEL. The LOEL and NOEL may correspond to an effect that is observable but is not adverse and of no practical importance.

Figure 4.2 shows a possible test result. The icons below the curve indicate the dilutions of effluent that were used. This is a geometric progression. Starting from 100% effluent, each lower dose decreases by half, so the dilutions are 50%, 25%, 12.5%, 6.25% effluent and lower to include a clean water control.

The percentage of test organisms showing the response is plotted against the percentage of effluent. A valid bioassay should show a generally increasing percent response for increasing percentages of effluent. The graph is typical in showing a sudden change, often 75% or more, between two of the effluent dilution levels. Sometimes this response is even more exaggerated, with no response at one dilution and 100 percent response at the next higher concentration.

The graph defines several measures of toxicity.

- EC_{50} is the level at which 50% of the organisms show an effect that is not necessarily death. (EC denotes effective concentration.) For some test species (e.g., *Ceriodaphnia dubia*) the point of death is not easy to specify so immobility is used as the response.
- NOEL is the no observable effect level. This is the highest tested level at which the responses is not significantly different statistically from the control (zero exposure). The NOEL is normally only used in chronic toxicity tests.
- LOEL is the lowest observable effect level. This is the lowest dose at which the response can be statistically distinguished from the control group. This occurs at 3.125%. The NOEL is the next lowest dose.



Not shown are the lowest observable adverse effect level (LOAEL) and the no observable adverse effect level (NOAEL). These differ from the LOEL and the NOEL because the effect is judged to be biologically adverse, either because of its severity or its frequency. The LOEL may be an effect that is observable but is not adverse and of no practical importance.

The bioassay results need to be converted to water quality criteria. Tests for a variety of species need to be examined so the most sensitive will be protected.

4.4 Water Quality Criteria for Toxic Chemicals

Water quality criteria are based only on data and scientific judgments about pollutant concentrations and their effects. Whether numeric or narrative in form, water quality criteria protect designated uses by describing the chemical, physical and biological conditions necessary for safe use of waters by humans and aquatic life. Definitions and examples of some criteria appear in Table 4.3.

Type	Definition	Example
Numeric Criteria	Lists the maximum pollutant concentration levels allowed in a water body.	The maximum concentration of lead that aquatic life can tolerate in a water body on a short-term (acute) basis is 65 micrograms of lead per liter of freshwater.
Narrative "Free From" Criteria	Describes the desired conditions for a water body as being "free from" certain negative conditions.	Free from excessive algae blooms
Narrative Biological Criteria	Describes the kinds of organisms expected in a healthy water body.	Capable of supporting and maintaining a balanced, integrated, adaptive community of diverse warm water aquatic organisms.

Table 4.3 Types of Water Quality Criteria (USEPA 2002, 2011)

Nationally recommended aquatic life criteria set numeric allowable thresholds concentrations of particular chemicals. Criteria are usually derived for both freshwater and saltwater organisms. The specified levels are intended to protect aquatic organisms from unacceptable effects assuming the following default exposures:

- Acute = Exposure to a 1-hour average concentration of the chemical does not exceed the criterion more than once every 3 years on average.
- Chronic = Exposure to a 4-day average concentration of the chemical does not exceed the criterion more than once every 3 years on average.

The acute toxicity criterion (*Criterion Maximum Concentration* or CMC) is an estimate of the highest concentration of a material in ambient water to which an aquatic community can be *exposed briefly* without resulting in an unacceptable adverse effect.

The chronic toxicity criterion (*Criterion Continuous Concentration* or CCC) is an estimate of the highest concentration of a material in ambient water to which an aquatic community can be *exposed indefinitely* without resulting in an unacceptable adverse effect (e.g., immobility, slower growth, reduced reproduction).

A biological community comprises fish, insects, snails, etc. in juvenile and adult stages of life. The tolerance may range from extremely sensitive to robust and tolerant. The sensitivity of different species can cover a wide range of LC_{50} or EC_{50} values. Figure 4.3 shows the LC_{50} concentrations for fifty aquatic species (fish, insects, etc.) that were exposed to copper. Ten percent of species had an LC_{50} of less than 25 μg/L, 50% were less than 260 μg/L and a few could tolerate more than 500 μg/L.

The criteria are set to protect the most sensitive organisms The minimum data requirement is acceptable acute values for at least eight taxonomic families of aquatic organisms, as shown in Table 4.4.

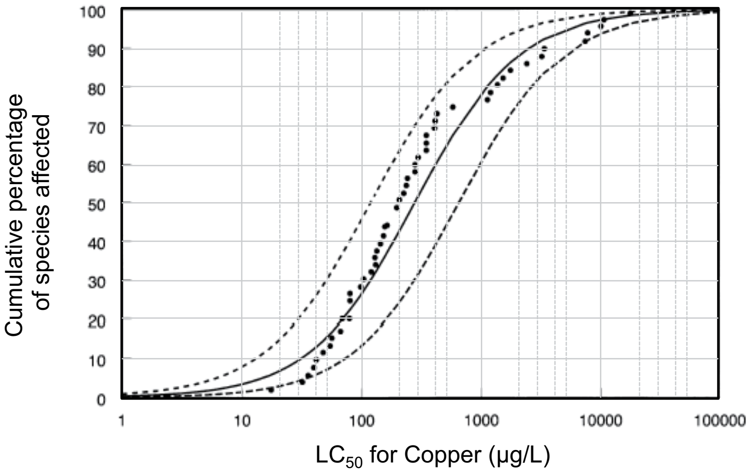


Figure 4.3 Species sensitivity to copper.

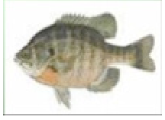
Three vertebrates:		**Five invertebrates:**	
Salmonid fish (e.g., trout or salmon)		Planktonic crustacean (e.g., daphnia)	
Fish from a family other than Salmonidae (bass, fathead minnow, etc.)		Benthic crustacean (e.g., crayfish)	
Species from a third chordate family (e.g., salamander, frog)		Insect (e.g., stonefly, mayfly)	
		Species from a phylum other than Chordata or Arthropoda (i.e., rotifer, annelid, or mollusk)	
		Species from another order of insect or a fourth phylum (e.g., an insect or mollusk not already represented above).	

Table 4.4 Minimum data asset requirement for establishing freshwater aquatic criteria.

The procedure to calculate the recommended acute criterion (CMC) is:

- Calculate the Genus Mean Acute Values (GMAV) for a minimum of eight families of organisms (Table 4.4).
- Rank order the GMAVs and estimate the 5th percentile organism (95% of organisms are more tolerant).
- Use the GMAVs to estimate the Final Acute Value (FAV).
- The Critical Maximum Concentration is half the FAV: CMC = FAV/2.

The FAV is set at half the CMC to establish a low level effect for the most sensitive 5th percentile genus, rather than a 50% effect.

Example 4.1 Calculation of the Genus Mean Acute Values (GMAV) for *Daphnia* sp.

Data from acute toxicity bioassays on three species of Daphnia, a small crustacean, yield the average EC_{50} values of 29, 38, and 42 µg/L. These three values are averaged to get an average for the Genus *Daphnia*. This gives the GMAV = 36 µg/L.

Daphnia magna	29 µg/L
Daphnia pulex	38 µg/L
Daphnia ambigua	42 µg/L
Genus Mean Acute Value =	36 µg/L

Example 4.2 Calculation of the Final Acute Value (FAV) and the Critical Maximum Concentration (CMC)

GMAVs have been determined for nine organisms and the sample ranking of the lowest four is given in Table 4.5. The percentile rank is $p = 100r/(n+1)$, where r = rank, n = number of ranked GMAVs, and p = percentile. For nine GMAVs this becomes $p = 100r/(9+1) = 10r$.

The GMAVs are plotted against the percentile rank in Figure 4.4 and a straight line is drawn to facilitate interpolation to find the FAV at the lower fifth percentile point.

FAV = 11 µg/L.
CMC = FAV/2 = 5.5 µg/L

Rank	GMAV (µg/L)	Species	EC_{50} (µg/L)	Percentile Rank
9		…		0.90
…	…	…	…	
4	100	Rainbow trout	100	0.40
3	36	Cladoceran, *Daphnia magna*	29	
		Cladoceran, *Daphnia pulex*	38	0.30
		Cladoceran, *Daphnia ambigua*	42	
2	25	Amphipod (*Gammarus p.*)	25	0.20
1	19	Amphipod (*Hyalla a.*)	19	0.10

Table 4.5 Example Genus Mean Acute Value data.

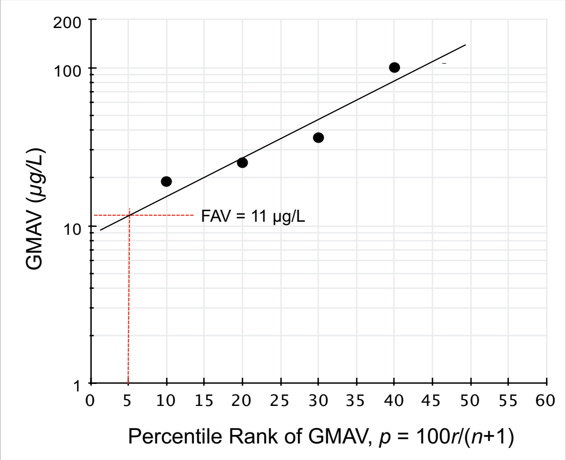


Figure 4.4 Ranked Genus Mean Acute Values (GMAVs) are used to graphically estimate the Final Acute Value that is converted to a Critical Maximum Concentration.

4.5 Site-Specific Water Quality Criteria

The toxicity of a substance may be increased or decreased by the presence of other substances. Stream water contains particles and organic carbon that may bind metals and other chemicals and render them less harmful, or some metals may form less active inorganic complexes. Water hardness (the amount of calcium and magnesium in the water) is known to moderate the toxicity of some metals.

The Water-Effect Ratio is one approach to deriving site-specific aquatic life criteria. At times it may seem that directly transcribing the USEPA criteria is overly protective. The water-effects ratio looks at relevant differences between the toxicities of a chemical in lab dilution water and in site water.

Two side-by-side toxicity tests are conducted, one using amended laboratory dilution water and one using amended site water. The concentrations used are established using water quality data from the affected site.

The end point obtained using site water is divided by the endpoint obtained using the lab dilution water. The quotient is the Water-Effect Ratio, which is multiplied by the national or state aquatic life criterion to obtain the site-specific criterion.

The Recalculation Method recalculates the water quality criteria after eliminating some organisms that were included in the USEPA calculation. For example, if rainbow trout were used to calculate the recommended criteria and rainbow trout are not found the location of interest, a new CMC is recalculated without trout. Using this approach requires stream surveys to identify the indigenous aquatic organisms.

4.6 Adjusting for Water Hardness

Water hardness – the amount of calcium and magnesium in the water – is known to moderate the toxicity of some metals. Figure 4.5 shows how the LC_{50} of copper increases (toxicity decreases) as the hardness increases. Similar results are seen for cadmium, chromium III, copper, lead, nickel, silver, and zinc.

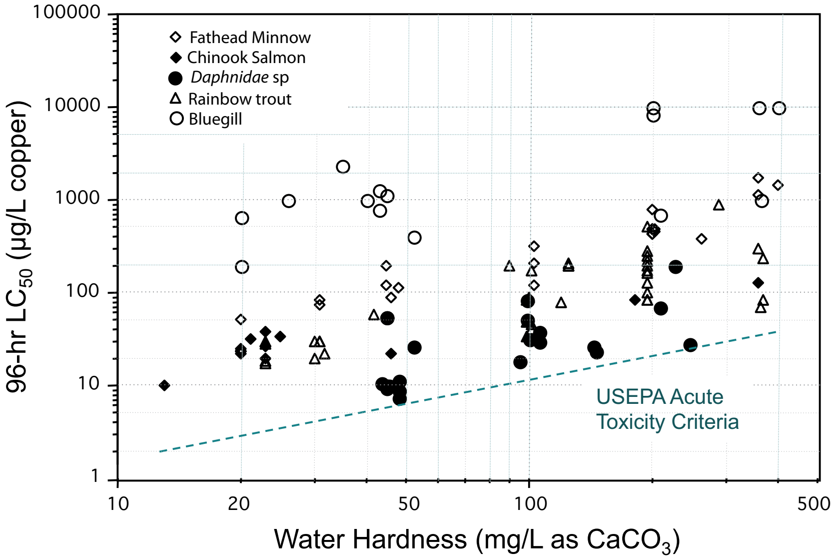


Figure 4.5 The toxicity of heavy metals decreases (the LC_{50} increases) as water hardness increases. Data for four fish species and Daphnidae sp show a wide range tolerance to copper.

The equations used to adjust acute and chronic toxicity aquatic criteria for heavy metals are

$$\text{Acute toxicity criterion } (\mu g/L) = CMC = \exp[m_A \ln(hardness)+b_A] \text{ x } CF$$

$$\text{Chronic toxicity criterion } (\mu g/L) = CCC = \exp[m_C \ln(hardness)+b_C] \text{ x } CF$$

Table 4.6 gives the values of *m* and *b* for seven heavy metals.

Chemical	m_A	b_A	m_C	b_C	***CF* = Freshwater Conversion Factors**	
					CMC	***CCC***
Cadmium	1.0166	-3.924	0.7409	-4.719	1.136672 – 0.041838 ln(hardness)	1.101672 – 0.041838) ln(hardness)
Chromium III	0.8190	3.7256	0.8190	0.6848	0.316	0.860
Copper	0.9422	-1.700	0.8545	-1.702	0.960	0.960
Lead	1.273	-1.460	1.273	-4.705	1.46203 – 0.145712 ln(hardness)	1.46203 – 0.145712 ln(hardness)
Nickel	0.8460	2.255	0.8460	0.0584	0.998	0.997
Silver	1.72	-6.59	—	—	0.85	
Zinc	0.8473	0.884	0.8473	0.884	0.978	0.986

Table 4.6 Parameters for calculating the acute and chronic toxicity for seven metals as a function of water hardness. (Federal Register, vol 56, no. 223, p. 58444, 1991)

Water hardness measures the amount of calcium (Ca) and magnesium (Mg) in water. The concentration is reported as mg/L $CaCO_3$. The conversion from mg/L Ca and mg/L Mg to mg/L $CaCO_3$ is

$$(1\ \text{mg Ca/L})(100\ \text{mg CaCO}_3/40\ \text{mg Ca}) = 2.5\ \text{mg/L CaCO}_3$$
$$(1\ \text{mg Mg/L})\ (100\ \text{mg CaCO}_3/24.3\ \text{mg Mg}) = 4.1\ \text{mg/L CaCO}_3$$

Water that contains 20 mg/L Mg and 50 mg/L Ca has a hardness of 80.4 + 125 = 205.4 mg/L $CaCO_3$

The conversion factor, *CF*, which is in the range 0.85 to 1.00, is an adjustment for the biological unavailability of bound metals.

Example 4.3 SITE SPECIFIC CRITERIA FOR COPPER AND LEAD

The river flow and the water hardness change during the year and seasonal chronic toxicity limits were needed for copper and lead. The hardness at summer low flow is 89 mg/L as $CaCO_3$. During the winter low flow it is 97 mg/L as $CaCO_3$.

The toxicity model parameters, from Table 4.3, are

Copper	$m_C = 0.8545$	$b_C = -1.702$
Lead	$m_C = 1.273$	$b_C = -4.705$

For Copper, the conversion factor is $CF_{Copper} = 0.960$

The chronic toxicity criterion for Copper in summer conditions is

$$CMC_{Copper} = \exp[0.8545 \ln(89)-1.702](0.960) = 8.1\ \mu g/L$$

The Copper criterion for winter is 8.7 µg/L.

For Lead, the conversion factor depends on hardness, $CF_{Lead} = 1.46203 - 0.145712 \ln(\text{hardness})$.

The chronic toxicity criterion for Lead in summer conditions is

$$CF_{Lead} = 1.46203 - 0.145712 \ln(89) = 0.808$$
$$CMC_{Lead} = \exp[1.273 \ln(89)-4.705](0.808) = 2.2\ \mu g/L$$

The Lead criterion for winter is 2.4 µg/L.

4.7 Ammonia Toxicity

Ammonia in water exists in two species: ammonia (NH_3), which is toxic, and ammonium (NH_4^+), which is not. Total ammonia is the sum of these two species:

$$\text{Total Ammonia Nitrogen } (NH_3\text{-N}) = \text{ammonia } (NH_3\text{-N}) + \text{ammonium } (NH_4^+\text{-N})$$

The notation NH_3-N means that the concentrations are reported as mg/L of Nitrogen (N). This gives both species the same units and the concentrations can be added.

The laboratory analysis for ammonia cannot distinguish the two species, so the measured values are total ammonia. The total concentration does not determine the toxicity, because the NH_4^+ is not toxic. The proportion of total ammonia that exists in each form can be calculated using the water temperature and pH. The details, which are omitted here, can be found in USEPA water quality standards (USEPA 2011).

Higher pH and higher temperatures cause more of the total ammonia to be in the toxic form, NH_3. Lower pH and lower temperature reduce the toxicity. The fraction of total ammonia in the toxic un-ionized form (NH_3) is shown in Figure 4.6. Table 4.7 gives the chronic toxicity limits for total ammonia at different levels of pH and temperature.

Example 4.4 Seasonal Ammonia Criteria

A municipal wastewater treatment plant effluent is currently creating ammonia concentrations of 8–10 mg/L NH_3-N in a small receiving stream. Seasonal ammonia criteria are needed for summer values of pH = 8.0 and T = 22°C. Sensitive life stages are present in summer. The winter values are pH = 7.5 and T = 8°C; sensitive life stages are absent.

From Table 4.7 the criteria are

Summer = 1.5 mg/L total ammonia (NH_3-N)
Winter = 6.64 mg/L total ammonia (NH_3-N)

From Figure 4.6, the fractions of un-ionized ammonia (NH_3) are

Summer = 4.5%
Winter = 1%

The approximate concentrations of the two ammonia species are

Summer:	0.07 mg/L NH_3-N and	1.43 mg/L NH_4^+-N
Winter	0.07 mg/L NH_3-N and	6.57 mg/L NH_4^+-N

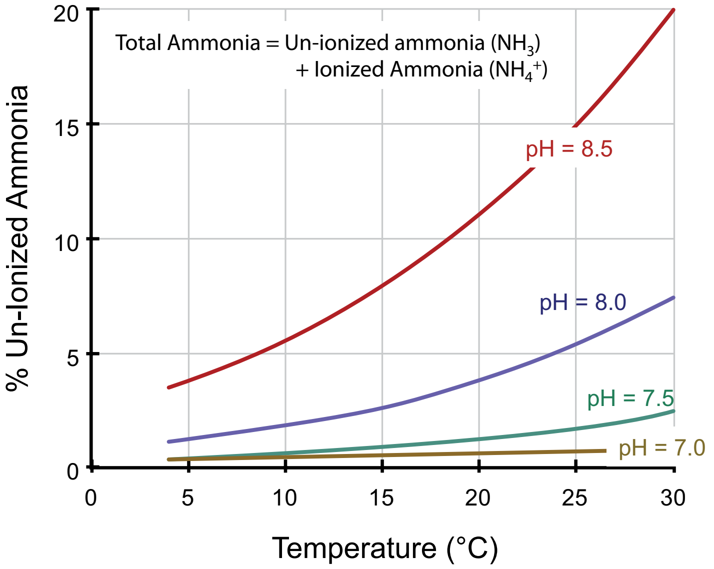


Figure 4.6 Percent Un-ionized ammonia as a function of water pH and temperature.

Chronic Continuous Concentration (CCC) – Early Life Stages Present (mg/L as N)									
pH	Temperature (°C)								
	14	16	18	20	22	24	26	28	30
6.5	6.67	6.06	5.33	4.68	4.12	3.62	3.18	2.80	2.46
7.0	5.91	5.37	4.72	4.15	3.65	3.21	2.82	2.48	2.18
7.5	4.36	3.97	3.49	3.06	2.69	2.37	2.08	1.83	1.61
8.0	2.43	2.21	1.94	1.71	1.50	1.32	1.16	1.02	0.897
8.5	1.09	0.990	0.870	0.765	0.672	0.591	0.520	0.457	0.401
Chronic Continuous Concentration (CCC) – Early Life Stages Absent (mg/L as N)									
pH	Temperature (°C)								
	8	9	10	11	12	13	14	15	16
6.5	10.1	9.51	8.92	8.36	7.84	7.35	6.89	6.46	6.06
7.0	9.00	8.43	7.91	7.41	6.95	6.52	6.11	5.73	5.37
7.5	6.64	6.23	5.84	5.48	5.13	4.81	4.51	4.23	3.97
8.0	3.70	3.47	3.26	3.05	2.86	2.68	2.52	2.36	2.21
8.5	1.66	1.55	1.46	1.37	1.28	1.20	1.13	1.06	0.99

Table 4.7 Chronic Water Criteria for Total Ammonia (mg/L as N).

4.8 Conclusion

The challenge is that toxic pollutants come in many forms and cause diverse harmful effects. Some accumulate in the flesh and organs of animals, some breakdown the environment, some are mobile while others are not, some cause cancer or birth defects after long exposure, some kill quickly at sufficiently high doses, and some upset normal body functions in subtle ways that we may overlook until the cumulative effect is serious disease.

The key decisions are

- Which chemicals must be controlled?
- What concentrations can be tolerated or accepted?

The aquatic bioassay is how we answer these questions for fish and other aquatic organisms. Acute toxicity and chronic toxicity tests are used to set acute (CMC) and chronic (CCC) water quality criteria.

5 Risk Assessment

5.1 Risk Assessment Models and Philosophy

People ask whether a practice, product, or condition is safe, knowing that nearly all we do entails some risk. If safe means ‘no risk’ then there is no such thing as safe. A better question would be ‘Is the risk acceptable?’

Acceptance of risk is subjective. Some people have faith in our ability to calculate impacts and risks, and to design protective measures as needed. Others are skeptical and believe that many failures have led to unanticipated environmental and health damage.

Risk assessment is a simplified model of the real world that relies on many assumptions and subjective judgments. The models are useful, but they are certain to be wrong with respect to some parts of the real world. Conclusions are vulnerable to error caused by gaps in the data that lead to gaps between the model and reality.

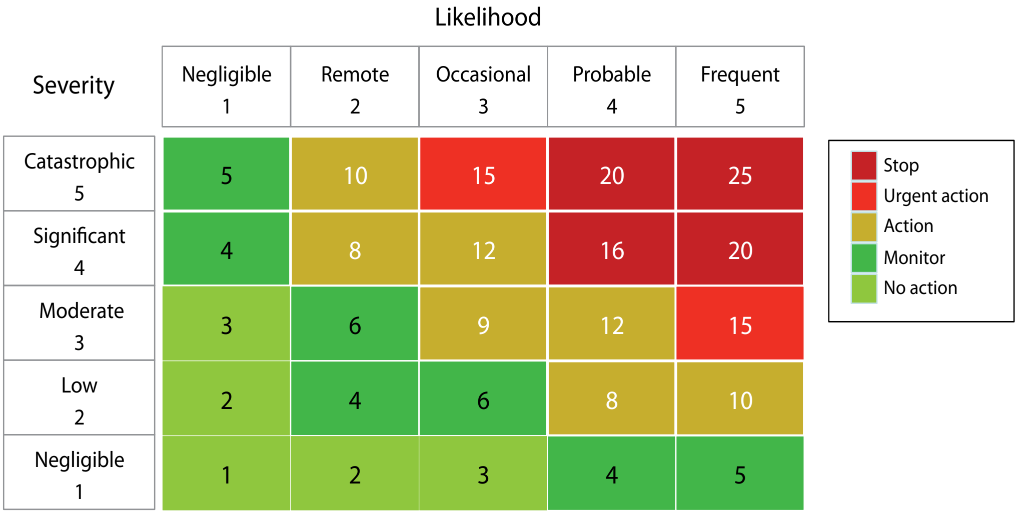
There are fundamental differences in worldview and they may arise in part from the differences in the time scale over which people think. The U.S. view of long-term is 30 to 100 years. In Europe the view of time can be quite different. You will see land that has been farmed for thousands of years. Vineyards that grew grapes for early civilizations still produce wine today. Lead used by Romans 2000 years ago persists in the soil. This should change our view of long-term sustainability.

5.2 Semi-Quantitative Risk Assessment

Risk mapping is a semi-quantitative risk management tool that combines subjective information (expert opinion) and objective information (measurements and calculations). Different approaches can be used depending on the amount and kind of information available. A hierarchy of decisions or actions can be prepared as part of the exercise.

Figure 5.1 is an example of a risk profile matrix. The likelihood of an accident or other hazardous or harmful event (which could include financial harm) is categorized on a subjective scale. Five categories are used in this example, but other schemes could be used. The likelihood of an event ranges from being near zero (say less than 3%) to frequent (say more than 90%). The severity of the consequences, should an event happen, range from a small inconvenience to catastrophic.

The combinations in the upper right-hand corner are serious. Proactive measures are needed before these take place. The goal should be to reduce the likelihood of the events and to mitigate the damage if they occur.



Likelihood

Severity	Negligible 1	Remote 2	Occasional 3	Probable 4	Frequent 5
Catastrophic 5	5	10	15	20	25
Significant 4	4	8	12	16	20
Moderate 3	3	6	9	12	15
Low 2	2	4	6	8	10
Negligible 1	1	2	3	4	5

🟥 Stop
🟥 Urgent action
🟨 Action
🟩 Monitor
🟩 No action

Figure 5.1 A risk profile matrix of a semi-quantitative risk assessment. The factors are the likelihood of an event occurring and the severity of the consequences if it does occur. The scales divide these two factors into five categories (more or less could be used) and they are arbitrarily given weights of 1 through 5. The numbers in the cells are the products of the marginal weights.

5.3 Hazards and Risks

A hazard is a situation that poses a threat to life, health, property, or the environment. Most hazards pose only a theoretical risk of harm. A toxic chemical becomes an active hazard (danger, harm) when toxicity and exposure are combined. Trucks and rail cars that haul hazardous materials are clearly marked with the familiar sign shown in Figure 5.2 so emergency crews will know exactly what hazard they face in case of an accident. This sign shows that materials can be hazardous in many different ways, by toxicity, flammability, and strong chemical reactions, including possible explosions.

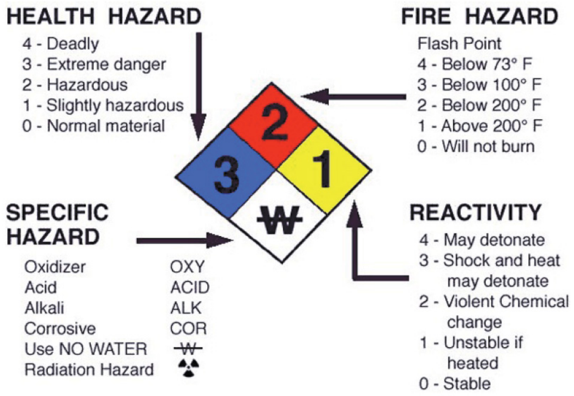


Figure 5.2 Hazardous material identification symbol showing the types of active hazard that could be created by an accidental release

Traffic accident	5 x 10^{-5} per person/year
Electrocution	10^{-5} per person/year
Accidental poisoning	10^{-5} per person/year
Hurricane, flood, tornado, etc.	10^{-6} per person/year
Insect bites	10^{-6} per person/year
Anesthesia complications during surgery	10^{-6} per person/year
Diphtheria, common cold	10^{-7} per person/year
Passenger on a plane	10^{-7} per person/year

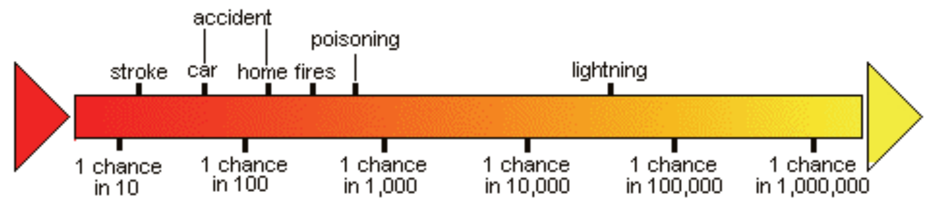


Figure 5.3 Annual risk of death (per person per year) for some "risky" activities.

Figure 5.3 shows the annual risk of death for some events that might happen in the course of ordinary activities. Obviously, if you never fly on an airplane you are not at risk of dying in a plane crash. If you could remove all causes of death from your life except flying on airplanes your expected lifetime would be 10,000,000 years.

To have actual harm there must be a hazardous event and exposure. Toxicity is an intrinsic property of some chemicals, just as heat of combustion is an intrinsic property of gasoline. The heat of combustion represents the potential for something to happen. Until the gasoline is burned, nothing happens. What happens can be safe and useful, as in driving an automobile, or it could be violent and dangerous.

Likewise, toxicity only represents a potential to do harm. Nothing will happen until an organism is exposed, and even then nothing bad will happen unless the level of exposure is high enough and for a sufficiently long time. *Risk assessment* is the business of learning what is 'high enough' and 'long enough'.

Risk is the probability that a *hazard* will happen. Risk depends on the probability of a critical event occurring and the probability of exposure.

Risk = (Probability of critical event)(Probability of exposure to event)

Figure 5.4 shows the risk of an individual getting cancer if exposed to a carcinogen that causes cancer once in every 100,000 exposures. The risk to the individual is one in one hundred thousand (1/100,000). The risk of added cancer deaths for an exposed population of 1,000,000 to a dose that causes cancer once in 100,000 exposures, is (1/100,000)(1,000,000) = 10 cases of cancer.

Risk assessment and risk management are used to evaluate risk of all kinds, including financial risks. Our discussion will be about toxic chemicals in air and water.

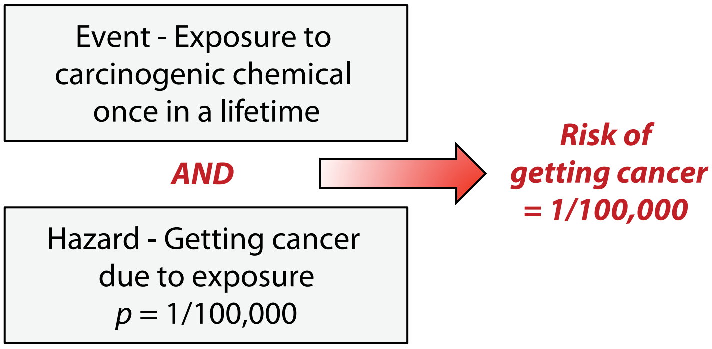


Figure 5.4 Illustration of risk as the combination of exposure and probability of exposure.

Good engineering can reduce the hazard by limiting either the dose or the exposure, or both. For example:

- Change raw materials used in manufacturing to eliminate the toxic substance.
- Provide waste treatment to reduce the discharge or emission of toxic substances.
- Encapsulate or contain the toxic substance to prevent exposure,.
- Install barriers to keep people away from the substance.
- Control how the material is transported.

This is the business of risk management.

5.4 Toxic Chemicals – The Regulator's Dilemma

It is upsetting when the media exclaims that a toxic chemical has been found in food or water or air. The excitement can be a false alarm because chemists routinely quantify chemical concentrations in the parts per billion range and they can detect chemicals at even lower levels. The important issue is not presence or absence of a chemical but 'Can the chemical cause harm at the concentration found?'

		Is this substance hazardous?	
		Yes	No
Should we ban or regulate this substance?	Yes	*Bravo!*	*Bad Mistake*
	No	*Mistake*	*Bravo!*

Figure 5.5 The regulator's dilemma is deciding whether a chemical or substance should be banned or regulated.

The regulator's dilemma, shown in Figure 5.5, is deciding whether a chemical or substance should be banned or regulated. There are two correct decisions and two that are wrong. The worst mistake is failure to ban or regulate a truly dangerous substance. We also want to not ban substances that are harmless because this mistake will waste time and money that could be better used on real problems.

Good epidemiological studies top all other information, but they do not exist for most chemicals. They evaluate the health of real people in the real world. The most definitive studies are of clearly identified groups of industrial workers, or very large groups of exposed people, such as smokers and long-term residents in cities with highly polluted air.

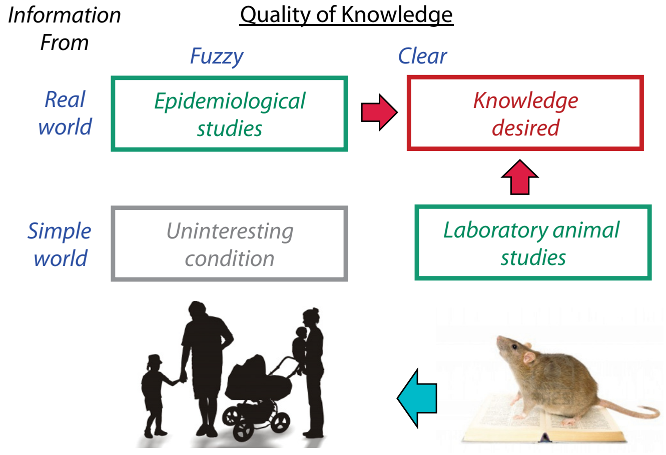


Figure 5.6 Epidemiological studies and laboratory studies provide different kinds of information. Both are needed and both are valuable. When clear epidemiological information does not exist data from laboratory studies are used to extrapolate risks in the real world.

Figure 5.6 suggests that these studies can give fuzzy results. This is because people move from farms to towns, and they change jobs and diets. Also, the number of people exposed to a hazard may be small or their exposure may be short, and this greatly reduces the chance that harm will be observed.

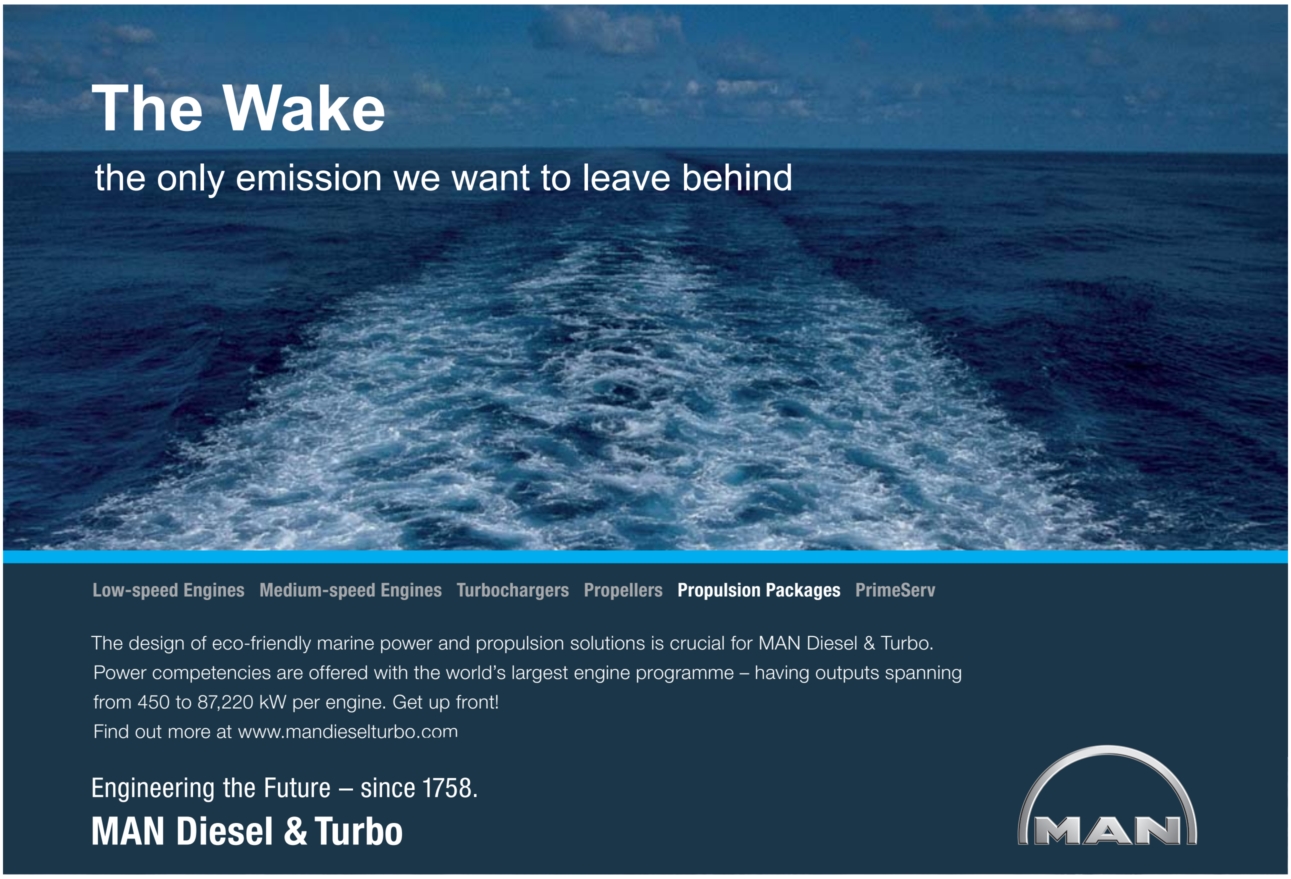
Laboratory studies provide data on the health of confined animals that have eaten or inhaled the substance of interest. The animal population is homogeneous, for example, rats of a certain breed that are housed and fed in identical conditions. These studies give a clear picture of risk in the idealized laboratory animal world, which poorly represents the messy real world where we live.

To help understand the difference between these two kinds to studies imagine all true knowledge about a toxic substance is written on the walls, floor, and ceiling of a dark room. You will be allowed inside the room for ten minutes with an ordinary flashlight (no cameras or iPhones). How will you use your few minutes?

You might read carefully what is written on a small section of one wall. This is like doing an animal laboratory study. You learn a lot of details, but they will not explain much about the world. Alternately, you might stand back and cast your light from spot to spot, scanning information about many things, but the information will have large gaps and spaces. This is like an epidemiological study. You have some useful ideas about a bigger, more complicated, and more realistic world. But the blank spaces in your knowledge frustrate efforts to answer many questions in detail.

Whichever choice you have made – scan or focus – you need professional friends who have done the opposite to help fill in the gaps. Epidemiologists and public health workers study the work of laboratory scientists, and vice versa. Over time, a collective body of knowledge emerges, and as more scientists exchange information the quality of knowledge becomes more reliable.

The difficulty is that we would like to know about thousands of potentially hazardous substances. The analogy is thousands of dark rooms that need exploration. The scientific problem is that truth is revealed incrementally in small steps. The economic problem is that entry to the room is not free. The aggregated cost of a useful level of knowledge is millions of dollars per chemical.



5.5 Tests for Genotoxicity

Genotoxic means able to damage genetic material. DNA (deoxyribonucleic acid) is the molecule that contains the genetic information responsible for cell growth, function, and reproduction. The gene is the portion of DNA that directs the formation of a single product. Alteration of DNA causes mutations. Mutations in reproductive cells may cause birth defects. Mutations in non-reproductive cells may cause cell death or cancer.

Long-term genotoxicity tests look for birth defects or cancer. These tests are expensive in terms of money, laboratories, scientists, and test animals. A long-term test using rats or mice might take 26 weeks to 3 years and cost millions of dollars. Other problems, aside from cost, are the need for many test animals and the need to use very high doses in order to stimulate an observable effect within the short life span of the test animals. There is also the uncertainty caused by the metabolic rate, size, surface area, and life span of animals being different than humans.

Short-term tests screen out the innocuous chemicals and focus attention on the serious troublemakers. Short-term tests use bacteria, yeast, plants, insects, isolated mammalian cells, and whole animals. They are used in a hierarchy of toxicity testing.

- Short-term tests to indicate potential hazard.
- Tests designed to confirm positive short-term tests and delineate the type of hazard.
- Long-term animal tests to validate the hazard and establish the dose-response curve needed for quantitative risk assessment.

Short-term genotoxic tests are based on detecting alteration of a cell's genetic material (DNA), usually by checking for one of these kinds of biological activity: (1) DNA damage and repair, (2) gene mutation (Ames Test, enzyme changes), (3) chromosome alteration (microscopic examination), (4) cancer-like cell formation, or (5) tumor formation.

A positive result in a short-term test is only a sign of potential danger; an indication that additional testing should be done. To reliably serve this purpose, the test must not indicate that a dangerous substance is safe. The opposite kind of error – indicating that a safe substance is dangerous – is tolerable because the error will be discovered when additional testing is done on suspect substances. (See the regulator's dilemma in Figure 5.5.)

5.6 The Reference Dose (RfD) for Non-Carcinogenic Chemicals

The dose response curve is different for carcinogens and non-carcinogens. For non-carcinogens there is a threshold concentration, below which there is no adverse effect. This is the 'hockey-stick' curve shown in Figure 5.7. The threshold value is a no observed adverse affect level (NOAEL), a low-level dose that a person can consume daily with no adverse effect after chronic (long term, low-level) exposure.

Carcinogens are assumed to have no safe threshold. The risk can be very small, but it never goes to zero.

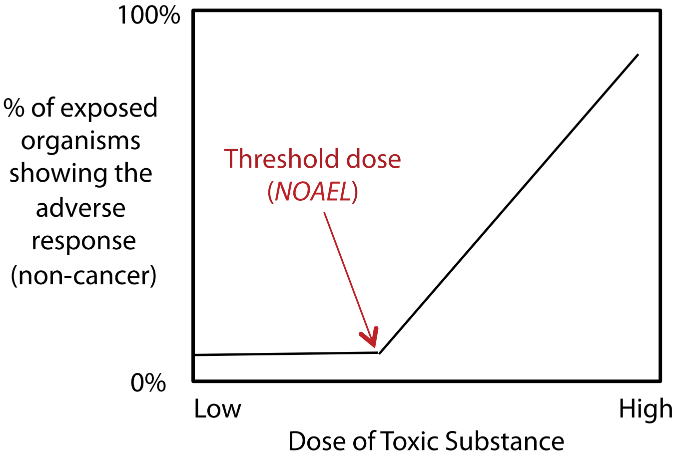


Figure 5.7 Dose response curve for non-carcinogens, such as heavy metals, have a threshold dose, below which there will be no adverse effect.

The *Reference Dose* (*RfD*) is the NOAEL is divided by uncertainty factors (UFs). The NOAEL and the *Rfd* are measured as mg/day of pollutant per kg of body weight, or mg/kg-day.

$$Rfd = \frac{\text{no observed adverse effect level}}{\text{uncertainty factors}} = \frac{NOAEL}{UF_1\, UF_2 \ldots UF_n}$$

The uncertainty factors account for differences between the test animals and the protected human population. If the *RfD* were determined from tests using human subjects the interspecies uncertainty factor would be 1, otherwise it is UF = 10. Additional safety factors can be applied to account for gaps in data.

Example 5.1 Determine the Acute RfD for the insecticide Chlorpyrifos (Wikipedia).

The EPA determined the acute *RfD* to be 0.005 mg/kg-day based on a study in which male rats were administered a one-time dose of chlorpyrifos. The observed response was Cholinesterase inhibition. The lowest dose tested was 1.5 mg/kg-day and this was specified as the lowest observed adverse effect level (LOAEL).

A NOAEL is estimated as one-third the LOAEL

$NOAEL = LOAEL/3 = 1.5/3 = 0.5$ mg/kg-day.

The NOAEL is divided by the standard 10-fold interspecies and 10-fold intraspecies uncertainty factors to get

$$Rfd = \frac{\text{no observed adverse effect level}}{\text{uncertainty factors}} = \frac{NOAEL}{(10)(10)} = 0.005 \text{ mg/kg-day}$$

Example 5.2 The Acute Population Adjusted Dose (Wikipedia).

An *RfD* derived with an additional uncertainty factor that only applies to certain populations is called a *population adjusted dose*. Studies showed that fetuses and children are more sensitive than adults to chlorpyrifos, so the EPA applied an additional ten-fold uncertainty factor to protect that subpopulation. This *acute population adjusted dose* applies to infants, children, and women who are breast feeding.

$$\textit{Acute Population Adjusted Dose} = \frac{Rfd}{10} = \frac{0.005}{10} = 0.0005 \text{ mg/kg-day}$$

Example 5.3 Determine the Chronic *RfD* for the Insecticide Chlopyrifos (Wikipedia).

The *RfD* for chlorpyrifos chronic exposure based was based on studies in which animals were administered low doses of the pesticide for two years. The LOAEL is 0.3 mg/kg-day. An uncertainty factor of 10 was used to get

$NOAEL = LOAEL/10 = 0.03$ mg/kg-day

Applying the 10-fold inter- and intra-species uncertainty factors for uncertainty factors gave

$RfD = 0.0003$ mg/kg-day

The chronic population adjusted dose for infants, children, and breastfeeding women is the *Rfd* divided by an additional uncertainty factor of 10, to give 0.00003 mg/kg-day.

5.7 The Dose Response Curve and the Slope Factor (SF)

Chemicals or mixtures may be studied in large animals to develop a dose-response curve that can be used to make predictions about human effects. A known dose of chemical is fed to an animal (rat, dog, monkey, etc.) in food or water, or as a gavage, or is introduced in the air supply. Animals that get sick or die are autopsied. Animals that survive a fixed test period are sacrificed and examined for tumors or other effects. The response is quantified as the proportion of exposed animals showing an effect.

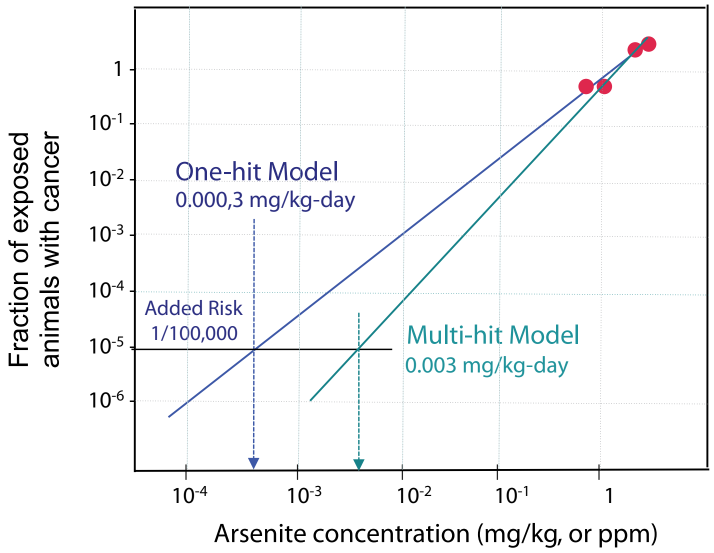


Figure 5.8 Dose response data for rats exposed to arsenite.

Figure 5.8 shows dose-response data for animals exposed to the carcinogen arsenic (arsenite). The arsenite dose, measured in mg arsenite/kg body weight (ppm), is constant over the term of the experiment. The four data points are in the upper right hand corner of the plot. The straight line is the extrapolation of risk. Note that extrapolation over more than a 100,000-fold range is necessary to predict the dose that gives an added risk of 10^{-5} or10^{-6}.

The use of 'heroic doses' is designed to provoke a response in a short time in a small population of test animals. The extrapolation to levels that give acceptable risk in humans is valid if what happens to an animal exposed to a very high dose is, in all important ways, similar to what will happen in a human at low exposure.

The USEPA will make a policy decision to specify a *de minimus* risk. That means 'a risk of minimum importance', more commonly called the *acceptable added risk*. The EPA has used acceptable risk values of 10^{-6} or10^{-4} (1/1,000,000 to 1/10,000) in different laws and policies, but most often the value is 10^{-6} or10^{-5}.

Added means that exposure to the carcinogen will add cases to the prevailing rate in the population. If a population currently has 5,000 deaths per million persons, an acceptable risk of 1 in 1,000,000 means that the rate would become 5,001.

The slope factor (*SF*), also known as the cancer potency factor, is the slope of the extrapolated dose-response model at a low concentration. It is the measure of added risk of cancer due to long-term exposure at a low dose. The units are (added risk)/(mg/kg-day), or $(\text{mg/kg-day})^{-1}$. (Slope factors can be found in the USEPA's IRIS database.)

The one-hit model is the simplest dose-response model and it rests on an assumption that one-hit of a carcinogenic chemical on a cell can, but does not always, cause a tumor. The one-hit model is linear at low doses and it gives the lowest "acceptable" concentration. The one-hit model in Figure 5.8 predicts that 0.0003 mg/kg-day gives an added risk of 10^{-5} (1/100,000).

Recent research on the metabolism of chemicals is providing justification for using models like the multi-hit and probit models. The USEPA model of choice is a multistage model. It is linear at low doses. As an additional safety factor, the upper 95 percent confidence limit of the fitted line is used to determine the acceptable dose.

Multi-hit or multi-stage means that multiple events must occur to initiate cancer. Presumably this combination or sequence of events is less likely than a single-hit and this increases the dose required to cause cancer. The multistage model applied to the data in Figure 5.8 would predict an acceptable dose of about 0.003 mg/kg-day. Note that it is the models, and not the data, that cause the approximate 10-fold difference in the predicted safe doses.

Example 5.4 Slope Factor (Cancer Potency Factor)

The one-hit model in Figure 5.8 predicts that 0.0003 mg/kg-day (ppm) gives an added risk of 10^{-5} (1/100,000).

$$\text{Slope factor} = SF = \frac{\text{Acceptable Risk}}{\text{Dose (mg/kg-day)}} = \frac{10^{-5}}{0.0003\ \text{mg/kg-day}} = 0.033\ (\text{mg/kg-day})^{-1}$$

This is the SF for the test animal. Scale-up to humans is usually done on the basis of body surface area, which is proportional to the cube root of the weight. For an average human of 70 kg and an average rat of 0.04 kg, the scale-up factor, F_A, is

$$\text{Area scale – up Factor} = F_A = \sqrt[3]{70/0.04} = 12.05$$

The adjusted slope factor for humans, based on this test, is

$$SF^* = SF(F_A) = 12.05[0.033\ (\text{mg/kg-day})^{-1}] = 0.40\ (\text{mg/kg-day})^{-1}$$

Example 5.5 Acceptable Concentration in a Stream

Calculate the concentration of chemical in a stream that corresponds to an acceptable risk of one in a million (10^{-6}) for a slope factor of 2.5 $(\text{mg/kg-day})^{-1}$.

$$\text{Acceptable dose} = \frac{\text{Acceptable Risk}}{SF^*} = \frac{10^{-6}}{2.5\ (\text{mg/kg-day})^{-1}} = 4x10^{-7}\ \text{mg/kg-day}$$

$$= 4x10^{-4}\ \mu\text{g/kg – day}$$

For a 70 kg adult the daily intake is (70 kg)(0.0004 µg/kg-day) = 0.028 µg/day. If this is ingested in 1.5 L of water per day, the acceptable concentration in the water is

$$\text{Acceptable concentration} = \frac{0.028\ \mu\text{g/day}}{1.5\text{L/day}} = 0.019\ \mu\text{g/L}$$

5.8 The Added Risk Concept

Cancer accounts for 1 out of 4 deaths and is the second most common cause of death in the U.S., exceeded only by heart disease. About 560,000 people are expected to die of cancer this year (2013), or 1500 people per day. The number of new cancer cases in the United States in 2012 was 1,638,910 (excluding skin cancers). The probability of developing invasive cancer from birth to death is 45% for men and 38% for women. About 55% of new cancer cases are diagnosed in people of age 55 years and older.

It is known how many cases of the different kinds of cancer are diagnosed each year and how many people die from the disease. That is the *background rate.* It is generally unknown what fraction of cancer cases are initiated by environmental exposure to chemicals and what fraction is determined by genetic predisposition and natural aging. Whatever the fractions may be, we presume that the fraction due to environmental exposure to chemicals will be increased if exposure is increased and, conversely, that the number of cases will be reduced by better risk management.

Added risk is the risk increment above the existing background risk:

$$\text{Total risk} = \text{background risk} + \text{added risk of dose } d$$
$$\text{Added risk} = A(d) = p(d) - p(b)$$

where $p(d)$ = the total risk to an individual
$p(b)$ = the risk when the dose is at the background level.

The notation p indicates that risk is the probability that an individual subjected to the stated exposure will develop, but not necessarily die from cancer.

The model for incremental individual risk to an exposed individual is

$$\text{Incremental individual lifetime cancer risk} = CDI \times SF$$

CDI is the chronic daily intake (the absorbed chemical dose averaged over a lifetime), measured in mg/day of chemical absorbed per kg body weight. For an average adult we assume the body weight is 70 kg and the average lifetime is 70 years. The slope factor (SF) has units of added cancers per year per mg/kg-day. The value calculated from dose-response data by the USEPA is an upper-bound estimate of the actual risk.

The expected number of Added Cancers (AC) per year in an exposed population of size *P* is

$$\text{Added cancer cases in an exposed population} = P \times CDI \times SF$$

In short, the population risk is the individual risk multiplied by the size of the exposed population.

Tables 5.1 gives the default values for body weight and consumption that are widely used for risk calculations. Fish consumption is included because bioaccumulation of carcinogens in the edible tissue may create a significant cancer risk. Table 5.2 lists some cancer potency factors and other characteristics for a few important chemicals.

Parameter	**Standard Intake Values**	
	Adult	**Child**
Average body weight	70 kg	10 kg
Amount of water ingested daily	2 L	1 L
Amount of air breathed daily	20 m^3	5 m^3
Amount of fish consumed daily	6.5 g	---
If exposure is for entire lifetime use	70 years	---

Table 5.1 EPA Recommended standard values for Daily Intake Calculations

Chemical	**Slope Factor**		**Bioaccumulation Factor (L/kg fish)**
	Oral route (mg/kg-day)$^{-1}$	**Inhalation route (mg/kg-day)$^{-1}$**	
Arsenic	1.75	50	44
Benzene	2.9×10^{-2}	2.9×10^{-2}	5.2
Cadmium	------	6.11	81
Carbon tetrachloride	0.13	-------	19
Chloroform	6.1×10^{-3}	8.1×10^{-2}	3.75
DDT	0.34	-----	54,000
1,1-Dichloroethylene	0.58	1.16	5.6
Dieldrin	30	-----	4,760
2,3,7,8-TCDD (dioxin)	1.56×10^{5}	------	5,000
1,1,1-Trichloroethane	-----	-----	5.6
Trichloroethylene (TCE)	1.1×10^{-2}	1.3×10^{-2}	10.6
Vinyl chloride	2.3	0.295	1.17

Table 5.2 Toxicity Data for Selected Potential Carcinogens

Example 5.6 Risk Assessment for Chloroform in Drinking Water (ADAPTED FROM MASTERS & ELA 2008)

Disinfecting drinking water with chlorine forms an undesired byproduct, chloroform ($CHCl_3$). Find the upper-bound lifetime cancer risk for a 70 kg person who drinks 2 L of water every day for 70 years with a chloroform concentration of 0.20 mg/L (twice the drinking water standard).

First, compute the CDI:

$$CDI\ \text{(mg/kg-day)} = \frac{\text{Average daily dose (mg/day)}}{\text{Body weight (kg)}} = \frac{\text{(0.2 mg/L)(2 L/day)}}{\text{70 kg}} = 0.00572\ \text{mg/kg-day}$$

The chloroform slope factor for ingestion is 6.1×10^{-3} (mg/kg-day)$^{-1}$. The incremental lifetime cancer risk is

$$\begin{aligned} Risk &= CDI\ x\ SF \\ &= 0.00572\ \text{mg/kg-day}\ x\ 6.1x10^{-3}\ (\text{mg/kg-d})^{-1} = 34.8x10^{-6} \end{aligned}$$

Thus, over a 70-yr period the upper bound estimate of the probability that a person will get cancer from chloroform in this drinking water is about 35 in a million.

If a city of 500,000 people also drinks the same amount of this water, how many extra cancers per year would be expected? Assume a standard 70-year lifetime.

$$500{,}000\ \text{people}\ x\ \frac{34.8\ \text{cancer}}{10^6\ \text{people}}\ x\ \frac{1}{70\text{yr}} = 0.24\ \text{cancers/yr}$$

Compare the extra cancers per year caused by chloroform in the drinking water with the expected number of cases from all causes for this city. The average annual cancer death rate in the U.S. is about 190 per 100,000. The expected number of cancer deaths in a population of 500,000 is about 950. It is unlikely that an additional 0.24 new cancers per year would be detectable.

Example 5.7 Inhalation of Ethylene oxide (EO) and PAHs

Air pollution by ethylene oxide (EO) and polyaromatic hydrocarbons (PAH) is a concern. Calculate the cancer risk if the annual average concentrations are 0.1 μg/m^3 for ethylene oxide and 0.05 μg/m^3 for PAH. The respective unit risk factors are 8.8×10^{-5} m^3/μg for ethylene oxide and 1.7×10^{-3} m^3/μg for PAH.

Cancer risk = (unit risk)(annual average concentration)

Cancer risk for EO = (0.1 μg/m^3)(8.8×10^{-5} m^3/μg = 8.8×10^{-6}
Cancer risk for PAH = (0.05 μg/m^3)(1.7×10^{-3} m^3/μg) = 8.5×10^{-5}

In an exposed population of 1,000,000 people this method estimates an additional 85 cancer cases due to PAH and 9 due to ethylene oxide, for a total of 94 additional cases.

Example 5.8 Inhalation risk of benzene and toluene

A ground level plume from an industry reaches nearby homes. The concentrations are 10 μg/m^3 toluene and 5 μg/m^3 benzene. The respective slope factors are 0.021 (mg/kg-day)$^{-1}$ and 0.029 (mg/kg-day)$^{-1}$. A 70-kg adult breathes 15 m^3 of contaminated air per day for 15 years. Assume that 75% of the inhaled chemicals are absorbed.

$$\text{Risk} = \frac{(\text{Air conc.})(\text{Slope factor})(\text{Breathing rate})(\text{Duration})(\text{Absorption})}{(\text{Ave. body weight})(\text{Lifetime})}$$

$$\text{Risk} = \frac{(10\ \mu\text{g/m}^3)(0.021(\text{mg/kg-day})^{-1}(15\ \text{m}^3/\text{d})(15\ \text{years})(0.75)}{(70\ \text{kg})(70\ \text{years})} = \frac{1\ mg}{1000\ \mu g} = 7.2 \times 10^{-6}$$

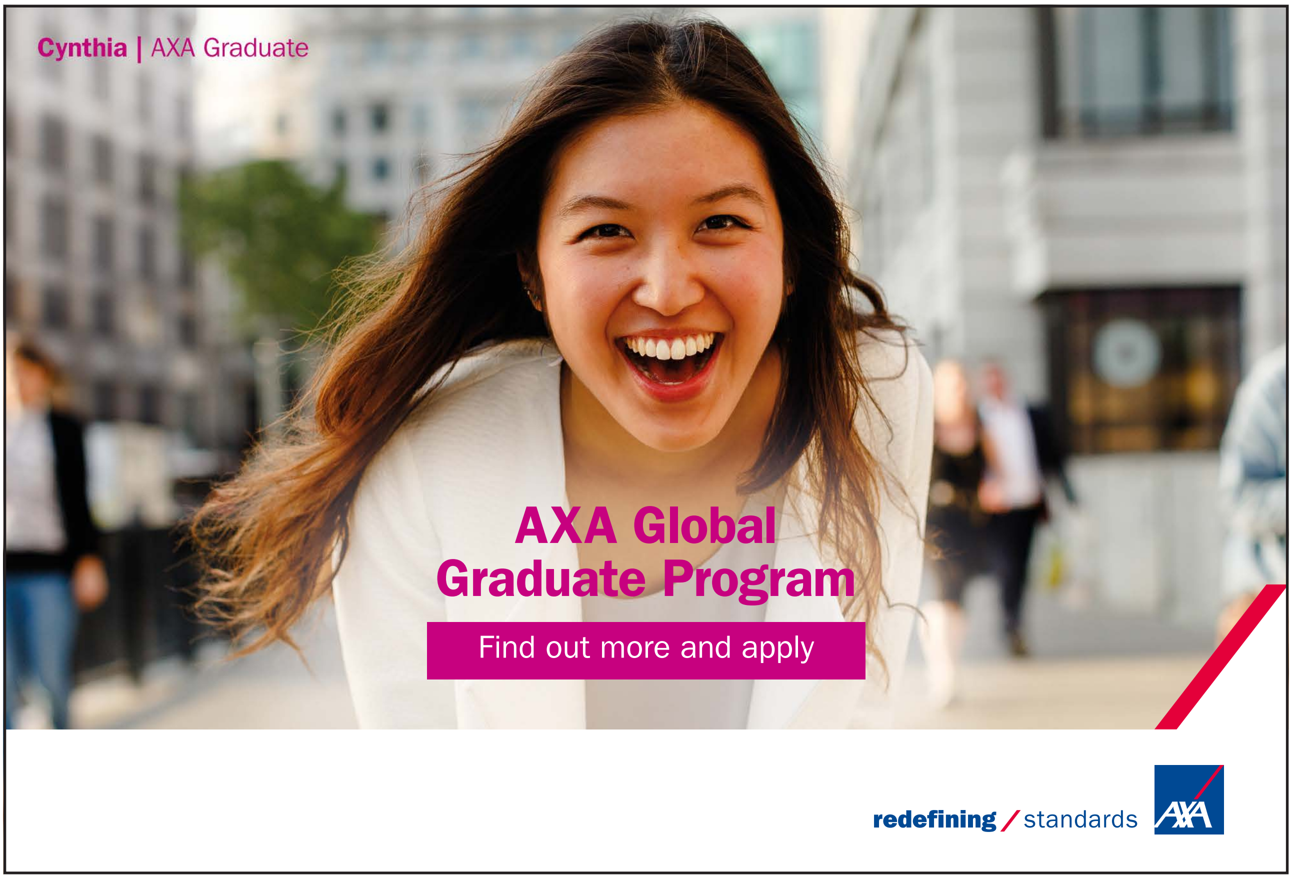
$$\text{Risk} = \frac{(5\ \mu\text{g/m}^3)(0.029(\text{mg/kg-day})^{-1}(15\ \text{m}^3/\text{d})(15\ \text{years})(0.75)}{(70\ \text{kg})(70\ \text{years})} = \frac{1\ \text{mg}}{1000\ \mu\text{g}} = 5.0 \times 10^{-6}$$

Total risk = $\text{Risk}_{\text{Toluene}} + \text{Risk}_{\text{Benzene}} = 7.2 \times 10^{-6} + 5.0 \times 10^{-6} = 12.2 \times 10^{-6}$
= 12 cases per 1,000,000 exposed people.

5.9 Risk-based Standards for Drinking Water

5.9.1 Relative Source Contribution

Drinking water, polluted air, and contaminated food are possible sources of pollutants that a person could face each day. Estimating health-protective levels of chemical in drinking water should consider the proportion of the total possible dose derived from water versus other sources. That proportion is the *relative source contribution* (RCS). This applies to chemicals that have a threshold toxicity.



The USEPA has used values of 0.2 to 0.8 (20% to 80%) of the total acceptable exposure for drinking water, with 0.2 (20%) being the default value in the absence of good data. The total exposure should not exceed the reference dose (*RfD*). This approach has been used to derive *public health goals* (*PHG*s) for 69 chemicals. Some of the values used in the derivation of public health goals are in Table 5.3.

Chemical	**Relative Source Contribution (fraction of total dose)**		
	USEPA	**WHO**	**Health Canada**
Antimony	0.4	0.1	0.38
Cadmium	0.25	0.1	0.12
Carbon tetrachloride	0.4	0.1	-
Dichlorobenzene	0.2	0.2	0.2
Endrin	0.2	0.1	-
Mercury (inorganic)	0.2	0.1	0.05 (total)
Nickel	0.2	-	-
Toluene	0.2	0.1	-

Table 5.3 A sample of Relative Source Contribution factors for drinking water (USEPA 2000).

5.9.2 Maximum Contaminant Level

The Maximum Contaminant Level Goal (MCLG) is a non-enforceable health-based goal. For known carcinogens, or cancer-causing agents, the goal is set at zero, assuming that any level of consumption presents a cancer risk. For non-carcinogens the MCLG level is based on the assumption that a person could consume two liters of drinking water containing the maximum level of the contaminant daily for 70 years without experiencing any known health effects

The Maximum Contaminant Level (MCL) is the highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration.

There is no MCL for turbidity, bacteria, protozoa, and viruses. Instead a Treatment Technique is established. Some calculations are

$$\text{Maximum Contaminant Level Goal (MCLG)} = \frac{Rfd \times BW \times RSC}{V}$$

where RfD = reference dose (mg/kg-day)
BW = body weight (kg)
RSC =-relative source contribution (value between 0.2 and 0.8)
V = volume of water consumed per day (L/day)

$$\text{Maximum Contaminant Level Goal (MCLG)} = \frac{(Rfd - \text{Other Sources}) \times BW}{V}$$

$$\text{Public Health Goal (PHG)} = \frac{NOAEL \times BW \times RSC}{UF \times V}$$

where $NOAEL$ = no observed adverse effect level (mg/L)
UF = uncertainty factor (dimensionless number)

A criterion that combines the consumption of drinking water and fish can be calculated using

$$\text{Ambient Water Quality Guidance} = \frac{RfD \times BW \times RSC}{(FI \times BAF) + V}$$

where FI = fish intake (mg/day)
BAF = bioaccumulation factor (dimensionless number)

Table 5.4 lists MCL values for a few chemicals. Appendix 1 is a more complete list.

Inorganic Chemicals	**MCL**	**Organic Chemicals**	**MCL**
Antimony	0.006	Atrazine	0.003
Arsenic	0.01	Benzene	0.005
Barium	2	Benzo(a)pyrene (PAHs)	0.0002
Beryllium	0.004	Carbon tetrachloride	0.005
Cadmium	0.005	Heptachlor	0.0004
Chromium	0.1	Lindane	0.0002
Copper	1.3	Methoxychlor	0.04
Cyanide (as free cyanide)	0.2	PCBs	0.0005
Fluoride	4	Pentachlorophenol	0.001
Lead	0	Tetrachloroethylene	0.005
Mercury (inorganic)	0.002	Toxaphene	0.003
Nitrate (as N)	10	1,2,4-Trichlorobenzene	0.05
Nitrite (as N)	1	1,1,11-Trichloroethane	0.005
Selenium	0.05	Trichloroethylene	0.005
Thallium	0.002	Vinyl chloride	0.002

Table 5.4. Maximum Contaminant Level (MCL) for selected chemicals taken from the U.S. Recommended Drinking Water Criteria (USEPA 2011).

Example 5.9 Hypothetical MCL Determination.

The acceptable daily intake of a non-carcinogen for a human of 70 kg body weight is calculated from the reference dose (*RfD*)

$$\text{Intake} = RfD \times BW$$

For $RfD = 1$ mg/kg-day,

$$\text{Intake} = (1\ \text{mg/kg-day})(70\ \text{kg}) = 70\ \text{mg/day}$$

Assuming 2 L/day of water intake, the allowable concentration in the drinking water is

$$\text{Drinking water concentration (mg/L)} = (70\ \text{mg/day})/(2\ \text{L/day}) = 35\ \text{mg/L}$$

Assuming that 20% of the total allowable daily intake will come from drinking water, the Maximum Contaminant Level (MCL) is

$$\text{MCL} = 0.2(35\ \text{mg/L}) = 7\ \text{mg/L}$$

If the chemical is a Class C carcinogen (suggestive evidence of carcinogenic potential), divide by uncertainty factor $UF = 10$.

$$\text{MCL} = (7\ \text{mg/L})/10 = 0.7\ \text{mg/L}$$

5.10 Risk Assessment of the Land Application of Sludge

5.10.1 Beneficial Use of Biosolids

Sewage sludge (biosolids) is the byproduct of processes that clean municipal wastewater in preparation for discharge to waterways. The USEPA reported in 1996 that US treatment plants produce an estimated 5.3 million metric tons of sludge per year.

Ocean dumping was banned in 1988. Landfilling and incineration carry high environmental and economic costs. This makes land disposal an attractive option. Also, the sludge is rich in nitrogen and phosphorus, which makes it useful as a soil amendment on farms, reclaimed lands, and forestland. One annual application of sludge can provide the nitrogen and phosphorus needed to grow corn, alfalfa, and soybeans.

Sewage contains food and fecal wastes from homes and businesses and a variety of products and contaminants, but also landfill leachate (in many cities) and contaminants leached from plumbing fixtures. The average composition of municipal sewage sludge in the U.S. is given in Table 5.5.

Nutrients	**Percent (dry weight basis)**	**Metal**	**Average metal concentration (mg/kg of dry sludge solids)**
Organic carbon (C)	20–40%	Arsenic (As)	10
Total nitrogen (N)	4–8%	Cadmium (Cd)	7
Phosphorus (P)	1–5%	Copper (Cu)	740
Potassium (K)	0.2–2%	Lead (Pb)	135
Sodium (Na)	0.5–2%	Mercury (Hg)	5
Calcium (Ca)	2–5%	Molybdenum (Mo)	9
		Nickel (Ni)	43
		Selenium (Se)	5
		Zinc (Zn)	1,200

Notes: Dry weight basis means that 100 kg of dry sludge solids will contain from 4 to 8 kg of total nitrogen.
100 kg of dry sludge solids will contain, on average, (100 kg)(10 mg/kg) = 1000 mg Arsenic.

Table 5.5 Average composition of sewage sludge.

Any metals that are removed by a municipal wastewater treatment plant become part of the biosolids (the sludge). Most are incorporated into the sludge solids, but some are soluble and thus mobile and bioavailable. The insoluble fraction may become bioavailable in the soil, depending upon pH and other factors.

Sludge that has a total solids concentration of 3% to 5% (dry solids) is handled as a liquid. Injection into the plow layer of soil is a common practice, but it can be sprayed if used for land reclamation or in forestland. Sludge that has been dewatered to a solids concentration of 18% can be handled as a solid (squeezing the sludge will not release any water).

5.10.2 The Risk Assessment Pathways

The Part 503 sludge regulations control nine metals and pathogenic microorganisms in sludge that will be applied to land. The EPA did not establish pollutant limits for any organic pollutants because it determined that none of the organics considered for regulation pose a public health or environmental risk from land application of sewage sludge (USEPA, 1992a).

The USEPA supports 'beneficial reuse of biosolids' and asserts that the practice is low risk. They evaluated each of the nine metals through 14 pathways to find the pathway resulting in the lowest concentration at the 'acceptable risk' level. The pathways are listed in Table 5.6. Most of these are shown in Figure 5.9.

The limiting pathway was a child ingesting sludge for arsenic, cadmium, lead, mercury, and selenium. Molybdenum was limited by an animal's diet. Copper, nickel and zinc were limited by direct toxicity to plants (phytotoxicity).

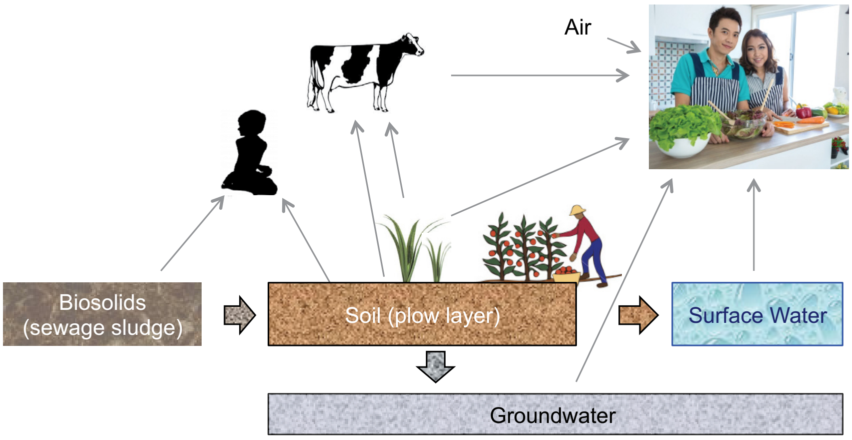


Figure 5.9 Pathways for risk assessment of the beneficial use of biosolids under the Part 503 regulations (USEPA 1992).

Pathway	Description of highly exposed individual
1 Sludge – soil – plant – human	Human (except home gardener) lifetime ingestion of plants grown in sludge-amended soil
2 Sludge – soil – plant – human	Human (home gardener) lifetime ingestion of plants grown in sludge-amended soil
3 Sludge – human	Human (child) ingesting sludge
4 Sludge – soil – animal – human	Human lifetime ingestion of animal products (animals raised on forage grown on sludge- amended soil)
5 Sludge – soil – animal – human	Human lifetime ingestion of animal products (animals ingest sludge directly)
6 Sludge – soil – plant – animal	Animal lifetime ingestion of plants grown on sludge-amended soil
7 Sludge – soil – animal	Animal lifetime ingestion of sludge
8 Sludge – soil – plant	Plant toxicity due to taking up sludge pollutants when grown in sludge-amended soils
9 Sludge – soil – organism	Soil organism ingesting sludge/soil mixture
10 Sludge – soil – predator	Predator or soil organisms that have been exposed to sludge-amended soils
11 Sludge – soil – airborne dust – human	Adult human lifetime inhalation of particles (dust) (e.g. tractor driver tilling a field)
12 Sludge – soil – surface water – human	Human lifetime drinking surface water and ingesting fish containing pollutants in sludge
13 Sludge – soil – air – human	Human lifetime inhalation of pollutants in sludge that volatilize to air
14 Sludge – soil – groundwater – human	Human lifetime drinking well water containing pollutants from sludge that leach from soil to groundwater

Table 5.6 Description of the pathways for risk assessment of the beneficial use of biosolids under the Part 503 regulations (USEPA 1992).

5.10.3 The Limitations on Metals in Land Applied Sludge

There are four limitations on metals, shown in Table 5.7. Two are sludge quality limits, specified in mg/kg of metal, and two are loading rates, specified with units of kg/hectare (kg/ha) and kg/hectare-year (kg/ha-yr).

Pollutant	Pollutant Concentration Limit in EQ sludge (mg/kg)	Ceiling Concentration Limit (mg/kg)	Cumulative Pollutant Loading Rate (CPLR) (kg/ha)	Annual Pollutant Loading Rate (APLR) (kg/ha-yr)
As	41	75	41	2
Cd	39	85	39	1.9
Cu	1,500	4,300	1,500	75
Pb	300	840	300	15
Hg	17	57	17	0.85
Mo	18	75		0.9
Ni	420	420	420	21
Se	36	100		5
Zn	2800	7500	2800	140

Table 5.7 The Part 503 limitations on heavy metals set in the Part 503 Rule for land disposal of municipal sewage sludge (USEPA 1992).

The *Cumulative Pollutant Loading Rate* (*CPLR*) is taken directly from the risk assessment results. The *Ceiling Concentration Limit* also considers the risk assessment, but less directly. Once the *CPLR* has been reached no more biosolids can be applied to that site. Even at the *CPL*, however, the pollutant loading is protective of public health and the environment.

The *Pollution Concentration Limit* is the most stringent. It defines no-adverse-effect biosolids that will be safe without the applier keeping track of cumulative pollutant loadings (as is required for *CPL* biosolids). The pollutant limits were derived from the limits identified in the risk assessment. These are based on an assumed application of 1,000 metric tons per hectare (tonne/ha) in which the cumulative pollutant loading rates would be met but not exceeded.

Biosolids that can be shown to meet the pollution concentration limits, as well as certain pathogen and vector control requirements, are designated *exceptional quality* (EQ). *EQ* biosolids can be land applied as freely as other fertilizers and soil conditioners without having to show that they meet the Part 503 management practices and general requirements.

Ceiling Concentration Limits identify the maximum allowable concentration of pollutants that can be land applied. These are minimum-quality limits to prohibit the lowest quality (highest pollutant concentration) biosolids from being land applied. Ceiling concentration limits are either the 95th-percentile concentrations of the National Sludge Survey or the risk assessment pollutants limits, whichever were least stringent.

The *Annual Pollutant Loading Rates* (*APLR*) apply only to biosolids that are sold or given away in bags or other containers. A common use of bagged sludge solids is in home gardens, or at parks and golf courses. They identify the amounts of pollutants that can be applied to a site in one year.

Example 5.10 CALCULATION OF THE ANNUAL WHOLE SLUDGE APPLICATION RATE (AWSAR)

Sewage sludge to be applied to land contains the 8 of the 9 regulated metals. The pollutant concentrations (mg/kg dry weight) are given in the table below. The APLR values come from Table 5.8.

The Annual Whole Sludge Application Rate (AWSAR) for each pollutant is calculated using

$$AWSAR = \frac{APLR}{0.001C}$$

where AWSAR = Annual whole sludge application rate (tonne dry sludge/ha-yr)
APLR = Annual pollutant loading rate (kg/ha-yr)
C = Metal concentration (mg metal/kg dry sludge)
0.001 = conversion factor (1000 kg = 1 tonne)

The AWSAR for the sludge is the lowest of the individual AWSARs calculated for the 10 regulated metals. The lowest AWSAR is copper (Cu). The limit is 20 tonne/ha-yr (410 lb/ft^2-yr).

	Metal conc. (mg/kg)	**APLR (kg/ha-yr)**	**AWSAR = APLR/0.001C (tonne/ha-yr)**
Arsenic	10	2.0	2/(10 × 0.001) = 200
Cadmium	10	1.9	1.9/(10 × 0.001) = 190
Chromium	1,000	150	150/(1,000 × 0.001) = 150
Copper	3,750	75	75/(3,750 × 0.001) = 20
Lead	150	15	15/(150 × 0.001) = 100
Mercury	2	0.85	0.85/(2 × 0.001) = 425
Nickel	100	21	21/(100 × 0.001) = 210
Selenium	15	5.0	5/(15 × 0.001) = 333
Zinc	2,000	140	140/(2,000 × 0.001) = 70

Table 5.9 Annual whole sludge application rate (AWSAR) calculations

5.10.4 The Risk Assessment Assumptions

The chapter introduction stated that the simplified model of the real world that we call risk assessment relies on many assumptions and subjective judgments. The models are vulnerable to error caused by gaps between the model and reality.

The land application risk analysis offers interesting points for discussion because there are multiple pathways and multiple pollutants and the fate of metals in soils is complicated. The available data is often less than one would like, leading to numerous assumptions and approximations.

The following are considered to be weaknesses in the EPA's risk assessment method (Harrison et al.1999).

Cancer risk was determined to be the most significant risk and the acceptable level was set at 1 in 10,000. The drinking water standards use a risk level of 1 in 1,000,000.

The risk assessment does not take into account the additive risk of exposure by multiple pathways, such as drinking water plus vegetables grown in sludge-amended soil. Likewise, it does not take into account the additive risk of consuming more than one of the regulated metals. Each may be at a no effect level, but this may not be true for the combination. The risk was calculated using the 'acceptable risk' for individual pathways and individual metals. An additive approach is usually used in other situations.

The regulations allow sludge application until each metal reaches the maximum level. The groundwater level could be pushed to the maximum along with the level on cropland. Without a very strong understanding of the pathways and processes, allowing the pollutants to reach maximum acceptable levels may be unwise.

As our understanding of pathways and impacts increases it may be desirable to reduce the acceptable values. (Levels for lead have decreased over the years.) Once the metals are in the soil, remediation is difficult.

The groundwater pathway is to protect a shallow well immediately downstream of a sludge field. The calculation assumes a large reduction of the peak metal concentration, through dilution or soil attenuation, by the time the leachate reaches the well. Groundwater contamination may be of concern where land spreading covers large areas, but not in the home garden setting.

The potential for a child to ingest sludge is much greater for sludge used by residential gardens that for sludge applied to field corn and the restrictions could be adjusted for this. At this time, an EQ sludge can be applied without any record keeping.

The ingestion rates may be too low. The soil ingestion rate of a child was taken as 200 mg/day (about the weight of an aspirin tablet). This may be low, and there may be inadvertent ingestion through a lifetime. There are estimates of 50–200 mg/day ingestion for adults.

Plant uptake of metals depends on soil pH, soil moisture, cation-exchange capacity, and other factors. It can be highly variable and it is not well understood. (Cadmium uptake rates used by the EPA vary by a factor of 10,000.)

Synthetic organic chemicals and radioactivity are not considered.

5.11 Conclusion

These are some general lessons regarding toxic chemicals in the environment.

The possible pathways through the environment are so subtle and numerous that even when we are alert to possible harmful effects we may not correctly predict where and when the substance could reach a harmful level.

We can use analogy and similarity between chemical families to try and foresee troublesome environmental routes, but we dare not rely only on these analogies to suggest that a substance is safe.

We can make statements about the concentration of materials in a local environment, or about the solubility of a substance, but the dynamic character of the environment makes it risky to assume equilibrium conditions or uniform distributions.

6 Waterborne Microbial Diseases

6.1 Promoting Public Health and Happiness

The World Health Organization (WHO) defines health as a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity. Access to safe drinking water is fundamental for health and happiness, a basic human right, and a component of effective policy for health protection.

The routes of disease transmission are broken by sanitation in food processing, wastewater treatment to reduce the pathogen discharge into rivers and lakes, filtration and disinfection of drinking water to kill pathogens, and managing the water cycle to protect sources of drinking water.

Safe drinking water presents no significant risk to health over a lifetime of consumption, including groups with different sensitivities. Those at greatest risk of waterborne disease are infants and young children, people who are debilitated or living under unsanitary conditions and the elderly.

A properly designed and well-operated drinking water treatment system is in force one hundred percent of the time for everyone in the service area. It will simultaneously protect all consumers against many different kinds of pathogens, including threats that may be unidentified.

6.2 An Important Public Health Event

A cholera epidemic in London in 1854 led to the discovery by Dr. John Snow that disease could be spread by contaminated water. The germ theory of disease had not yet been developed, so Snow did not understand the mechanism by which the disease was transmitted. He was a skeptic of the then-dominant miasma theory that stated that diseases such as cholera and bubonic plague were caused by a noxious form of “bad air”. His simple, but brilliant, removal of the handle to the Broad Street water pump stopped the epidemic.

His observation of the evidence led him to discount the theory of foul air. In 1849 he published his theory in an essay, *On the Mode of Communication of Cholera*, in which he stated these conclusions about cholera.

- Cholera was not likely transmitted through the air via miasmas.
- Cholera was likely transmitted through something eaten or drunk.
- The ferocious diarrhea that characterized cholera was likely a factor in the spread.
- Pollution of wells and other water supplies produced outbreaks.
- Cholera was likely due to some parasite or other tiny germ.

Snow wrote in a letter to the editor of the Medical Times and Gazette:

> "…I found that nearly all the deaths had taken place within a short distance of the [Broad Street] pump. There were only ten deaths in houses situated decidedly nearer to another street-pump. In five of these cases the families of the deceased persons informed me that they always went to the pump in Broad Street, as they preferred the water to that of the pumps which were nearer. In three other cases, the deceased were children who went to school near the pump in Broad Street…
>
> With regard to the deaths occurring in the locality belonging to the pump, there were 61 instances in which I was informed that the deceased persons used to drink the pump water from Broad Street, either constantly or occasionally…
>
> The result of the inquiry, then, is, that there has been no particular outbreak or prevalence of cholera in this part of London except among the persons who were in the habit of drinking the water of the above-mentioned pump well.
>
> I had an interview with the Board of Guardians of St James's parish, on the evening of the 7th inst [Sept 7], and represented the above circumstances to them. In consequence of what I said, the handle of the pump was removed on the following day."

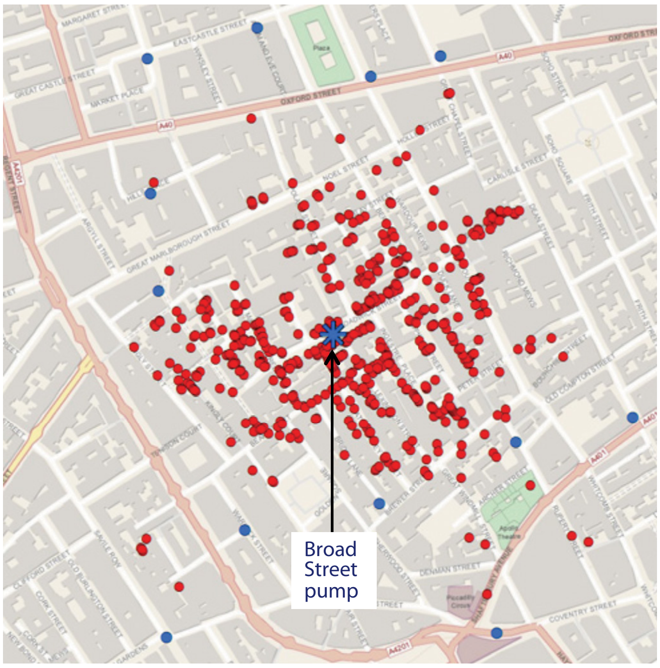
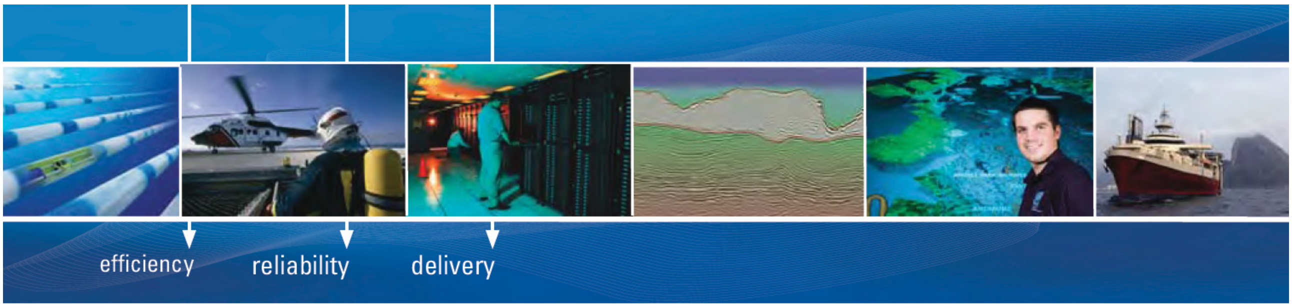


Figure 6.1 A colorized version of the original map by John Snow showing the clusters of cholera cases (red dots) in the London epidemic of 1854 and the locations of wells in the neighborhood. The Broad Street well is the blue dot at the center of the cluster. This well was the source of the cholera infection.

Snow used a dot map (Figure 6.1 is a modern version) to illustrate the cluster of cholera cases around the pump. His use of statistics to illustrate the connection between the water source and cholera cases was a major event in the history of public health and geography. It is the founding event of the science of epidemiology.

Cholera is an infectious disease that affects the absorption of water in the small intestine. It is caused by the bacterium, *Vibrio cholera*. In severe cases it produces violent diarrhea within only a few days. The dangerous aspect of cholera is the vast and rapid loss of fluid that if untreated can be fatal within 24 hours of developing the disease. Treatment is simple: replace the fluid with the right mix of sugar and salts – water alone is not adequately absorbed. Bad cases require admission to hospital where fluids can be administered straight into the bloodstream via a drip. Cholera is related to standards of hygiene and the quality of drinking water. This is true of many other serious diseases. Improved sanitation and hygiene are still the basic foundation of the fight against waterborne diseases. It is more cost-effective than putting people in hospitals.

Waterborne disease was still a problem in the United States in the early 1900s. One in 10 infants died in their first year of life from typhoid fever or diarrheal disease, including cholera. One cause was known to be unsafe water and chlorine was thought to be the solution. John Snow had used chlorine in London and the first patent for a chlorination system in the U.S. was granted in 1888.



But how much chlorine? A dose that would make water safe in one location would be too weak in another. Abel Wolman worked out the chemistry that let treatment plant operators inject the effective dose of chlorine and chlorination rapidly became a widespread practice (Okun 1971). The number of typhoid cases fell from 16.2 per 100,000 in 1913 to 2.5 in 1936. It has been estimated that chlorination has saved 179 million lives.

6.3 Water-borne Infectious Microorganisms

Fortunately, most bacteria and other microbes do not cause disease. Most – in the sense of number of species and mass – are beneficial.

‘You are mostly not you. That is to say, 90 percent of the cells residing in your body are not human cells. They are microbes…. These bacteria that live on us and in us, aid our digestion and help defend us from pathogens. A healthy biota in our guts make the pH inhospitable and even toxic to many pathogens (Buhler 2011).’

This section is mostly about water-borne bacterial disease, with brief attention to a few viruses and protozoans. Water-related parasitic diseases, like malaria, yellow fever, schistosomiasis (bilharzia), and trypanosome, are not discussed.

The human body is a comfortable environment for many pathogens, especially those of the gastrointestinal tract that pass from infected individuals into the food supply or water supply and cause disease when exposure exceeds a person’s limit of tolerance. Most pathogens do not survive long once outside the body, but they may live long enough to be transmitted to a new host. To prevent disease we must block transmission, increase the rate of pathogen die-off and dilution, and effectively kill the pathogens. Water borne pathogens can infect thousands of people simultaneously, which creates an unmanageable burden for health care facilities. Engineered preventive medicine is much preferred to letting people get sick and then hoping that the medical profession can cure them.

Organism	Reason for concern
Protozoan pathogens	
Endamoeba hystolytica	Amoebic dysentery. Endemic cases are by personal contact, food, and possibly flies. Rare epidemics are waterborne.
Cryptosporidium parvum	Cryptosporidiosis is an acute gastrointestinal illness, including diarrhea, nausea, and stomach cramps. As few as 30 oocysts can cause infection. Can be fatal in individuals with weakened immune systems. Waterborne from animals to man. Cysts are resistant to chlorination, but they can be removed from water by coagulation-sedimentation-filtration.
Giardia duodenalis	Formerly known as *Giardia lamblia*. Giardiasis causes diarrhea. Waterborne from animals (beavers, cats, dogs, sheep) to man. Forms cysts that are resistant to chlorination. As few as 10 to 25 cysts can cause infection, but they can be removed from water by coagulation-sedimentation-filtration.
Bacterial pathogens	
Escherichia coli	There are several strains of *E. coli* that cause diarrhea. *E. coli* O157:H7 causes hemorrhagic colitis that can be fatal.
Leptospira sp.	Causes Leptospirosis, a flu-like disease in the early stages, which may become more serious and even fatal in advanced cases. Transmitted via animal urine. Can be waterborne.
Salmonella typhi	Typhoid fever. Only lives in humans. Spread only fecally-orally via food and water. Infectious dose is below 1000 organisms and may be below 10 organisms.
Salmonella paratyphi	Paratyphoid fever. Only lives in humans. Spread only fecally-orally via food and water.
Shigella dysenteriae	Causes severe and possibly fatal diarrhea only in humans and primates. Highly infectious by fecal-oral route via water, milk, food, flies, or direct contact. Up to 109 viable organisms per gram of feces in the early stages of infection.
Vibrio cholera	Cholera. Initial wave of epidemic is waterborne; secondary cases by contact, food, flies.
Viral pathogens	
Poliovirus	Infectious dose is around 10^5 to 10^6 infectious particles. Causes aseptic meningitis, encephalitis, and paralytic poliomyelitis. Infection is usually by ingestion of fecally contaminated material.
Hepatitis A	Viral hepatitis – liver damage. Humans are considered the only host.
Hepatitis E	Viruses are acquired orally. Hepatitis E appears to be exclusively spread by drinking water
Rotavirus, Adenovirus	Viral gastroenteritis causes 3 to 5 billion cases and up to 10 million deaths per year, mostly in infants and young children due to dehydration from to diarrhea and vomiting.
Enterovirus	Subgroups are Poliovirus, Coxsackie virus A & B, Echovirus, and Enterovirus.

Table 6.1 Pathogenic organisms in water and sewage (WHO 2011).

It has been estimated that known pathogens accounted for an estimated 38.6 million illnesses each year in the United States due to known pathogens from all exposures, including food, water and other routes. It was estimated that 5.2 million cases are from bacterial pathogens; 2.5 million are due to parasites, and 30.9 million due to viral pathogens (Soller 2006, USEPA 2010).

Of those 38.6 million, 13.8 million were thought to be foodborne, leaving 24.8 million illnesses that were due to waterborne routes and other exposures. About 9% were protozoans (Cryptosporidium and Giardia), which are waterborne. Less than 3% were due to bacterial infection, and the rest were viral diseases (55.6% Norwalk-like viruses, and 15.6% Rotavirus). Norwalk viruses are transmitted by fecally contaminated food or water, and by person-to-person contact, and via aerosols. They are the most common cause of viral gastroenteritis. Rotavirus enters the body through the mouth via contaminated food or water, and is easily spread by contaminated objects, such as hands and toys. It is very contagious and spreads from child-to-child.

Table 6.1 lists bacteria, viruses, and protozoans that must be controlled in order to have safe drinking water. The WHO Guidelines (2011) include fact sheets on these organisms that explain their role in water-borne disease.

Waterborne transmission of the pathogens listed has been confirmed by epidemiological studies and case histories. Part of the demonstration of pathogenicity involves reproducing the disease in suitable hosts. Experimental studies in which volunteers are exposed to known numbers of pathogens provide relative information. As most studies are done with healthy adult volunteers, such data are applicable to only a part of the exposed population, and extrapolation to more sensitive groups is an issue that remains to be studied in more detail.

6.4 Risk Assessment for Pathogenic Organisms

The WHO Guidelines for Drinking-water Quality (WHO 2011) explain how the risk assessment methods behind the guidelines for microbiological quality bring together the data collected on pathogen exposure, dose-response, severity and disease burden.

The use of 'guidelines', as opposed to 'standards' or 'mandatory limits', is in recognition that while the minimum requirements for safety are universal, the nature and form of drinking water standards may vary among countries.

Risk assessment for pathogenic organisms is not as well developed a science as risk assessment for carcinogens and other toxic chemicals. The infective dose is hard to determine, but estimates have been made.

Pathogen doses are inherently discrete. Chemical doses are expressed in mass units (e.g., mg/kg or mg/L). Pathogen doses are expressed as counts of organisms per volume of water (e.g., count/liter) or as an average dose.

Drinking water exposures are usually low, often below 0.0001 organisms per liter. For low exposure, the maximum risk of infection is related to the probability of exposure. If the average dose was 0.0001 and the pathogen was 100% effective in causing an infection, one individual out of 10,000 exposed would become infected, on average.

The organism count has a distribution of values. Not every liter of water contains the average count; some contain more and some less. The distribution of counts often has a *Poisson* probability distribution. This means that for an average dose of 0.5 organisms per liter, 60% of one-liter portions contain no organisms, 30% contain a single organism, and 10% contain 2 or more.

The *exponential* model estimates the probability of being infected from ingestion of one organism as

$$p(d) = 1 - e^{-rd}$$

where $p(d)$ = cumulative probability of infection for dose d in the exposed population
d = average pathogen dose in infectious units (organisms)
r = probability of infection given ingestion of one organism

The *Beta-Poisson* model predicts

$$p(d) = 1 - (1 + d/\quad)^{-}$$

where $p(d)$ and d are as defined above, and α and β are parameters that are used to fit the model to the data. Infectivity is larger when α and β are large.

Values for r, α and β are given in Table 6.2 along with the probability of being infected by exposure to a single organism and the exposure that is predicted to cause a 1% risk of infection.

Microorganism	α	β	**Probability of infection from exposure to 1 organism**	**Dose that infects 1% of exposed individuals**
Beta-Poisson Model				
Campylobacter jenuni	0.145	7.59	0.0178	0.6
Salmonella (non-typhoid)	0.1324	51.45	0.0025	4.1
Salmonella typhi	0.1086	6,097	0.000,018	590
Shigella	0.21	42.9	0.0048	2.1
Vibrio cholera	0.25	16.2	0.015	0.6
Poliovirus 1	0.1097	1524	0.000,0072	0.67
Poliovirus 3	0.409	0.788	0.285	0.20
Echovirus 12	1.3	75	0.017	0.06
Rotavirus	0.2531	0.4265	0.236	0.02
Entamoeba histolytica	13.3	39.7	0.282	0.04
Cryptosporidium p.	0.06	0.095	0.1364	0.02
Exponential Model				
Cryptosporidium parvum	r = 00042			
Giardia lamblia	r = 0.0199		0.020	0.5
Hepatitus A virus	r = 0.5486		0.422	0.18
Legionella	r = 0.06		0.058	0.17

Table 6.2 Probability of infection for some pathogenic microorganisms. (USEPA 2012).

Example 6.1 Risk of infection from *Rotavirus* using the Beta-Poisson model.

Calculate the risk of infection from ingesting one *Rotavirus* organism using the Beta-Poisson model with $\alpha = 0.2531$ and $\beta = 0.4265$ from Table 6.2, the model is

$$p(d) = 1 - \left(1 + \frac{d}{0.4265}\right)^{-0.2531}$$

The probability of infection for $d = 1$ organism is

$$p(d) = 1 - \left(1 + \frac{1}{0.4265}\right)^{-0.2531} = 0.263$$

Figure 6.2 was generated using this model over a wide range of doses.

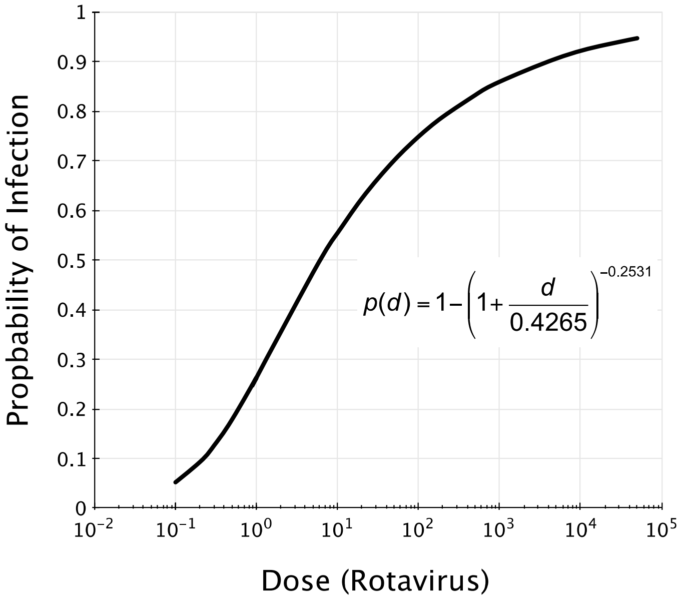


Figure 6.2 Probability of infection by Rotavirus as predicted by the Beta-Poisson model

The probability of infection can be estimated as the product of the exposure from drinking water and the probability that exposure to one organism would result in infection. Not all infected individuals will develop clinical illness; asymptomatic infection is common for most pathogens. The percentage of infected persons that will develop clinical illness depends on the pathogen, but also on other factors, such as the immune status of the host.

6.5 The DALY Metric for Evaluating Public Health Risk

WHO (2011) has used DALYs to evaluate public health priorities. A DALY is a Disability Adjusted Life Year and it is equivalent to one year of healthy life lost due to a health condition. It aggregates different effects and combines quality and quantity of life. It focuses on actual rather than potential hazards and promotes rational public health priority setting. The difficulties in using DALYs relate to availability of data on exposure and on epidemiological associations.

The basic principle of the DALY is to weight each health effect for its severity from 0 (normal good health) to 1 (death). This weight is multiplied by the duration of the effect and by the number of people affected by a particular outcome. It is then possible to sum the effects of all different outcomes due to a particular agent. The duration is the time during which disease is apparent. When the outcome is death, the "duration" is the remaining life expectancy.

The DALY is the sum of years of life lost by premature mortality (YLL) and years lived with a disability (YLD), which are standardized by means of severity weights. Thus:

$$\text{DALY} = \text{YLL} + \text{YLD}$$

This reflects the acute end-points (e.g., diarrhoeal illness) and also mortality and the effects of more serious end-points. Disease burden per case varies widely. For example, the disease burden per 1000 cases of rotavirus diarrhea is 480 DALYs in low-income regions, where child mortality is frequent, but only 14 DALYs per 1000 cases in high-income regions where hospital facilities are accessible to the great majority of the population.

Condition	***Cryptosporidium***	***Campylobacter***	**Rotavirus**[a]
Health outcome target	10^{-6} DALYs per person per year	10^{-6} DALYs per person per year	10^{-6} DALYs per person per year
Raw water quality	10 org/L	100 org/L	10 org/L
% reduction by water purification	99.994%	99.99987%	99.99968%
Drinking-water quality	1 per 1600 L	1 per 1800 L	1 per 32,000 L
Consumption of untreated water	1 L/d	1 L/d	1 L/d
Exposure by drinking-water	0.00063 org/day	0.00056 org/day	0.000032 org/day
Probability of infection per organism	0.004/organism	0.018/organism	0.27/organism
Risk of infection	0.00092 per year	0.00083 per year	0.0031 per year
Risk of diarrhoeal illness given infection	0.7	0.3	0.5
Risk of diarrhoeal illness	0.00064 cases per yr	0.00025 cases per yr	0.0016 cases per yr
Diseases burden per case	0.0015 DALYs/case	0.0046 DALYs/case	0.14 DALYs/case
Susceptible % of population	100%	100%	6%
Disease burden per year	$1x10^{-6}$ DALYs/yr	$1x10^{-6}$ DALYs/yr	$1x10^{-6}$ DALYs/yr

[a] Data from high-income regions. In low-income regions, severity is typically higher, but drinking-water transmission is unlikely to dominate.

Table 6.3 Method for linking tolerable disease burden and source water quality for reference pathogens: example calculation for an acceptable disease burden of 1×10^{-6} DALYs per year. No accounting is made for effects on immune-compromised persons (e.g., cryptosporidiosis in HIV/AIDS patients), which is significant in some countries.

Example 6.2 Risk of illness for *Cryptosporidium*

The numbers in Table 6.3 can be interpreted to represent the probability that a single individual will develop illness in a given year. For example, a risk of diarrhoeal illness for *Cryptosporidium p.* of 0.00064 per year indicates that, on average, 1 out of 1560 consumers would contract Cryptosporidiosis from drinking water, assuming the raw water quality of 10 organisms per liter.

A few of the calculations are:

Risk of infection per year = (365 day/yr)(0.00063 org/day)(0.004/org) = 0.00092 per year
Risk of diarrhoeal illness = 0.7(0.00092 per year) = 0.00064 per year
Disease burden = (0.00064 per year)(0.0015 DALYS per case) = 1×10^{-6} DALYs per year

6.6 Drinking Water Treatment and Disinfection

We do not like to think of our drinking water as recycled sewage, but most of it has been used many times. The reuse cycle is to take water from a river, lake or well, treat it in a drinking water purification plant, process the used water through a wastewater treatment plant, discharge the treated effluent (usually to a river where additional purification occurs), and once again through a drinking water purification plant. Wastewater treatment and drinking water treatment both include disinfection. Disinfection is not sterilization; it is not designed to kill all microorganisms in the water.

Public water supplies were always desired by cities but drinking water treatment to prevent disease was not common until nearly the 20th century. Until 1870 no water filtration plants existed in the United States. In the 1870s, slow sand filters were built in Poughkeepsie and Hudson, NY, followed by those at Lawrence, MA in 1893. Slow sand filters will remove bacteria, protozoa, parasites, and also turbidity. By 1897, 100 more slow sand filters had been built, and by 1925, 587 rapid sand filters and more than 1090 slow sand filters were delivering about 19 million m^3/d (5 billion gallons per day) of safe water to city dwellers. This greatly reduced the incidence of diseases like cholera, typhoid fever, and dysentery among the people served.

At the turn of the 20th century a great step forward came about through chlorination for bacterial disinfection. Chlorination does not kill all microorganisms in water, but it is very effective against water-borne pathogenic bacteria and viruses. Chlorination subsequently became the universal resort of the sanitarian, both in water and sewage treatment. Pasteurization of milk became widely used at about the same time. The dramatic historical decrease in typhoid fever is due to these two factors.

Drinking water purification involves a sequence of steps to remove turbidity, hardness, or unpleasant tastes and odors. The final step before distribution to the consumer is disinfection, usually with chlorine. Water that is safe for drinking when it leaves the treatment plant has to be kept safe until it reaches the consumer. A low concentration of chlorine is maintained in the water as it travels through the mains to protect against recontamination.

Disinfection effectiveness depends on the form and concentration of chlorine, time of contact, pH and temperature of the water, and species of organism to be inactivated. Most important is the time-concentration (*Ct*) factor. This is captured in Chick's Law (Chick 1908, Okun 1971). Chick's law defines the fraction of organisms inactivated as

$$\frac{N_t}{N_0} = e^{-kCt} \quad \text{and} \quad N_t = N_0 e^{-kCt}$$

N_t and N_0 are the bacterial concentrations at times t and $t = 0$, C is the disinfectant concentration or intensity, t is the time of contact or exposure to the disinfectant, and k is a rate coefficient that depends on temperature, pH, and type of organism.

For a contact basin of fixed volume (fixed contact time) the most practical control is variation of the concentration or intensity. The job can be done with intense exposure (high concentration of chlorine or intense UV radiation) and a short contact time, or with low exposure for a longer time. Figure 6.3 shows the *Ct* requirements for 99% kill of bacteria, virus and protozoa. Table 6.4 provides more detailed information. Higher pH requires a higher *Ct* ; lower temperature requires a higher *Ct*.

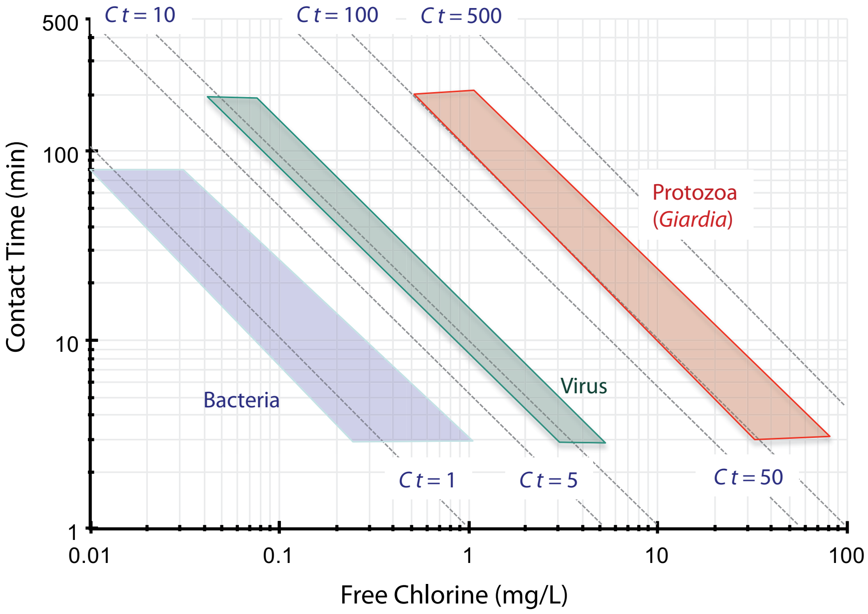


Figure 6.3 The colored bands show the Ct required for 99% kill or inactivation of bacteria, virus and protozoans. Cryptosporidium is not inactivated at these conditions.

Chlorine (Cl_2) is applied as a gas dissolved in water. The Cl_2 reacts with water to form hypochlorous acid (HOCl) and hypochlorite (OCl^-). Both forms, known as free chlorine, are powerful disinfectants.

Free chlorine will react with ammonia to form the chloramines, NH_2Cl and $NHCl_2$. These are called combined chlorine. Combined chlorine is a less powerful disinfectant than free chlorine, but it is more persistent and this makes it desirable as a residual in the water distribution system.

Treatment Process	**Enteric Pathogen**	**Percent Removal**		
Membrane Filtration				
Microfiltration	Bacteria	99.9%–99.99%,		
	Viruses	< 90%		
	Protozoa	99.9–99.99%		
Ultrafiltration	Bacteria	Complete removal with adequate membrane integrity		
Nanofiltration &	Viruses	Complete removal with adequate membrane integrity		
	Protozoa	Complete removal with adequate membrane integrity		
Reverse Osmosis				
Disinfection		**(*Ct* for 99% inactivation (mg-min/L)**		
		Ct	**Temp. (°C)**	**pH**
Chlorine	Bacteria	0.08	1–2	
		3.3	1–2	8.5
	Viruses	12	0–5	7–7.5
		8	10	7–7.5
	Protozoa (*Giardia*)	230	5	7–7.5
		100	10	7–7.5
	Cryptosporidium		not killed	
Monochloramine	Bacteria	94	1–2	7
		278	1–2	8.5
	Viruses	1240	1	6–9
		430	15	6–9
	Protozoa (*Giardia*)	2550	1	6
		1000	15	6
	Cryptosporidium		not inactivated	
Ozone	Bacteria	0.02	5	6–7
	Viruses	0.9	1	6–7
		0.3	15	6–7
	Protozoa (*Giardia*)	1.9	1	6–9
		0.63	15	6–9
	Cryptosporidium	40	1	6–9
		4.4	22	6–9
UV radiation			**Radiation for 99% inactivation**	
	Bacteria		7mJ/cm^2	
	Viruses		59mJ/cm^2	
	Protozoa (*Giardia*)		5mJ/cm^2	
	Cryptosporidium		10mJ/cm^2	

Table 6.4 Reduction of bacteria, viruses and protozoa achieved by chlorination and membrane processes. *Ct* is the product of disinfectant concentration (mg/L) and contact time (min). Inactivation is directly proportional to the *Ct* values. *Ct* and UV radiation levels apply to microorganisms in suspension, not embedded in particles.

Example 6.3 *Ct* VALUES AS A FUNCTION OF TEMPERATURE.

Inactivation is proportional to *Ct*. Table 6.4 indicates that 99% inactivation of *Giardia* with ozone when pH is in the range of 6-9 requires $Ct = 1.9$ at 1°C and $Ct = 0.63$ at 15°C.

For an ozone contact chamber of fixed contact time *t* the ozone concentration at 1°C must be 3 times larger than at 15°C to achieve 99% inactivation.

$$\frac{Ct_{1°C}}{Ct_{15°C}} = \frac{1.9}{0.63} = 3.0$$

Example 6.4 CHICK'S LAW FOR DISINFECTION.

Estimate the *Ct* value for ozone that will give 99.9% and 99.99% inactivation of *Giardia* at 1°C. The required condition is $Ct = 1.9$ at 1°C and pH 6-9.

Chick's Law $\frac{N_t}{N_0} = e^{-kCt}$ can be rewritten as $\ln\left(\frac{N_t}{N_0}\right) = -kCt$

For 99% inactivation, $N_t/N_0 = 0.01$

$$\ln(0.01) = -4.605 = -kCt = -1.9k$$
$$k = 2.4237 \text{ (mg/L – min)}^{-1}$$

For 99.9% inactivation, $N_t/N_0 = 0.001$

$$\ln(0.001) = -6.908 = -2.4234Ct$$
$$Ct = 2.84 \text{ mg/L – min}$$

For 99.99% inactivation, or $N_t/N_0 = 0.0001$

$$\ln(0.0002) = -9.210 = -2.4234Ct$$
$$Ct = 3.8 \text{ mg/L – min}$$

6.7 Animal Waste Management

Animal waste contamination of drinking water and recreational water is a serious threat in many parts of the world, including the many rich agricultural areas of the United States. Animal waste management has often been careless but new awareness of the transmission of disease, especially protozoans like *Cryptosporidium*, make this an important problem.

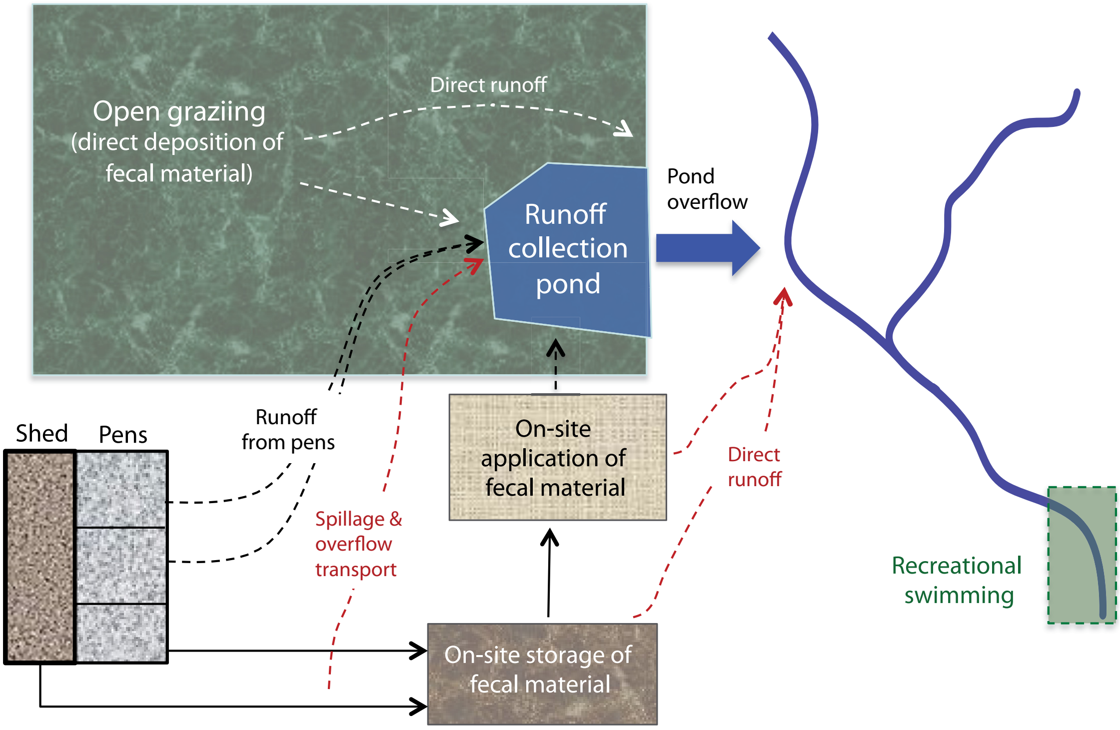


Figure 6.4 Animal husbandry can contribute pathogens by direct contamination by animals in the water body as well as runoff from pens, storage ponds and cropland. The on-site storage of manure, the runoff collection pond, and a green buffer zone between the stream and the source area help to reduce pollution.

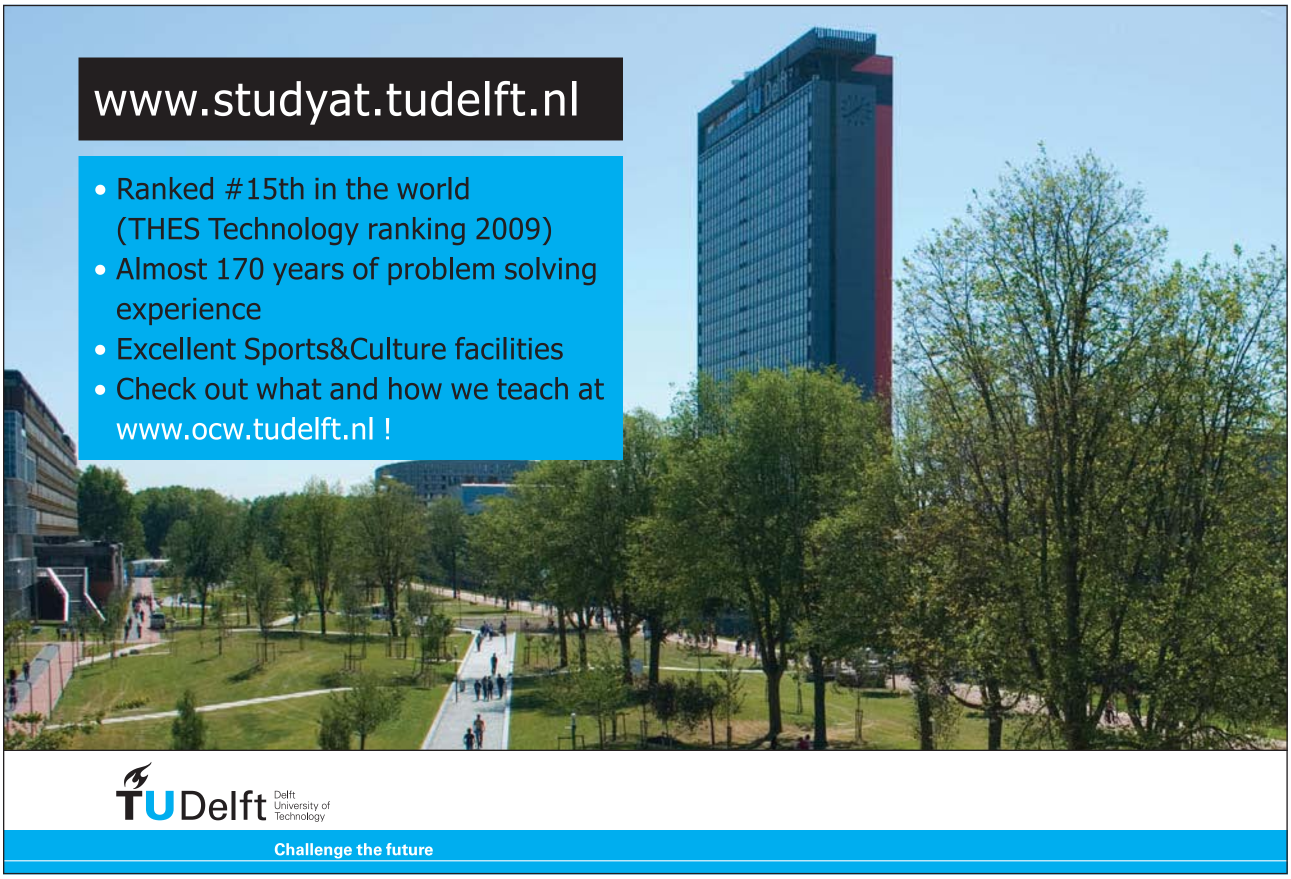


Figure 6.4 shows stream-loading scenarios from livestock pens and pasture. Direct contamination occurs when fresh undiluted fecal material is deposited into a water body. Indirect contamination occurs during transport from adjacent land into a water body via rainfall runoff. The distinction between direct and indirect contamination is that the source material for direct contamination is feces from an individual or individuals; for indirect contamination the source material of interest is a composite of many animals.

Quantitative risk assessment on freshwater impacted by agricultural sources of fecal contamination assumed that fresh cattle manure, pig slurry, and poultry litter (fecal materials) are land-applied at standard agronomic (maximum U.S. allowable) rates adjacent to a freshwater beach; pathogens from the fresh land-applied fecal materials reach the freshwater beach via runoff from an intense rainfall event. There is primary contact recreation (e.g., swimming) in the undiluted runoff; and exposure to reference pathogens occurs through water ingestion during recreation. Taken together, these conditions maximize the risk of infection.

The load of organisms entering a water body is estimated for each pathogenic species or indicator organism of interest using

$$N_i = \frac{f_i n_i M_{manure}}{V_{runoff}}$$

where N_i = density of organism i in runoff water (organisms/volume)
V_{Runoff} = net runoff during the storm event (volume)
f_i = fraction of organism i on land mobilized during the entire event
n_i = density of organism i in the land-applied manure (organisms/mass)
M_{manure} = mass of manure applied to the plot generating the runoff

This mass of organisms is used to estimate a concentration at the swimming area. The runoff is diluted in the stream or lake and there will be some die-off between the point of entry and the swimming area. The resulting concentration, along with the volume of water ingested by a swimmer (Figure 6.5), gives the dose that would be used to estimate the cumulative risk of infection in the exposed population. The risk is calculated using the Beta-Poisson dose-response model as illustrated in Section 6.4.

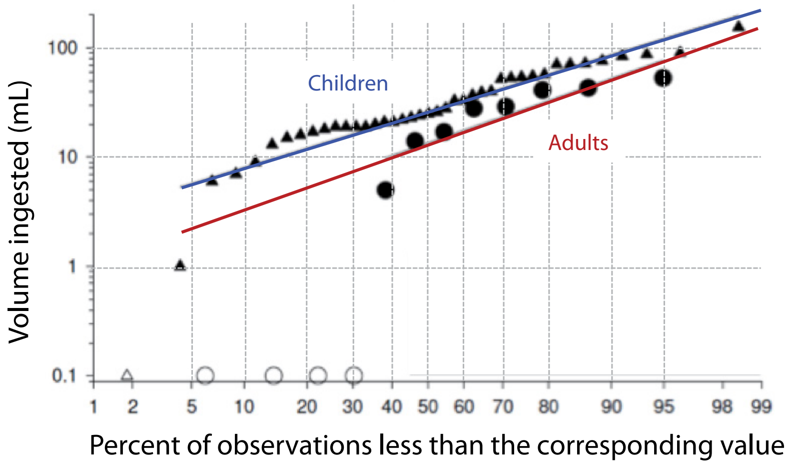


Figure 6.5 Distribution of the volume of water ingested by swimmers during 45 minutes of activity. 80% of children ingested more than 10 mL of water, 60% ingested more than 20 mL, and 20 % ingested more than 50 mL. (Source USEPA 2010)

The mass of manure applied to the land and the net runoff during the storm are known more precisely than the other values. The density of organisms and species depends on the kind of animals and their pathogen shedding abundance. The fraction of organisms mobilized depends on the rainfall intensity, rainfall duration, antecedent soil moisture, how the manure was incorporated into the soil, and vegetation protecting the soil and the stream bank.

A single value estimate of the risk of infection has little meaning in the face of so many highly variable factors (rainfall, manure applications, amount of runoff, etc.) and so many uncertainties in microbial densities, fraction mobilized, die-off, dilution, and the like. A useful approach to risk assessment in this situation is to calculate thousands of risk estimates using values selected at random from the range of realistic possibilities. This method is called Monte Carlo simulation because the element of random selection in each estimation can be imagined as a computerized spin of a roulette wheel or a toss of the dice. Sometimes you lose and get sick – sometimes you win and stay healthy.

The Monte Carlo results shown in Figure 6.6 are the additive risks due the five major pathogens (*E. coli* 0157, *Campylobacter*, *Salmonella*, *Cryptosporidium*, and *Giardia*). The horizontal line is the risk of infection (about 1 in 50) for the current recreational water quality criteria.

The bars in the boxes indicate the median of all the simulated estimates, which are about 0.0001 for chicken litter, 0.01 for pig slurry, and about 0.02 for cattle manure. The boxes bound the middle 50% of the simulated values. The bars on the extended lines bound 99% of the estimated values.

The analysis shows that there is about a 40% chance that the current recreational water quality criteria (RWAC) will be exceeded for cattle manure. The probability of exceeding the RWAC is roughly 25% for pig slurry, and perhaps 5% chance for chicken litter.

If these odds are unacceptable then better management methods are needed for handling animal manure.

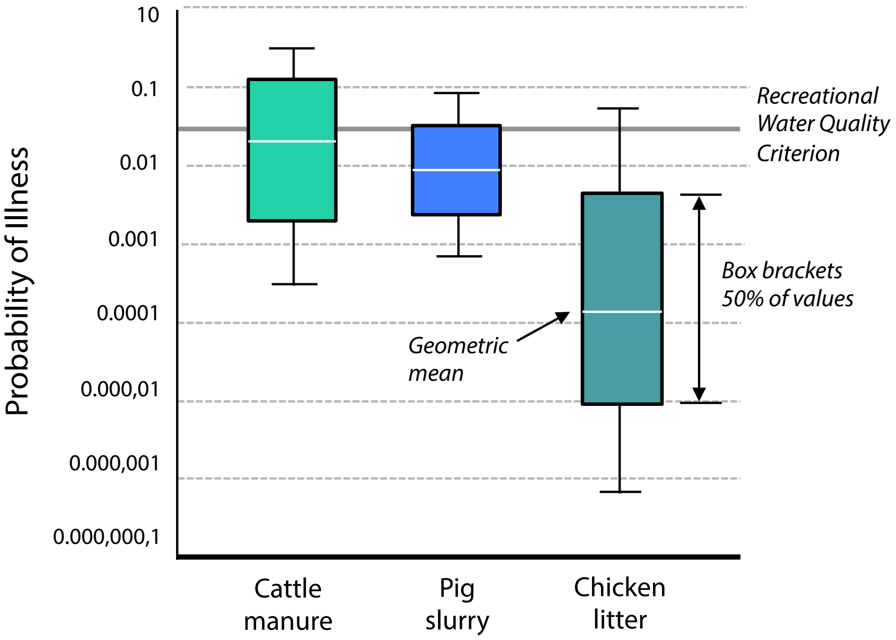


Figure 6.6 Risks estimates from a Monte Carlo simulation for the five major pathogens in recreational water contamination by pig, cattle, and chicken manure. The horizontal line is the risk of infection for the current recreational water quality criteria. The bars in the boxes indicate the median values, the boxes bound the middle 50% of the estimated values, and the bars on the extended lines bound 99% of the estimated values. (USEPA 2010)

6.8 Natural Die-Off of Microorganisms

The purity of drinking water in United States cities is so excellent it is easy to overlook the need for protecting water supplies in rural areas, and this includes vast parts of the world where safe drinking water is lacking and where even a decent volume of contaminated water may come at a high price. Contamination by animals can be a serious problem, and the microbial agents of disease, once in a water supply can persist. Table 6.5 summarizes some of these concerns.

Pathogen	**Health significance**	**Persistence in water supplies**	**Resistance to chlorine**	**Relative infectivity**	**Important animal source**
Bacteria					
Campylobacter jejuni, C. coli	High	Moderate	Low	Moderate	Yes
Escherichia coli (pathogenic)	High	Moderate	Low	Low	Yes
E. coli – Enterohaemorrhagic	High	Moderate	Low	High	Yes
Legionella spp.(a)	High	Multiply	Low	Moderate	No
Salmonella typhi	High	Moderate	Low	Low	No
Shigella spp.	High	Short	Low	Moderate	No
Vibrio cholerae	High	Short	Low	Low	No
Yersinia enterocolitica	High	Long	Low	Low	Yes
Viruses					
Adenoviruses	High	Long	Moderate	High	No
Enteroviruses	High	Long	Moderate	High	No
Noroviruses and sapoviruses	High	Long	Moderate	High	Potentially
Rotaviruses	High	Long	Moderate	High	No
Protozoa					
Acanthamoeba spp.	High	Long	High	High	No
Cryptosporidium parvum	High	Long	High	High	Yes
Cyclospora cayetanensis	High	Long	High	High	No
Entamoeba histolytica	High	Moderate	High	High	No
Giardia duodenatis	High	Moderate	High	High	Yes
Toxoplasma gondii	High	Long	High	High	Yes
Helminths					
Dracunculus medinensis	High	Moderate	Moderate	High	No
Schistosoma spp.	High	Short	Moderate	High	Yes

(a) spp. Means species (plural)

Table 6.5 Waterborne pathogens and their significance in water supplies and recreational waters (partial list from WHO 2011)

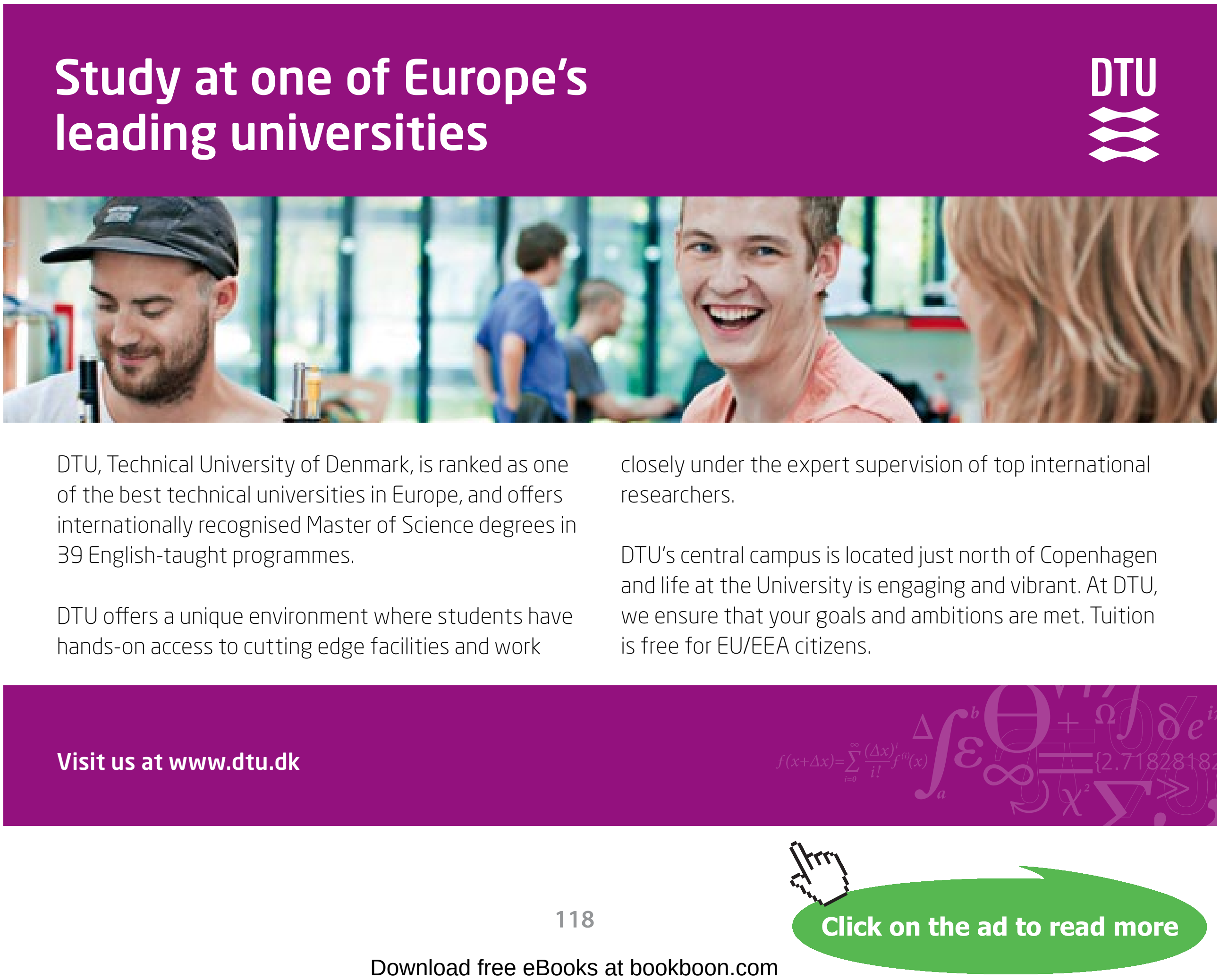
Conditions in conventional wastewater treatment processes are not hospitable to most pathogens, so they tend to die away. Disinfection of sewage effluents is required nationwide. This requirement may be waived during cold weather in northern states when contact water sports are not being enjoyed. The predominant method of wastewater disinfection is with ultraviolet light, which has mostly replaced chlorination.

Effluent discharged to a river or lake is diluted and the pathogen concentration is further decreased by die-off due to dilute food supply, cool temperature, and sunlight. Thus, wastewater treatment, dilution, and natural die-off can reduce the pathogen population to a level that leaves the water clean enough for recreational use, and clean enough to be used as a source for drinking water, provided that adequate additional water purification is done.

Enteric organisms, including the pathogens, die away in rivers and in groundwater according to the exponential model

$$C_t = C_0 e^{-K}$$

where C_0 is the count of bacteria at time $t = 0$, C_t is the count at time t, and K is the disappearance rate coefficient. A few values of K are given in Table 6.6



Microorganism	**Disappearance Rate Coefficient, *K* (1/day)**	
	In rivers	**In groundwater**
Bacteria		
E. coli	0.23–0.46	0.063–0.36
Enterococci	0.17–0.77	0.9–4.0
Faecal streptococci		0.03–0.24
Salmonella typhi		0.13–0.22
Vibrio cholera	can survive for long periods of time	
Protozoans		
Cryptosporidium sp.	0.057–0.046	
Giardia	0.023 – 0.23	
Virus		
Hepatitis A	0.05–0.2	
Rotavirus	0.24–0.48	

Table 6.6 Disappearance rate coefficients, *K*, for selected microorganisms in rivers and in neutral groundwater. (Blanc & Nasser 1996, Mathess et al. 1988)

Example 6.5 DIE-OFF OF BACTERIA IN A STREAM

Wastewater effluent containing 10,000 coli/mL is discharged to a river. The bacterial count after dilution is 4,000 coli/mL. Natural die-off occurs according to

$$C_t = 4000e^{-0.46t}$$

The coliform count downstream is

after 1 day $C_1 = 4000e^{-0.46(1)} = 2525$

after 2 days $C_2 = 4000e^{-0.46(3)} = 1594$

after 5 days $C_3 = 4000e^{-0.46(5)} = 400$

6.9 Management of Sludge Applications to Land

Land application of wastewater sludge is widely used. The pathogen levels in typical anaerobically digested sludge are: virus = 100–1,000 per 100 mL, fecal coliform bacteria = 30,000–6,000,000 per 100 mL, Salmonella bacteria = 3–60 per 100 mL. These levels can be greatly reduced by composting, or by holding the sludge at high temperature or high pH for a specified time and this broadens the possible ways for using the material as a soil amendment. The Part 503 sludge regulations specify the treatment conditions for making exceptional quality sludge that can be applied freely as a soil conditioner.

Generally these microorganisms do not leach through the soil, unless it is sandy or unless the distance between the sewage discharge and the drinking water supply is too short. Viruses are too small to be removed by filtration in soil interstices, but they will be removed by adsorption. Reduced survival is caused by high temperature, low moisture content, low organic content, high or low pH, the presence of predators, and decreased adsorption to soil particles. Following land application, a 99% reduction is expected for *Salmonella* spp. in 12 days and for fecal coliforms in 18 days.

Well water is protected by separating wells and septic tanks by at least 15 meters (50 ft), and by locating the well upstream from the septic tank (upstream as viewed by the flow of groundwater). Additional protection can be obtained by filtering the water as it leaves the tap in the home.

Protection against runoff to streams and lakes is provided by 25 m to 150 m grassy buffer strips between the treated field and the waterway.

6.10 Monitoring the Microbial Quality of Drinking Water

One might reasonably expect that the presence of pathogens would be determined by measuring the number of pathogens in samples of the drinking water. There are problems with this approach. Some pathogens are difficult to grow in the laboratory. Others can be grown and identified in the laboratory, but we have no good quantitative test for population density. Some, like Cryptosporidium spores, can be seen easily under a microscope, but we have no simple and reliable way of telling whether the spores are able to reproduce and infect. One might also question the wisdom of growing pathogens in a water purification plant laboratory.

Water safety is monitored by quantifying indicator organisms that have a life-cycle and sensitivity to environmental factors that are approximately the same as pathogens. As a practical matter, if the indicator organisms are absent in a water supply, pathogens are also absent and the water is safe to drink. The important indicator organisms are listed in Table 6.7.

Organism	Description
Coliform bacteria	A grouping of many bacteria that are commonly found in soil and in the feces of humans, birds, and animals. Used as an indicator of the hygienic quality of water. An absence of coliforms indicates a presumptive absence of pathogenic bacteria.
Escherichia coli	The predominant species of coliforms found in the human gut in temperate climates. May survive and grow in pristine waters in the tropics.
Fecal coliforms	Sub-group of coliforms that originate in the intestinal tract of warm-blooded animals. Provides a more specific indication of fecal contamination than the total coliform screening.
Fecal streptococci	Sub-group of streptococcus that originates in the intestinal tract of warm-blooded animals.
Enterovirus	Subgroups are Poliovirus, Coxsackie virus A & B, Echovirus, and Enterovirus. Relatively easily cultured markers of fecal pollution.

Table 6.7 Easily cultivated organisms that are reliable indicators of fecal contamination in water (WHO 2011).

One gram of feces from a healthy human contains billions of harmless bacteria of many different kinds and possibly some pathogenic bacteria. The number of infected people in a normal healthy population who are shedding pathogens in their feces is small. The sewage from these infected individuals contains relatively few pathogens. Looking for pathogens is a "needle in the haystack" problem.

A useful indicator organism should:

- Be absent in unpolluted water and present when a source of pathogenic microorganisms is present.
- Be present in greater numbers than the pathogenic microorganisms.
- Respond to natural environmental conditions and water treatment processes in a manner similar to the pathogenic microorganisms.
- Be easy to isolate, identify and enumerate.

The coliform group of bacteria is the most commonly used indicator of bacterial water pollution and drinking water safety. Total coliform refers to a group of bacteria, many of which are harmless and originate in soil and animals and not in human feces. Fecal coliforms come from the intestinal tract of warm-blooded animals. The dominant intestinal coliform in temperate climates is *E. coli.* Another useful indicator is fecal streptococci, which are native to the gut of warm-blooded animals. Any of these may be used as indicator organisms. Note that none of these is a pathogen, except for certain virulent strains of *E. coli.*

We will skip the details of the test procedures and just say that the simplest test is for total coliforms. A positive test (coliforms are present) is presumptive evidence of contamination. A second stage of testing can be done for confirmation. These tests are quantitative. Bacterial counts are reported as the most probable number of coliforms per 100 milliliter (mL).

The USEPA limit for wastewater effluents is less than 400 fecal coliforms per 100 mL.

The USEPA Maximum Contaminant Level Goal (MCLG) is zero coliforms. The Maximum Contaminant Level (the enforceable limit) is that no more than 5% of samples can be coliform-positive in a month. The numbers of samples that must be analyzed increases as the population served by the water utility increases. Every sample that has total coliforms must be analyzed for fecal coliforms. There can be no fecal coliforms of *E. coli*. These limits apply to water in the distribution system (EPA Drinking Water Quality Standards website).

The WHO guideline is that total coliform bacteria should not be detected in any 100 mL sample collected from the distribution system.

6.11 Conclusion

Microbial diseases, many of them water-borne, sicken and kill millions of people each year. The technology exists to cheaply and easily reduce this terrible number. Some of the solutions depend on the input of money to build water purification plants, but many do not. Simply better managing the disposal of human and animal wastes would be a big step.

This is a worthy challenge to raise the level of health and happiness in the world.

7 The Fate of Pollutants in Air

7.1 Introduction

Pollutants may be discharged to a body of water (lake, stream, estuary, or ocean), into the atmosphere, onto the land, into the groundwater, or deposited underground. After discharge a pollutant will be transported by water or air and it will be diluted and dispersed. So the fate of pollutants, once discharged, can be complicated.

The objective of this chapter is to explain some basic problems and mechanisms about the fate of pollutants in air and how that fate is modeled. Chapter 8 does the same for the fate of pollutants in water, and Chapter 9 is about the fate of pollutants in soil and groundwater. A few simple equations and calculations are used, but a detailed description of complex models is beyond our scope.

In theory, a mathematical model can be constructed to predict the fate of any pollutant anywhere in the air or in a river or lake for existing or proposed emissions or discharges. In practice, building a model that adequately represents reality is often limited by the data that are available to verify the model. This chapter will give an idea of the complexities of developing environmental fate and transport models.

A useful model takes into account the variation in local conditions (stream flow, temperature, etc.); the specific pollutants and their tendency to react, adsorb, volatilize, or deposit; the existing ambient conditions and environmental quality; and the likely future development that could add pollution load or new environmental stress. In short, the model must capture all of the important characteristics of the receiving environment and the possible effects of specific pollutants on the flora and fauna in that environment.

The USEPA provides a variety of free modeling software packages for estimating how chemical and biological reactions, adsorption, and sedimentation will change the concentration of pollutants in streams, or groundwater, or air currents. Free software does not mean that modeling is cheap. Information costs money. Expertise will be needed in chemistry, biology, hydrology, hydrogeology, soil science, statistics, and computing. Expertise costs money.

7.2 Natural and Engineered Systems

Natural systems are deceptively simple and deceptively complex. There are no obvious networks of pipes and pumps and heat exchangers, or valves and thermometers and pressure gauges, or mechanics with oilcans, or operators watching computers. Still, all the manipulations an engineer could make in a processing plant are made in a natural system. There are conveyance systems and pumps, feedback loops, self-adjusting mechanisms, amplifiers, and shock absorbers. It is just hard to see where and how it happens. It is hard to model natural systems, and it is hard to change a system when we don't like what is happening.

Table 7.1 lists some of the differences between natural and engineered systems. The two that dominate are variability and uncontrollability.

Natural Systems (atmosphere, rives, lakes, estuaries, oceans)	**Engineered Systems (separation and transformation processes)**
Understanding may require knowledge of hydrology, geology, meteorology, biology, ecology, microbiology, chemistry, thermodynamics, hydraulics	Understanding may require knowledge of hydraulics, thermodynamics, chemistry, microbiology
Complex flow patterns	Simple flow pattern
Small differences in density may be important in determining direction of flow and mixing	Mixing dominated by mechanical means. Density differences of fluids are usually not important. (see note a)
Variations may be extreme (i.e., maximum river flow = 100 times minimum river flow; maximum and minimum temperatures differ by 60°C; wind velocities from 0 to 150 km/hr)	Variations generally are within known limits and are small in comparison to possible natural variations.
Variations are seasonal and diurnal	Variations are seasonal and diurnal; shift related in industry (see note a)
Variations may be random (accidents, floods, hurricanes, etc.)	Variations may be random (accidental spills,) equipment failure, etc.)
System can be monitored, but control (e.g. reservoir operation) may be restricted or absent.	System can be monitored (flow rates, temperature, pH, etc.) and controlled (pumping, heating, pH adjustment, etc.)
Chemical transformations controlled by natural conditions. Transformations by living organisms may dominate.	Chemical transformations can be controlled by addition of reagents and catalysts, and by intentional changes in temperature and pressure. Living organisms may be involved, but in controlled conditions.
Flow of energy is controlled by solar radiation, wind, etc.	Flow of energy can be controlled by heating and cooling, and by pumping.
Gravity and meteorological conditions control the flow of material. Transport is usually is in the atmosphere or in open channels (exception is groundwater).	Gravity, pumping liquids, and compressing gases control the flow of material. Transport is usually in pipes and conduits.
Biology – micro and macro-	Biology – usually microbial
Chemistry – organic and inorganic	Chemistry – organic and inorganic
'Reactor' or 'process' is a large volume or area that is not naturally homogeneous. The complex real system usually must be subdivided into more nearly homogeneous compartments or cells.	Reactor is reasonably homogeneous or can be mixed to make it so. (see note b)

Table 7.1 Comparison of natural and engineered systems.

(a) Diurnal change in municipal wastewater flow and strength is 3-fold to 5-fold (more if storm water is entering the sewer system). Seasonal change in wastewater temperature in Wisconsin (for example) is 10–15°C.

(b) Landfill is an engineered system that is in many ways like a natural system. It is connected to soil, groundwater, and atmosphere. Reactions are at ambient temperature; can be monitored but control is limited once constructed.

7.3 Global Dispersion of Pollutants

Air pollutants can travel around the globe and do damage on a global scale. One example is the damage to the ozone layer; another is greenhouse gases and climate change.

Figure 7.1 shows how rapidly sulfur dioxide was dispersed after the eruption of Mt. Pinatubo on June 15, 1991. The eruption ejected roughly 10,000,000,000 tonnes of magma, and 20,000,000 tonnes of SO_2. Over the following months, the aerosols formed a global layer of sulfuric acid haze. Global temperatures dropped by about 0.5°C (0.9°F), and ozone depletion temporarily increased (Wikipedia).

These global issues are important, but this chapter will focus on local and regional conditions.

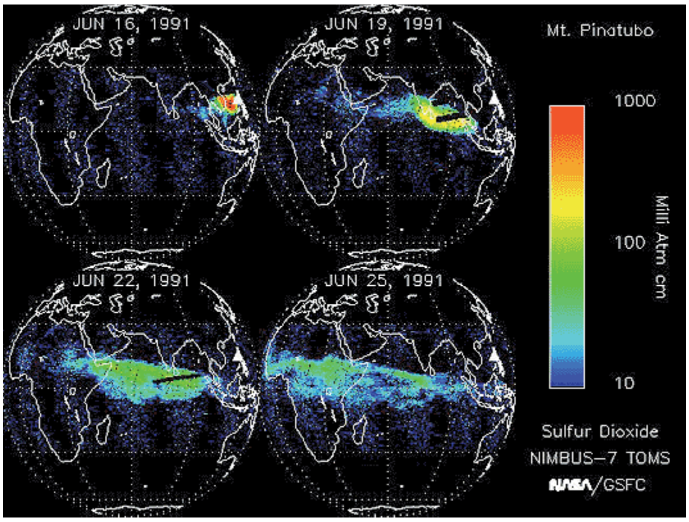


Figure 7.1 The spread of sulfur dioxide aerosols released by the June 15, 1991, eruption of Mt. Pinatubo, Philippines. (Source: NASA)

7.4 Dispersion of Air Pollutants

Different mixing patterns of pollutants in air give rise to different problems. There can be important near-field toxic effects, such as tetraethyl lead in automobile exhaust fumes and carcinogens in diesel exhausts. An industrial exhaust of a toxic chemical could be drawn into the ventilation system of an adjacent building, or it could move near ground level and cause a health threat to the local population.

Far-field effects might be dioxins adsorbed onto particles and then deposited at a great distance, or very fine particles, which are a health threat, migrating from industrial areas to suburban and rural areas.

Ozone is a special case. It is not emitted. It forms in the atmosphere, usually at some distance from the source of the ozone initiators.

Figure 7.2 Bouyant plume rise and dispersion of stack emissions. The height of plume rise depends on the temperatures of the ambient air and the gaseous emission. For power plants and many other industries the emission is warm and will rise above the stack, thus giving an effective stack height that exceeds the actual height. (Photo credit: pixabay)

How a pollutant moves – upward and away from people or being trapped near the ground – and how it is diluted and dispersed are the subjects of air pollution modeling. Data are needed on wind speed and direction, air temperatures, and the physical and chemical characteristics of the pollutant. Because these factors may change during a day, and certainly will change during the year, predictions are made for a variety of conditions. Figure 7.2 shows the bouyant rise and dispersion of a stack emission.

7.5 A Worst-Case Model for Pollutant Dispersion

It can be useful to do a simple screening analysis before making a more complete analysis. A *worst-case analysis* will quickly identify the order of magnitude of the expected concentrations and may even show that no problem exists.

Figure 7.3 is a highly simplified picture of a rectangular plume spreading downwind of the source. The plume is assumed to grow in proportion to the distance from the source. What makes this the 'worst-case' estimate of ground level concentration is assuming that the pollutant concentration is uniform over the cross-section. The maximum concentration of a real plume is at the centerline of the plume and the ground level concentration is less.

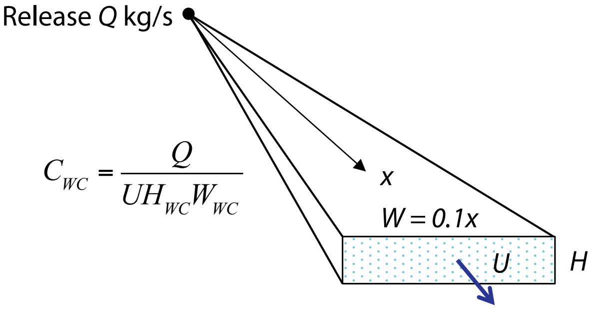


Figure 7.3 A worst-case analysis can be done using a highly simplified picture of a dispersion plume.

The release rate at the source is Q, with units of mass/time. The flux of pollutant through a cross-section at any distance x must equal the source release rate Q. As the plume moves it entrains more air and the mass of pollutant carried in 1 m^3 of air near the source is diluted into a larger volume. The flow of air through a cross-section of area is UWH m^3/s so the dilution from the near-source concentration is by a factor of $1/UWH$.

The worst-case average concentrations downwind of a point source is

$$C_{WC} = \frac{Q}{UH_{WC}W_{WC}}$$

where C_{WC} = worst case concentration (mg/m^3)
Q = source emission rate (mg/s)
x = distance from the source (m)
U = worst case wind speed at height $z = 10$ m, usually 1 m/s
W_{WC} = worst case plume width (m); usually assume $W = 0.1x$
H_{WC} = worst case plume depth (m); usually assume $H = 50$ m

This shows three fundamental conditions that must be satisfied by all plume models:

1. The mean concentration is inversely proportional to mean wind speed.
2. The mean concentration is directly proportional to the emission release rate.
3. The mean concentration is inversely proportional to the plume cross-sectional area.

Example 7.1 Worst-case Analysis of an Accidental Release of Chemical.

A small amount, 0.9 kg (900,000 mg), of noxious chemical is accidentally released over a period of 30 minutes (1800 sec). Assuming a light wind, say a velocity of U = 1 m/s, does this release pose any risk to the students in a school located 1000 m downwind?
The release rate = $\underline{Q}$ = (900,000 mg)/(1800 s) = 500 mg/s
Worst-case wind velocity = U = 1 m/s
Worst-case plume height = H_{WC} = 50 m
Worst case width of the width of the plume at the school = $W_{WC} = 0.1x$ = 0.1(1000 m) = 100 m

$$C_{wc} \quad \frac{Q}{UH_{WC}W_{WC}} = \frac{(500\ \text{mg/s})}{(1\ \text{m/s})(50\ \text{m})(100\text{m})} = 0.1\ \text{mg/m}^3 = 100\ \mu\text{g/m}^3$$

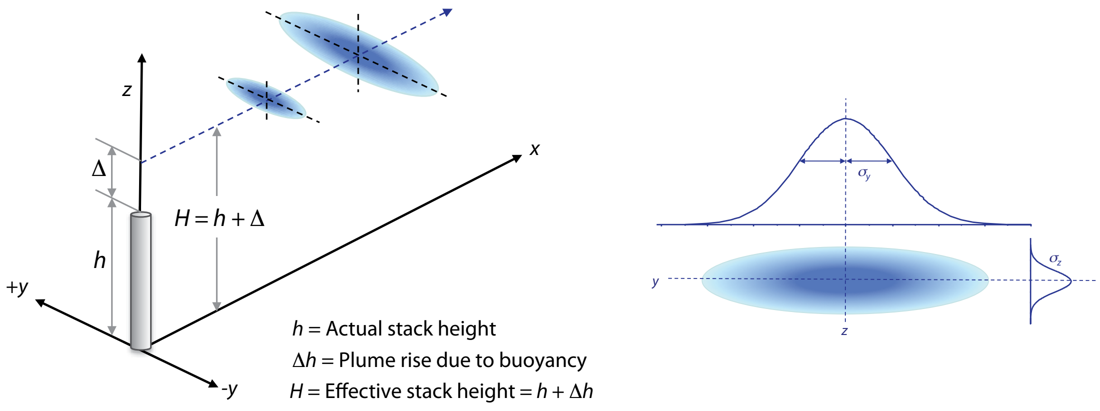
This can be compared to the acute toxicity standards for the chemical. Ammonia, for example, has a personal exposure limit associated with negative health effects due to prolonged exposure of 33,000 µg/m^3. If the chemical were ammonia we could safely say there is no risk and no more modeling is needed.

7.6 The Gaussan Model for Air Pollutant Dispersion

The behavior of a real plume can include:

- Coning – in stable conditions the plumes enlarges in the shape of a cone; a major part of the pollutant may be carried a long distance before reaching the ground.
- Looping – Large eddies and strong winds cause both upward and downward movement; high ground level concentrations may occur near the stack.
- Fanning- Pollutants disperse at stack height, horizontally in the form of a fan.
- Fumigation – Upward movement is restricted by an inversion so the pollutants move downward. The resulting fumigation can cause high ground level concentrations.
- Lofting – Upward mixing is uninhibited and downward movement is restricted. Pollutants may be carry a very long distances with no significant effect at ground level.

The plume shown in Figure 7.2 is for stable conditions, and it can be predicted using the so-called Gaussian model. The peak concentrations are along the centerline of the plume and concentrations away from the centerline decrease to give a bell-shaped (Gaussian) distribution, as shown in Figure 7.4. Note that particulate pollutants may settle toward the ground and the change in concentration due to this effect is not accounted for in the model.



(a) Definition sketch for the Gaussian plume model

(b) Symmetrical distribution of concentration within the plume

Figure 7.4 Ideal Gaussian plume dispersion. (a) Dispersion of a plume released under stable conditions at an effective height H. The pollutant disperses laterally and vertically as the plume moves downwind. (b) A view of the plume looking down the centerline shows the peak concentration is at the centerline and the the bell-shaped (Gaussian) distributions of concentration.

The total concentration for a plume spreading in free air is

$$C(x,y,z)=\frac{Q}{U}\frac{1}{\pi\sigma_y\sigma_z}\left(\exp\frac{-y^2}{2\sigma_y^2}\right)\left(\exp\frac{-(z-H)^2}{2\sigma_z^2}\right)$$

where $C(x,y,z)$ = pollutant concentration in the plume at the point (x, y, z) from the source ($\mu g/m^3$)
Q = emission rate of pollutants ($\mu g/s$)
h = actual stack height (m)
$H = h + \Delta$ = effective stack height (m)
Δ = rise of the buoyant plume above the stack (m)
x = distance directly downwind from the source (m)
y = lateral distance from the centerline (may be + or –) (m)
z = height of the plume above the ground (m)
$z - H$ = vertical distance of the plume from the centerline (m)
σ_y = lateral dispersion coefficient (standard deviation) (m)
and σ_z = vertical dispersion coefficient (standard deviation) (m)

There are charts and empirical expressions for estimating σ_y and σ_z. One approach is based on turbulent wind speed fluctuations (turbulence intensities) in the z and y directions. The formulas are

$$\sigma_y = I_y x \text{ and } \sigma_z = I_z x$$

Turbulent intensities increase, especially in the vertical direction, as atmospheric conditions become more unstable. Table 7.2 gives typical values for different atmospheric conditions

Thermal Stratification	**Lateral Intensity (I_y)**	**Vertical Intensity (I_z)**
Extremely unstable	0.40-0.55	0.15-0.55
Moderately stable	0.25-0.40	0.10-0.15
Near Stable	0.10-0.25	0.05-0.08
Moderately stable	0.08-0.25	0.03-0.07
Extremely stable	0.03-0.25	≤ 0.03

Table 7.2 Lateral and vertical turbulence intensities for different wind conditions.

If the pollutant released is near the ground the plume will 'hit' the ground. The plume cannot spread into the ground, so it is assumed to be reflected. This is modeled by adding an imaginary underground source (a mirror image) of the same strength placed at the same distance from the source but 'underground'. The concentrations of the real and imaginary plumes are added to estimate the total concentration.

$$C(x,y,z) = \frac{Q}{U}\frac{1}{\pi\sigma_y\sigma_z}\left(\exp\frac{-y^2}{2\sigma_y^2}\right)\left[\left(\exp\frac{-(z-H)^2}{2\sigma_z^2}\right)+\left(\exp\frac{-(z+H)^2}{2\sigma_z^2}\right)\right]$$

If only ground-level concenetrations are required, to assess the exposure of crops or humans, the model, with $z = 0$, is

$$C(x, y, z = 0) = \frac{Q}{U}\frac{1}{\pi\sigma_y\sigma_z}\left(\exp\frac{-y^2}{2\sigma_y^2}\right)\left(\exp\frac{-H^2}{2\sigma_z^2}\right)$$

The maximum concentration occurs when $\sigma_z = H / \sqrt{2}$.

The center-line pollutant concentration at ground level is

$$C(x, y = 0, z = 0) = \frac{Q}{U}\frac{1}{\pi\sigma_y\sigma_z}\left(\exp\frac{-H^2}{2\sigma_z^2}\right)$$

Example 7.2 GAUSSIAN DISPERSON MODEL

Calculate the ground-level, center-line concentration for $x = 500$ m for an emission of 500,000 µg/s, wind velocity of $U = 3$ m/s, effective stack height of $H = 20$ m, and dispersion coefficients $\sigma_y = 50$ m and $\sigma_z = 30$ m. The simplified model with these values inserted is

$$C(x = 500\text{ m}, y = 0, z = 0) = \frac{500{,}000\ \mu\text{g/s}}{3.1416(3\text{ m/s})(50\text{ m})(30\text{ m})}\exp\left(-\frac{20^2}{2(30^2)}\right) = 28.3\mu\text{g/L}$$

At $x = 1000$ m, σ_y and σ_z are twice their values at $x = 500$m, and

$$C(x = 1000\text{ m}, y = 0, z = 0) = 8.36\ \mu\text{g/L}.$$

7.7 Advanced Air Quality Models

The simple Gaussion model is instructive, but it has limited application, as suggsted in Figure 7.5. Complexities in the region of interest, such as multiple sources, obstructions to air movement by buildings or topographical features, physical or chemical changes in the pollutants, and particulate deposition, require more complicated air quality models (Daly & Zanetti 2007).

		Complexity of Effects	
		Low	*High*
Complexity of dispersion	*High*	Gaussian model or Advanced models	Advanced models (AERMOD, CMAQ, CMB, & Risk-assessment models)
	Low	Modeling rarely needed	Special purpose models

Figure 7.5 The applicability of different models depending on the complexity of dispersion and the complexity of effect.

Dispersion modeling uses meteorological data to characterize the dispersion of a pollutant from a source to selected downwind receptor locations. These models are used to determine compliance with National Ambient Air Quality Standards (NAAQS) and for State Implementation Plans (SIP). AERMOD is a steady-state model for continuous, buoyant plumes. Plume deposition behavior includes wet or dry deposition of particulates and/or gases. Releases may be at the surface, near surface, or elevated. It is available on the internet (USEPA 2004).

Photochemical models are large-scale models. They are used to assess control strategies for ozone and reactive chemicals. The EPA's Community Multi-scale Air Quality (CMAQ) modeling system includes state-of-the-science capabilities for conducting urban to regional scale simulations of multiple air quality issues, including tropospheric ozone, fine particles, toxics, acid deposition, and visibility degradation.

Receptor models (Figure 7.6) are mathematical or statistical procedures for identifying and quantifying the sources of air pollutants at a receptor location. Unlike photochemical and dispersion air quality models, receptor models do not use pollutant emissions, meteorological data and chemical transformation mechanisms. Instead, receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to quantify source contributions to receptor concentrations. The EPA has developed the Chemical Mass Balance (CMB) and UNMIX models, and also the Positive Matrix Factorization (PMF) method. CMB fully apportions receptor concentrations to chemically distinct source-types depending upon the source profile database. UNMIX and PMF generate source profiles from the ambient data.

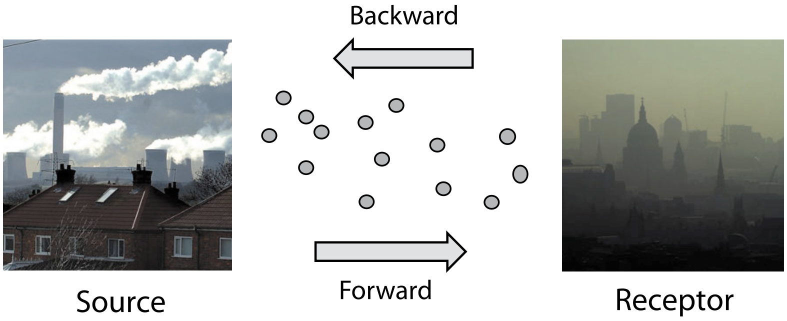


Figure 7.6 A receptor model can be run forward or backward in time to predict source emission or conditions at the receptor.

7.8 Case Study: Detroit Multi-Pollutant Pilot Project

In each chapter about the fate of pollutants (chapters 7, 8 and 9) we will summarize one case study of a complicated modeling project. The goal is to outline the impressive capability that has grown from the very simple models that were explained earlier in the chapter. This capability has developed because of advanced understanding of mechanisms, but more important have been the availability of reliable data and massive computing power.

This section is about the Detroit multi-pollutant project that used a hybrid of two air quality models and added risk assessment and benefit cost analysis. The goals were attainment/maintenance of all NAAQS, reductions in specified industrial sectors, and risk reductions of hazardous air pollutants (HAPs). The project included visibility, energy, climate, and ecosystems. Another goal was to make effective integrated use of land use and transportation.

The traditional single-pollutant approach selects control strategies to separately address ozone and fine particulate matter ($PM_{2.5}$) at non-attainment locations. A least-cost approach for successively meeting each standard may not necessarily produce the most efficient strategy for meeting multiple air quality objectives or for obtaining the greatest health and environmental benefit for a given expenditure.

The National Research Council recommended that the USEPA transition from a pollutant-by-pollutant approach to air quality management to a multi-pollutant, risk-based approach. This strategy is aimed at reducing population risk from exposure to ozone, $PM_{2.5}$ and toxics while still addressing ozone and $PM_{2.5}$ non-attainment.

The multi-pollutant approach was expected to be more efficient than the traditional approach (the status quo) because many air quality problems share common precursors while current NAAQS requirements are focused pollutant-by-pollutant. The release, control, and chemical formation of pollutants are interrelated. An approach that takes these facts into account can simultaneously seek reductions of pollutants posing the most significant risks while receiving the greatest benefits and reducing administrative overhead.

No one had actually implemented a multi-pollutant air quality management effort until the Detroit pilot project (Wesson et al 2009, 2010; USEPA 2008). Detroit provides an excellent test bed because there are multi-pollutant issues with ozone, $PM_{2.5}$ and toxics.

Also, the region is rich in technical data. The Detroit Air Toxics Initiative (DATI) monitored over 200 compounds from April 2001–April 2002 (Simon et al., 2005). Analysis identified 13 chemicals of highest concern: methylene chloride, naphthalene, benzene, acrylonitrile, formaldehyde, 1,4-dichlorobenzene, arsenic, carbon tetrachloride, 1,3-butadiene, acetaldehyde, cadmium, nickel, and manganese. Acrolein and diesel exhaust were important to consider for mitigation of air toxics health risks.

A significant innovation was combining the dispersion model (AERMOD) and the photochemical model (CMAQ) into one model output (via post-processing). This preserved the fine grid of AERMOD while properly treating chemistry/transport offered by CMAQ.

CMAQ modeling offers multi-pollutant (ozone, particulates, toxics, acid deposition, and nitrogen loading) capability by means of comprehensive description of gaseous and aqueous chemistry and aerosol dynamics. CMAQ was run with a 12 km × 12 km horizontal grid resolution centered on Detroit.

AERMOD modeling is EPA's preferred air quality impact assessment tool for inert pollutants that are emitted from a variety of sources for transport distances of up to 50 km. AERMOD was run with a 1 km × 1 km rectangular receptor grid. A concentration is predicted at each of these receptor locations so the output is very dense in comparison with the CMAQ model. The pollutants modeled include primary organic carbon, elemental carbon, benzene, cadmium, nickel, diesel particulate matter (DPM), formaldehyde, naphthalene, 1,3-butadiene, 1,4-dichlorobenzene, and methylene chloride.

The significant innovation was the combination of the CMAQ and AERMOD output to simultaneously deal with the many varied pollutants and increase the resolution of the analysis. Figures 7.7 and 7.8 show the benefits of this hybrid approach.

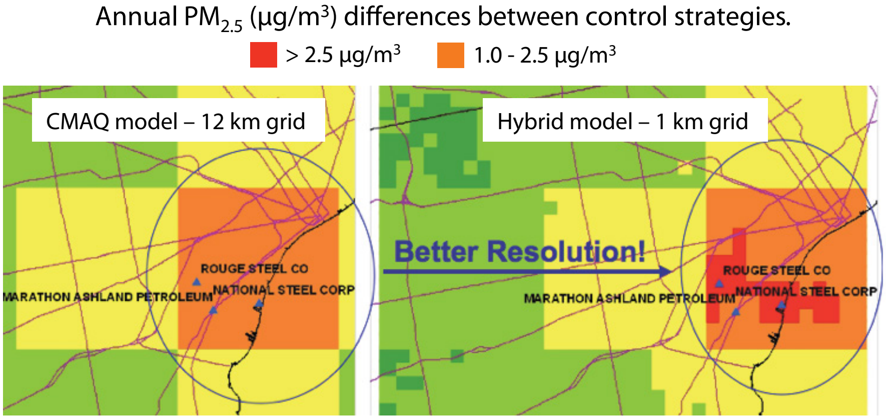
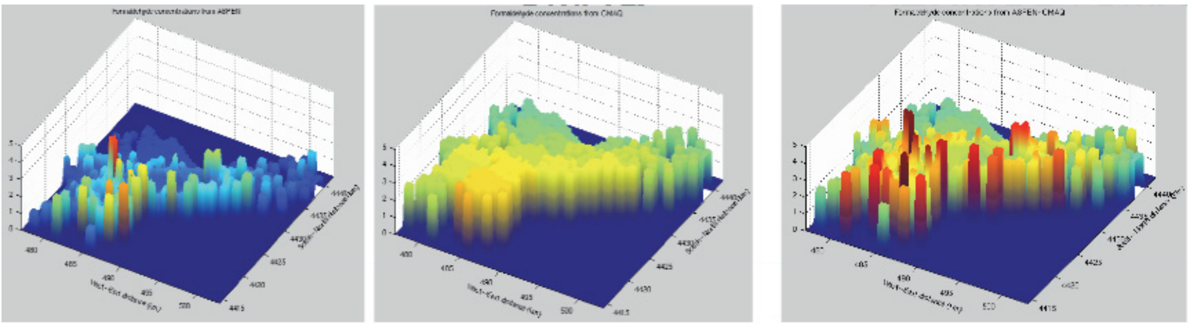


Figure 7.7 The AERMOD model uses a 1 km x 1 km grid size, compared with 12 km x 12 km for the CMAQ model. This provides 144 AERMOD receptor estimates for each CMAQ estimate, and these are for different pollutants. The hybrid approach merges the two outputs and gives better resolution and better management decisions. (Wesson et al 2009, 2010; USEPA 2008)



AERMOD Model

CMAQ Model

Combined AERMOD + CMAQ

Figure 7.8 The outputs of the dispersion model (AERMOD) and the photochemical model (CMAQ) were combined into one model output. (Wesson et al 2009, 2010; USEPA 2008)

Cost or Benefit		Single-pollutant approach	Multi-pollutant approach
Change in population weighted $PM_{2.5}$ exposure ($\mu g/m^3$)	Regional	0.16	0.1666
	Local	0.2703	0.7211
Change in population weighted O_3 exposure ($\mu g/m^3$)	Regional	0.0005	0.0006
	Local	0.0318	0.0583
Total benefits (million $2006)		*$1,127*	*$2,385*
Total costs (million $2006)		*$56*	*$66*
Cost per $\mu g/m^3$ $PM_{2.5}$ reduced		$0.50	$0.32
Cost per $\mu g/m^3$ O_3 reduced		$2.60	$0.58
Net Benefits (million $2006)		*$1,071*	*$2,319*
Benefit-Cost Ratio		*20.1*	*36.1*

Table 7.3 Some selected values from the benefit-cost comparison of the conventional modeling approach and the multi-pollutant hybrid model approach. (Wesson et al 2009, 2010; USEPA 2008)

Data from the air quality modeling was used as input into the environmental Benefits Mapping and Analysis Program (BenMAP) and the Human Exposure Model-3 (HEM-3). BenMAP relates ambient changes in air pollution to reductions in adverse health impacts, and it estimates the health impacts and monetary benefits. HEM-3 estimates cancer and non-cancer risk for toxic air pollutants, assuming an individual breathes the ambient air at a receptor site 24-hours per day over a 70-year lifetime. This assumption, while not realistic, is consistent with the EPA's approach to estimating risk for regulatory decisions (Wesson et al. 2010).

The single-pollutant and the multi-pollutant approaches both identified policies that would achieve attainment for ozone and $PM_{2.5}$. Both led to about the same number of tonnes of pollutants being targeted for reduction, but the pollutants were different because of the risk-based assessment. A few pollutant emissions are higher under the multi-pollutant plan.

The multi-pollutant plan is more protective of public health. For $PM_{2.5}$ and ozone impacts, premature mortality, asthma and other respiratory problems, lost work days, etc. are double that estimated for the traditional approach.

Table 7.3 summarizes the estimated costs and benefits. The results for the multi-pollutant approach are impressive. The benefits are twice as large for a 20 percent increase in cost.

7.9 Conclusion

After discharge an air pollutant will be transported and diluted and dispersed. Some disappear or become immobilized and can be forgotten within a fairly short time. Others persist, and are transported a great distance, even around the globe. Exactly what happens will depend on the physical and chemical properties of the pollutants and the meteorology.

The simplest model is the Gaussian distribution of pollutants in a buoyant plume. This can be developed to handle multiple pollutants, both mobile and stationary, and a variety of conditions for terrain and meteorology. It does not deal with chemical reactions, such as the photochemical production of ozone, but other models do, as illustrated in the Detroit air pollution case study.

Predicting the fate of pollutants in the air environment requires good data and appropriate models. We have sophisticated models and the computing power to execute large and complex environmental simulations of pollutant concentrations. Having computing power and good modeling software does not mean that modeling is easy or cheap. It is not. Information and expertise cost money.

8 The Fate of Pollutants in Water

8.1 Introduction

The five kinds of water receptors of pollutants – groundwater, rivers, lakes, estuaries, and the ocean – present different problems so they are discussed separately. Groundwater is discussed in Chapter 9 in connection with soil pollution, since it is not intentionally used as a receptacle for pollution.

Rivers are the easiest. Conditions change in one-dimension, along the length of the river. Vertical and horizontal variations are rarely important, except in very wide, slowly moving rivers like the Ganges.

Lakes and reservoirs are three-dimensional problems, or four-dimensional if one counts the annual cycle as a dimension. There can be important variations in temperature and water quality with depth. The distance from the inlet to the outlet of a reservoir can be up to 160 km (100 mi), and the width and depth will change along this distance. Mixing at the inlet may be controlled by differences in density due to temperature or silt load. Changes in water temperature throughout the year may cause stratification and turnover.

Estuaries have characteristics of rivers and reservoirs, with the added complication of tidal movement and salinity gradients.

The ocean is another three-dimensional problem, but generally more simple because the goal is maximum dilution of any pollutants that are discharged there.

8.2 Fate of Pollutants in Rivers

8.2.1 Basic Issues

For many years pollution control in rivers was about organic carbon compounds that would degrade the dissolved oxygen concentration as they were consumed by microorganisms in the river. These problems have been largely solved and today we are more concerned about toxins and the fertilizing effects of nitrogen and phosphorus.

The change in dissolved oxygen (DO) depends on the rate of consumption of organic carbon (the measure of this is BOD) and the rate of reaeration by transfer of oxygen from the air to the water. Reaeration is the mechanism that gives a river a capacity to absorb biodegradable organic pollution. Ignoring this assimilative capacity and using the same standards for all dischargers raises the total cost of pollution control. On the other hand, to determine the assimilative capacity and allocate it fairly to dischargers requires costly fieldwork and mathematical modeling. If the effluents are very low in organic carbon, the dissolved oxygen levels will normally be satisfactory.

Rivers usually wash out plankton faster than it can grow and periodic flood flows wash the streambed of rooted plants. As a result the lowest layer in the benthic pyramid is detritus feeding invertebrates, which in turn support macro invertebrates and fish. This makes rivers less sensitive to the discharge of nitrogen and phosphorus than other aquatic environments.

8.2.2 The Mixing Zone

Effluent is most often discharged at the stream bank and it takes some time (distance) to thoroughly mix into the river. The length of the mixing zone may be up to three times the width of the river. This is based on the assumption that most discharges are about the same density as river water and will mix freely. If this is not true, as with heated discharges, the mixing will be slower and special calculations will be needed.

For conservative pollutants, i.e. those that neither settle nor decay, the concentration in the river at the downstream boundary of a mixing zone will be

$$C_3 = \frac{Q_1 C_1 + Q_2 C_2}{Q_3}$$

Q_1 and Q_2 are volumetric flows of the river upstream and of the effluent, as shown in Figure 8.1. The flow after the river and effluent have mixed is $Q_3 = Q_1+Q_2$. C_1, C_2 and C_3 indicate concentrations at the three locations of interest. The pollutant will be further diluted as it moves downstream by tributaries, groundwater inflow, and overland runoff, assuming these flows do not make an additional contribution of the pollutant.

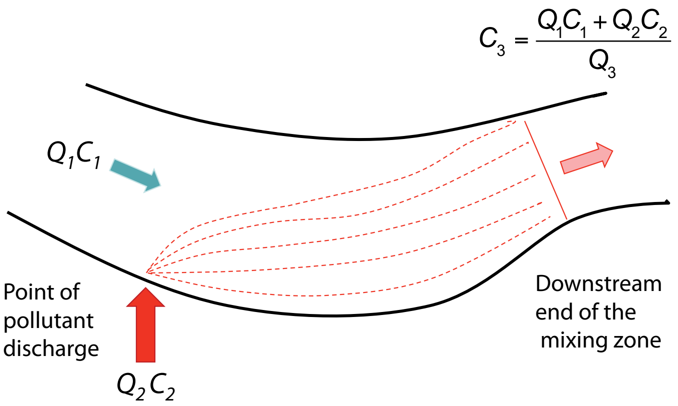


Figure 8.1 Zone of mixing for a bankside discharge of pollutant may be up to three times the width of the river. At the downstream end of the mixing zone the pollutant is thoroughly mixed and diluted in the river water.

The usual assumption is that any reactions within the mixing zone can be neglected. It is a good assumption for biological reactions, but may not be for rapid chemical oxidations. Ambient water quality criteria are usually imposed at the boundary of the mixing zone. If toxicity within the mixing zone is a problem, it may be worthwhile to discharge away from the bank or to use multiple discharge points.

Example 8.1 MIXING OF A POLLUTANT IN A RIVER

Wastewater with pollutant concentration C_2 = 50 mg/L is discharged to a stream at a rate of Q_2 = 5,000 m³/d. The river flow above the discharge is Q_1 = 15,000 m³/d with a pollutant concentration of C_1 =10 mg/L. The total flow at the end of the mixing zone is Q_3 = 5,000 + 15,000 = 20,000 m³/d. The pollutant concentration is

$$C_3 = \frac{Q_1C_1 + Q_2C_2}{Q_3} = \frac{(15{,}000\ \text{m}^3/\text{d})(10\ \text{mg/L}) + (5{,}000\ \text{m}^3/\text{d})(50\ \text{mg/L})}{20{,}000\ \text{m}^3/\text{d}} = 20\ \text{mg/L}$$

8.2.3 Transport by Convection and Longitudinal Dispersion

A pollutant that is released steadily into a river is assumed to move at the same velocity as the river. Turbulence will cause some longitudinal dispersion (upstream and downstream mixing) but any transport by this mechanism is unimportant compared with the convective flow.

The fate of a slug injection of pollutant is different. The sharp peak in pollutant concentration that is created by the spill will be carried along by convection, but turbulent mixing along the axis of flow will also be obvious. This will mix the pollutant into a larger volume of water and decrease the peak concentration. Figure 8.2 shows that concentration pattern that will develop. If the pollutant is non-reactive the mass of pollutant remains the same in the affected volume of water, which expands with travel downstream. This dilution of the peak is important to downstream consumers, especially if the spilled pollutant is toxic, causes off tastes or odors, or is otherwise objectionable.

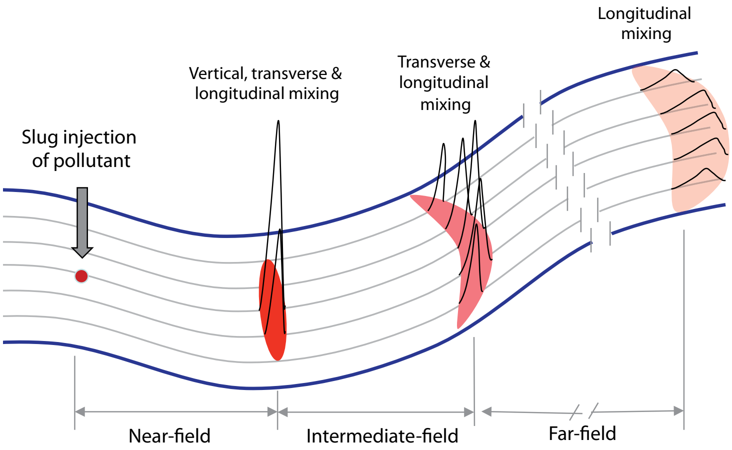


Figure 8.2 Dispersion of a non-reacting pollutant spill in a river. The height of the curve indicates the concentration at three locations below the point of the injection (or spill). The peak concentration decreases with distance from the spill as turbulence mixes the pollutant with a larger volume of river water.

8.2.4 The Exponential Decay Model for Pollutant Disappearance

Some pollutants are reduced by reaction, adsorption, or settlement. An exponential decay model can represent all of these mechanisms

$$C(t) = C_0 e^{-kt}$$

Where C_0 is the concentration at $t = 0$, that is, at the upstream boundary of the river section of interest. This may be the end of a mixing zone for an effluent discharge or a tributary. $C(t)$ is the concentration after travel downstream for time t. Indicating distance downstream as x and stream velocity as V, the time of travel is $t = x/V$.

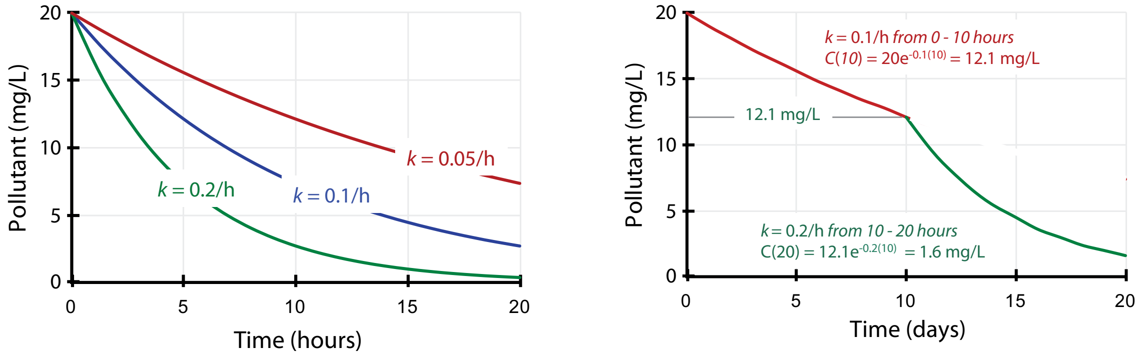
The coefficient k indicates how rapidly the pollutant disappears from the water; high k means faster disappearance. k has units of 1/time (time^{-1}). If travel time is measured in days, k has units of day^{-1}; if measured in hours then k has units of hr^{-1}.

Example 8.2 THE EXPONENTIAL DECAY MODEL FOR POLLUTANT DISAPPEARANCE IN A RIVER.

Assume the interesting behavior starts at the end of the mixing zone. Using the C_0 = 20 mg/L chemical concentration from Example 8.1, the concentration after 10 hours of travel for k = 0.05 hour^{-1} is

$$C(10) = (20 \text{ mg/L})e^{-(0.05)10} = 12.1 \text{ mg/L}$$

Figure 8.3a shows three pollutants decaying at different rates. The decay coefficients in these figures have units of 1/hour. Twenty hours travel in a river is 100 km, assuming an average velocity of 5 km/h (3 mile/h). It is unlikely that conditions will be constant for that distance, so a more realistic result may be that shown in Figure 8.3b, where for some reason the rate coefficient changes from k = 0.05/h to k = 0.2/h. A change like this could occur if the velocity is reduced and the removal efficiency increases due to settling. The chemical might disappear due to volatilization or the river might become more turbulent, which would increase the rate of removal. If the removal mechanism is biodegradation, the river might enter a shallow reach where the water is warmer and benthic activity accelerates the removal rate.



(a) Three pollutants decay at different rates

(b) Fate of one pollutant where the rate of decay changes after 10 hours

Figure 8.3 (a) Exponential disappearance of three pollutants at different rates. (b) Exponential disappearance of one pollutant where the rate changes after 10 hours.

8.2.5 Oxygen Depletion in a River

The level of dissolved oxygen (DO) required for a healthy fishery is 6 mg/L or higher. Below this spawning is inhibited and growth and activity decline. DO in the range of 3–5 mg/L is stressful to fish, but can be tolerated for 12–24 hours. DO below 3 mg/L will not support fish populations.

The earliest water quality model, by Streeter and Phelps (1925), was used to predict dissolved oxygen concentrations in the Ohio River as a function of pollution load. The 'sag' describes the shape of the response curve, with DO being high before the pollutant is added and then decreasing to some minimum and later recovering toward the original level as the pollution is dissipated.

Dissolved oxygen (DO) and biodegradable organic substances are simultaneously consumed by bacteria. The rate of DO depletion is proportional to the concentration of organics.

As oxygen is being depleted it is also being replenished by algal photosynthesis and by the transport of oxygen from the atmosphere into the water. We will assume in this discussion that photosynthesis is negligible. (It is negligible at night and it may be unimportant in the daytime if turbidity is high.) The rate of transport of oxygen from air to water increases as the DO decreases. This is fortunate because when bacterial activity has reduced the oxygen level, reaeration is working at a higher rate to regain the balance.

The simplest model that captures these two competing mechanisms is the Streeter-Phelps model.

$$DO(t) = DO_{sat} - \frac{k_1 P_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) - DO(0)e^{-k_2 t}$$

$DO(t)$ = the dissolved oxygen concentration at t days flow downstream (mg/L).
DO_{sat} = dissolved oxygen saturation concentration (mg/L).
$DO(0)$ = the dissolved oxygen concentration at $t = 0$ (mg/L).

P_0 = concentration of biodegradable pollutant at time $t = 0$ (mg/L).
k_1 = exponential decay coefficient for the degradation of organic pollutants (day^{-1})
k_2 = reaeration rate coefficient (day^{-1})

This is usually written in terms of the dissolved oxygen deficit (the gap between DO saturation concentration and the existing DO), so the equation in most other books looks different but describes the same mechanisms.

The dissolved oxygen saturation concentration for water is a function of temperature. The saturation concentration in fresh water at 20°C is 9.2 mg/L, at 15°C it is 10 mg/L. The saturation concentration in saline waters is lower than in fresh water.

P_0 is the concentration of the pollutant at the head of the river segment being modeled. This may be at the downstream end of an effluent mixing zone, the mixing zone of an incoming tributary, or at the beginning of a river segment that is physically different than its upstream segment (i.e. different velocity or depth).

Values for the biodegradation rate coefficient, k_1 are in the range of 0.05 to 0.5 day^{-1}. The reaeration rate coefficient, k_2, can range from 0.25 day^{-1} for sluggish streams to 0.45–0.7 day^{-1} for large streams of normal velocity to 1.15 day^{-1} for swift turbulent streams. The value for rapids and waterfalls is greater than 1.15. Both k_1 and k_2 depend on temperature; higher temperatures give higher k values, which means that everything happens faster.

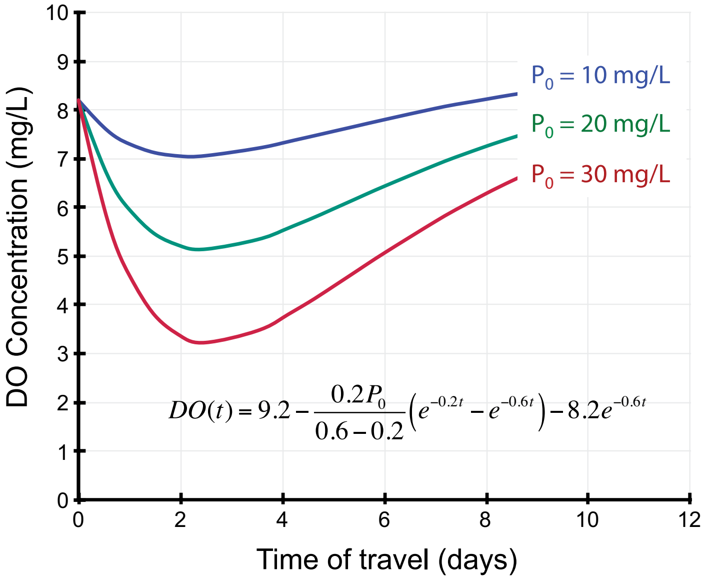


Figure 8.4 Dissolved oxygen concentrations predicted for the conditions given in Example 8.3 for 10 mg/L, 20 mg/L, and 30 mg/L of pollution. More pollution drives down the dissolved oxygen to levels that become harmful to stream biota.

Example 8.3 Dissolved oxygen concentration calculation in a river.

The upstream dissolved oxygen is $DO(t=0) = 8.2$ mg/L, the water temperature is 20°C so $DO_{sat} = 9.2$ mg/L. The reaeration rate coefficient is $k_2 = 0.6$ day^{-1} for the local river temperature, velocity, and depth. The biodegradation rate coefficient is $k_1 = 0.2$ day^{-1}. Inserting these values

$$DO(t) = 9.2 - \frac{0.2P_0}{0.6{-}0.2}\,(e^{-0.2t} - e^{-0.6t}) {-} 8.2e^{-0.6t}$$

The pollutant disappears according to the exponential model, in general

$$P(t) = P_0 e^{-k_1 t}$$

and for $k_1 = 0.2$

$$P(t) = P_0 e^{-0.2t}$$

Figure 8.4 shows the predicted dissolved oxygen concentrations for three levels of pollution. At a pollution level of $P_0 = 10$ mg/L the DO levels will support a healthy biological population, including all species of fish (unless they prefer cooler water temperatures). At $P_0 = 20$ mg/L the DO is acceptable, but at $P_0 = 30$ mg/L fish will be under great stress.

8.3 Segmented River Models

Advanced models include modifications of the simple model of the last section to account for photosynthesis, sediment oxygen demand, biodegradation, sedimentation, sediment scouring, adsorption, the influence of nitrogen and phosphorus, and dynamic conditions of loading and river flow. These models are basically still a prediction of the balance between oxygen consumption and oxygen replenishment. A widely used software package for advanced water quality modeling is QUAL2K, which is available from the USEPA.

One characteristic of all advanced models is that the river is segmented so that the model parameters (k_1, k_2 and others that may be needed for algae growth, ammonia oxidation, etc.) can be changed from segment to segment.

The calculations to do this are extremely simple, as Figure 8.5 shows, because once the known values of the k's and the times are substituted, the exponential terms become numerical values, and the equations become simple linear equations that are easily solved. The subscript notation is cumbersome and a more convenient system is used. The first letter of the variable indicates pollutant (P) or dissolved oxygen (D), the second indicates the upstream (U) or downstream (D) end of the segment, and the number is the segment identifier, giving, for example, DU1 = dissolved oxygen upstream segment 1, PD2 = pollutant concentration downstream segment 2.

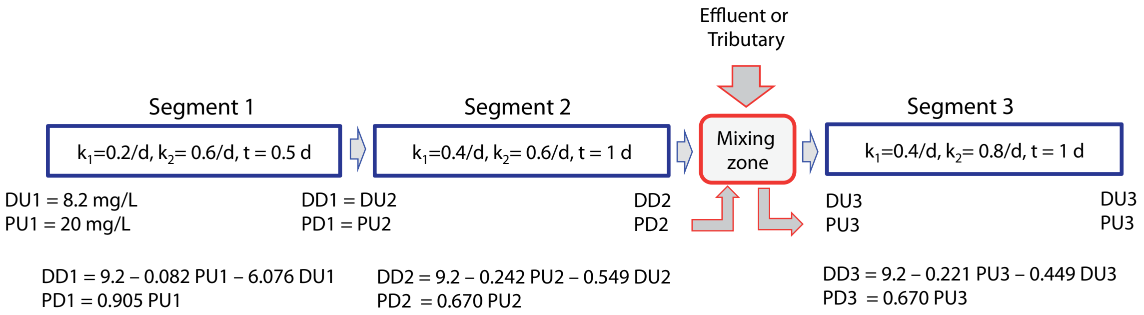
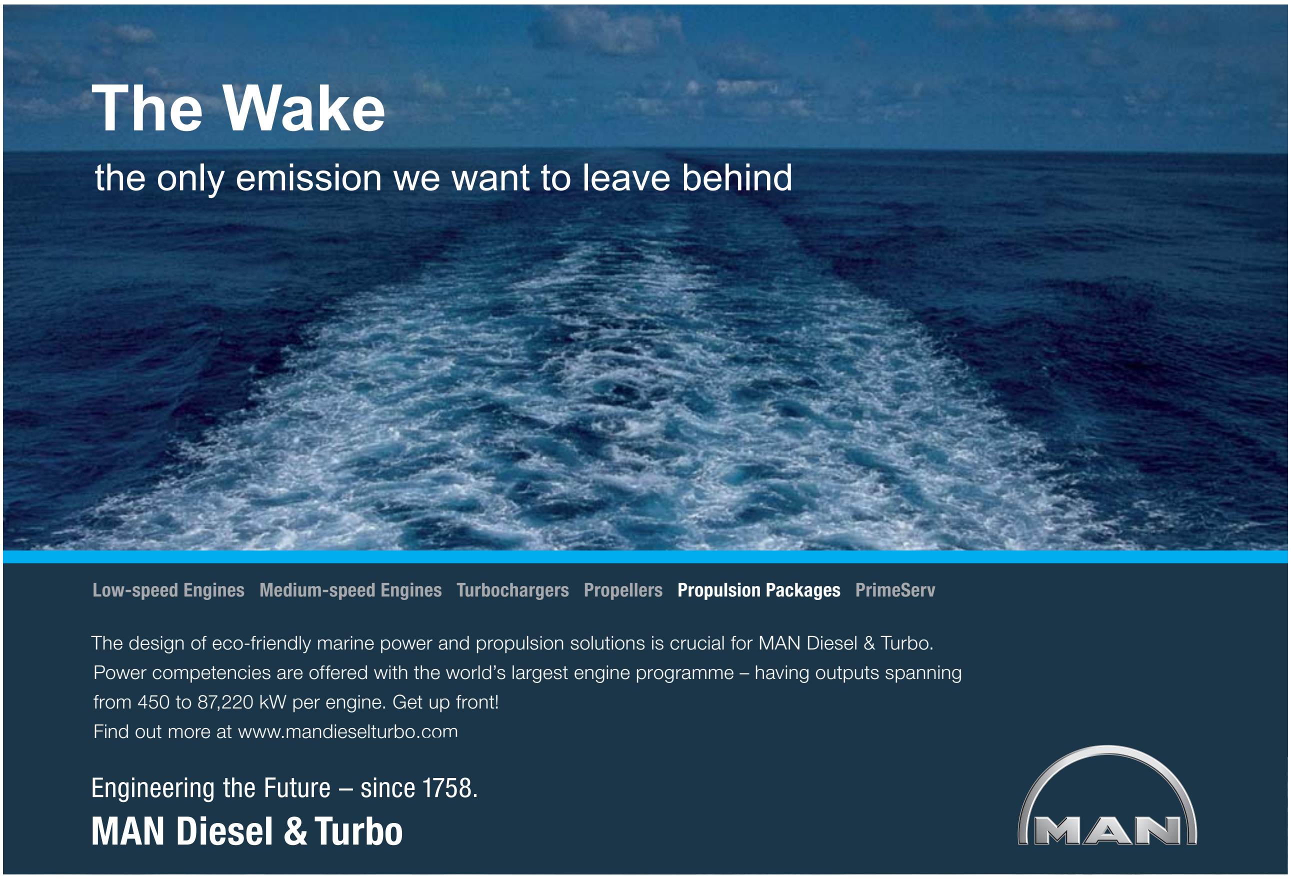


Figure 8.5 Segmented river model for a biodegradable pollutant and dissolved oxygen. The first letter of the variable indicates pollutant (P) or dissolved oxygen (D), the second indicates the upstream (U) or downstream (D) end of the segment, and the number is the segment identifier.

If there is no mixing zone the downstream value of one segment becomes the upstream value of the next. If there is a tributary or effluent to be mixed with the river, the values of P and D leaving the mixing zone become the initial values for the next segment.

When the initial conditions are known, the solution proceeds from upstream to downstream. When a specified critical condition must be maintained in the river, for example if DY3 must be 5 mg/L or higher, the calculations are done by working upstream.



Example 8.4 Segmented River Model

Using the initial values from Example 8.3, and the notation in Figure 8.5, the

$$DD1 = 9.2 - \frac{0.2PU1}{0.6-0.2}\left(e^{-0.2t} - e^{-0.6t}\right) - DUIe^{-0.6t}$$

The exponentials are $e^{-0.2(0.5)} = e^{-0.1} = 0.905$, $e^{-0.6(0.5)} = e^{-0.3} = 0.741$ and the model becomes

$$DD1 = 9.2 - 0.5\,PU1(0.905 - 0.741) - DU1\,(0.741) = 9.2 - 0.082\,PU1 - 0.741\,DU1$$

The initial values are $DU1 = 8.2$ mg/L and $PU1 = 20$ mg/L and

$$DD1 = 9.2 - 0.082(20) - 0.741(8.2) = 1.48 \text{ mg/L}$$

For the pollutant

$$PD1 = PU1\,e^{-0.2(0.5)} = PU1\,e^{-0.1} = 0.905\,PU1 = 18.1 \text{ mg/L}$$

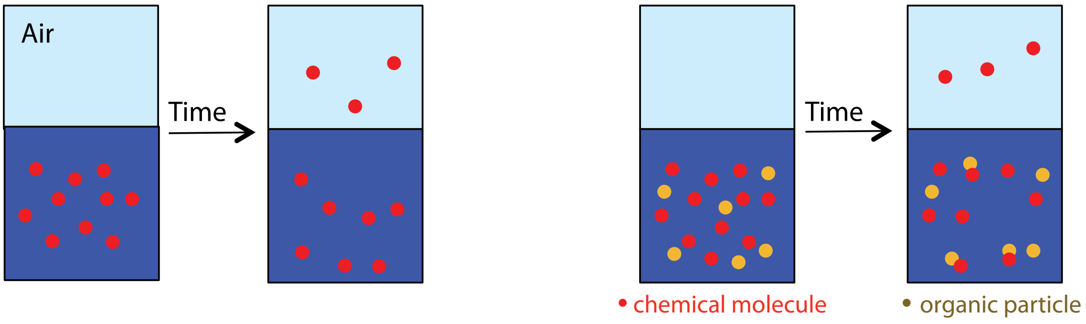
8.4 Partitioning of Pollutants between Water, Air and Solids

A brief explanation of chemical partitioning is given because the term is used in the following sections. It refers to the ability of many organic chemicals to exist as a vapor, as a soluble molecule, and as an adsorbed molecule. What happens depends mainly on the chemical's solubility. Water is a polar solvent. Most synthetic organic chemicals are non-polar compounds. They have a low solubility in water and a high affinity for organic matter in soil and suspended particulates. These compounds also tend to concentrate in the fatty tissues of living organisms.

Figure 8.6 is a graphical explanation of *partitioning* between air and water, and between dissolved and particulate material in the water.

Figure 8.6a shows 10 parts of a conservative chemical spilled into the water. After some time passes there are still 10 parts of chemical, but they are partitioned with 3 parts in the air and 7 parts in the water. Henry's Law defines the partitioning between liquids and gases. Figure 8.6b shows three parts of chemical adsorbed to organic particles and three parts going to the air, leaving four parts in the soluble form. The tendency to adsorb is inversely proportional to the chemical's solubility.

A reactive (non-conservative) chemical would disappear via chemical or biological reactions and there would be less than ten parts remaining, but whatever remained would still be partitioned between air and water.



(a) Volatilization
(air-water partitioning)

(b) Adsorption & Volatilization
(air-water-solid partitioning)

Figure 8.6 (a) Volatilization is partitioning between air and water (in general between a gas and a liquid). The relative concentrations at equilibrium are defined by Henry's Law. (b) Adsorption of chemical to solids (light colored particles) and partitioning between the air and water.

8.5 Case Study: PCBs in the Fox River, Wisconsin

Polychlorinated biphenyls (PCBs) were manufactured by adding chlorine to biphenyl. The resulting product was a mixture of chlorinated biphenyl groups, some with only 2 chlorine atoms attached, and some with seven or eight. Figure 8.7 shows examples of 7-Cl, 5-Cl and 4-Cl congeners. The biphenyl group has 10 positions where a Cl-atom can be attached, so there are many possible congeners. There are 169 congeners with 4 or more chlorine atoms.

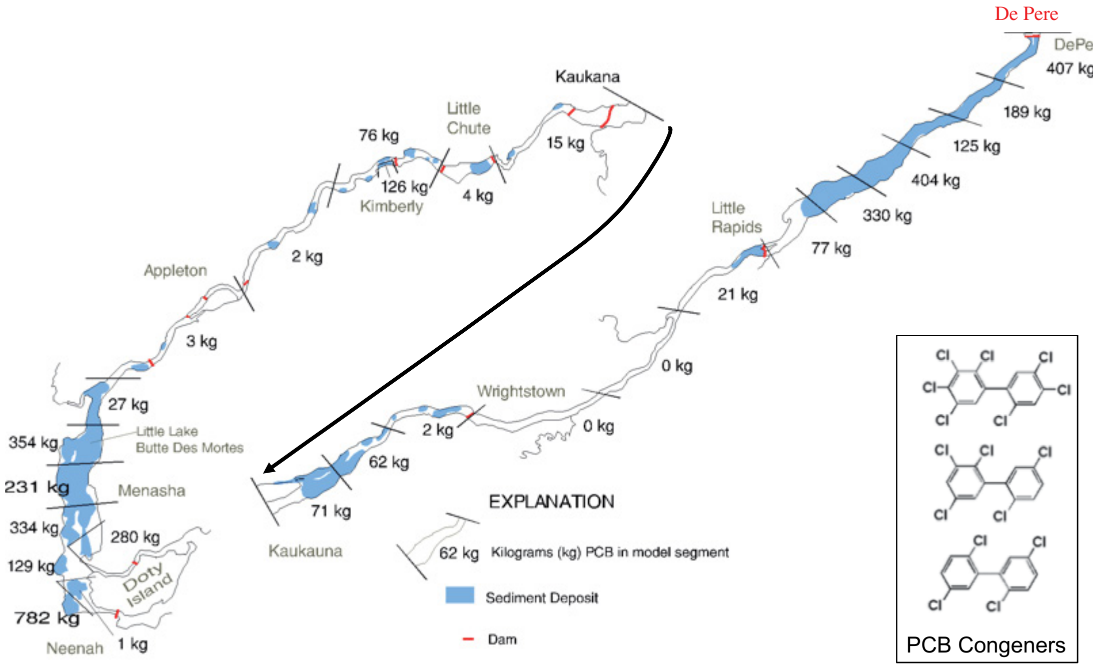


Figure 8.7 Map of the Fox River, Wisconsin. The map cuts the river into two lengths, above Kaukana and below Kaukana. The shaded areas show the deposits of PCB-contaminated sediments. The numerical values are the estimated inventory of PCBs (adapted from Velleux 2001).

A different kind of model is needed to deal with special chemicals, such PCBs. Figure 8.7 is a map of the Fox River, Wisconsin, showing areas of PCB contamination and the estimated PCB inventory in the sediments. The PCB model incorporates a number of transport and partitioning mechanisms. PCBs can be dissolved in water, volatilize to the atmosphere, settle and be resuspended from sediments, adsorb to dissolved organic carbon (DOC), or adsorb to particulate matter.

Dissolved organic carbon (DOC) is a broad classification for organic molecules of varied origin and composition within aquatic systems. The "dissolved" fraction of organic carbon is an operational classification. Many researchers use the term "dissolved" for compounds below 0.45 micrometers, but 0.22 micrometers is also common, saving 'colloidal' or 'particulate' designations for larger particle sizes.

Particles subside into the sediments during low flow but are resuspended in high flow. Some forms can volatilize. Some PCB congeners are slowly biodegradable in the presence of oxygen, but not in conditions like river sediments where there is no oxygen. Others decompose in the sediments without oxygen. The more highly chlorinated PCBs adsorb strongly to organic matter, including soil and sediment.

It was estimated that the Fox River was discharging 140 to 220 kg/yr into Green Bay (Lake Michigan) and the goal was to keep the PCBs out of the lake (Fitzgerald & Steur 1996). There has been no input of PCBs to the river for many years, so the PCBs are carried on sediments that accumulated years ago and are scoured from the river bottom during times of high flow. The issue was whether the contaminated sediment should be dredged from the river, left in place, or somehow covered up to restrict migration. Leaving them in place could result in intermittent transport during high flow conditions due to resuspension of surface sediments. Subsurface sediments would only be released if high flow caused severe scouring of the river bottom.

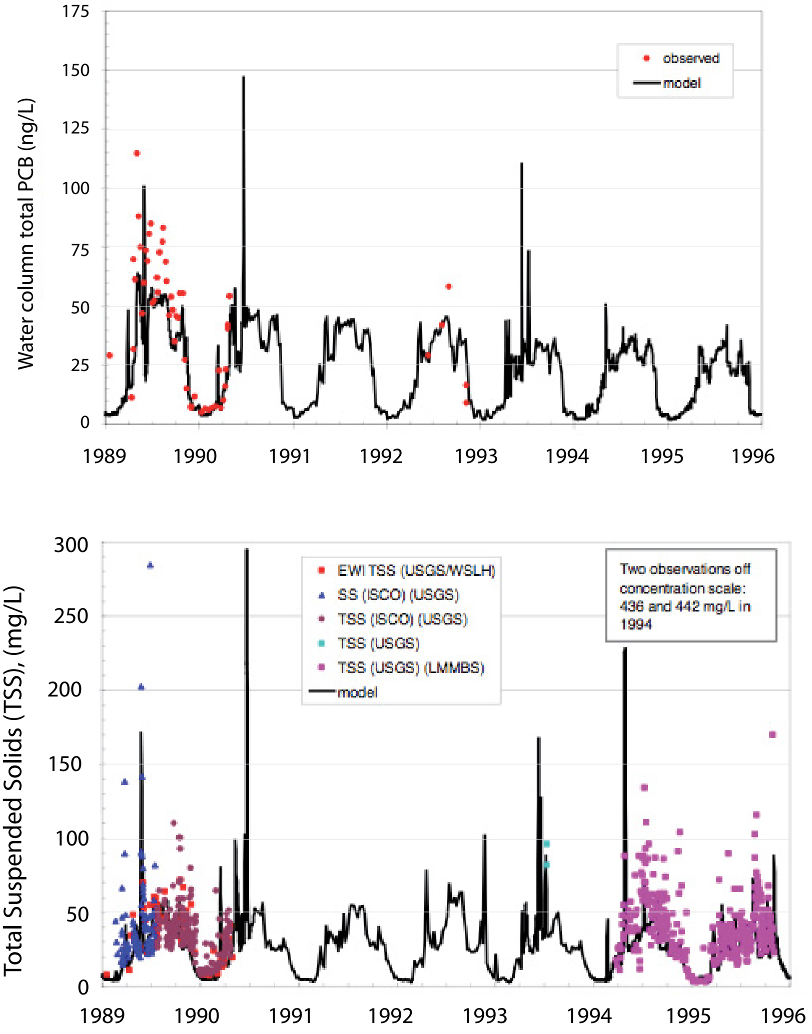


Figure 8.8 Observed and simulated concentrations for total suspended solids (TSS) and PCBs at the De Pere dam on the Fox River, Wisconsin, from 1989 to 1996. The observed values are shown as dots and the predicted values are the solid lines. (Figures adapted from Velleux 2001)

The model was used to simulate total suspended solids and PCB concentrations at several locations for a period from 1989 to 1996. The results for the De Pere dam are shown in Figure 8.8. The daily river flows (not shown) are low for most of the year, but increase in the spring and early summer with seasonal rain and snow melt, which is when the TSS and PCB concentrations increase. The top panel shows measured (dots) and predicted (line) PCB concentrations, in nanograms per liter (ng/L). The bottom panel is measured and predicted total suspended solids (TSS). The TSS results are important because a large part of the PCB load is adsorbed to solids. Particulate PCB was in the range of 0.5 to .25 mg/kg dry solid particulates. The model under-predicts the peak concentrations (most models do), but it captures the main features of TSS transport.

A 10-yr, $700 million dredging to remove 7.5 million cubic yards of PCB-contaminated sediments from critical locations began in 1999. This is the largest PCB remediation project in the world. The dredged slurry is processed with hydrocyclones to remove sand, the fine sediment fraction is dewatered using plate-and-frame filters, the filtrate is treated by filtration and carbon filters. In the first phase (September–December 1999) 640 kg of PCBs were removed from the river, 14.5 kg were transported downstream, 2.6 kg were volatilized, and 0.1 kg were returned to the river as treated filtrate (USGS 2000).

8.6 Fate of Pollutants in Lakes

8.6.1 Importance of Temperature and Density

The dynamics of a lake are driven by changes in temperature and water density. Pure water has its maximum density at a temperature of 4°C. As warmer water cools to 4°C, its mass stays the same but volume decreases so it is more compact. As it cools below 4°C the density decreases until it freezes. When water freezes at 0°C, its volume expands by 9 percent because a rigid open lattice of hydrogen-bonded molecules is formed. It is this open structure that makes ice less dense than liquid water.

Table 8.3 shows that the density difference between 4°C and 6°C is only 0.03 kg/m^3. A density difference this small is neglected in most engineering situations but it is important in deep lakes and reservoirs.

Temperature (°C)	0	4	6	8	10	15	20
Density (kg/m^3)	999.84	999.97	999.94	999.85	999.70	999.10	998.20

Table 8.3 Density of water at 0 to 20°C (Handbook of Chemistry and Physics, 53rd ed., 1972)

The water column may be uniform vertically in the winter and during spring and fall turnover. Turnover is when the lake water mixes thoroughly from top to bottom. If the water temperature during the year gets below 4°C a deep lake will stratify because of differences in water density. It may be covered with ice, thus blocking the entry of oxygen from the atmosphere. In the summer the water column will have a wind-mixed upper layer with dissolved oxygen and an active biota (the epilimnion), a relatively stagnant bottom layer (the hypolimnion), and an intermediate layer (the thermocline).

Figure 8.9 shows water temperature and dissolved oxygen in the Cherokee Reservoir of the Tennessee Valley Authority system on 11 March, 15 April, and 25 June in the year 1969. This seasonal pattern is consistent year to year. In March the reservoir is homogeneous; the temperature is a nearly uniform 5°C and dissolved oxygen of 10 mg/L. One month later, in April, the reservoir is stratifying, with warmer water near the surface and the colder water at the bottom. The dissolved oxygen levels in the deep water are starting to decline. By June the stratification is strongly established, as can be seen in the temperature profile, but even more clearly in the dissolved oxygen concentrations.

Another problem in discharging to lakes is to calculate the spatial changes in water quality. In the simplest case, where the water is well mixed vertically, the size and shape of the mixing zone is dependent on the pattern, direction, duration and velocity of the wind induced current, although advection through the lake may play some part. The temperature difference between the discharge and the lake water may also play a part in controlling the degree of mixing. Thermal stratification virtually eliminates the mixing of the surface layer (epilimnion) with the deeper water (hypolimnion). Only during the spring and autumn turnovers is there likely to be complete mixing of the discharge, otherwise it will tend to mix with the epilimnion.

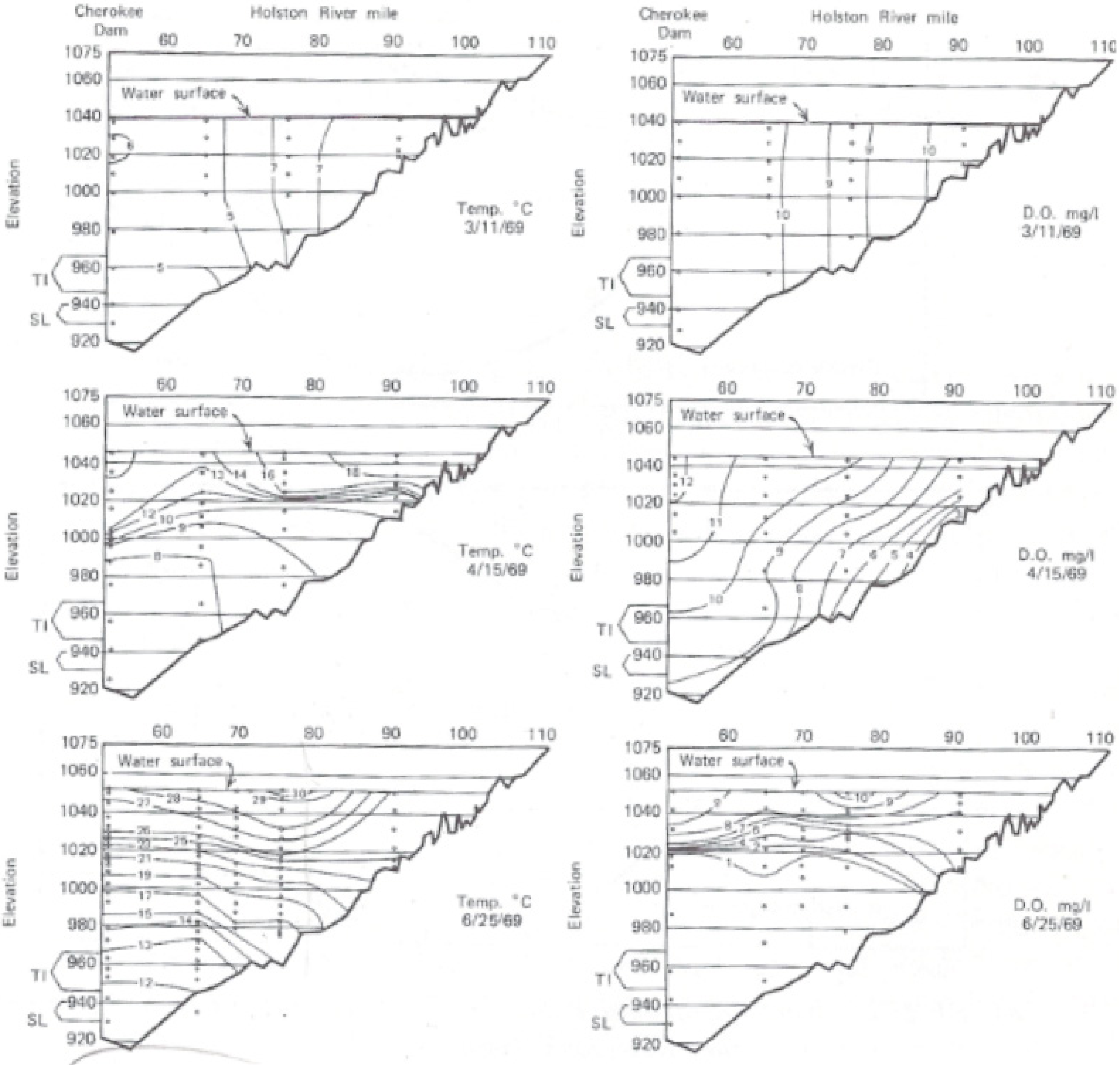


Figure 8.9 Stratification in the Cherokee Reservoir of the Tennessee Valley Authority (TVA) (Courtesy of John A Gordon, 1969). The elevation is in feet (above sea level) and the disatance (in miles) is measured across the top. TI indicates the depth of the turbine intakes and SL indicates rhe depth of the sluice. In the TVA system all water is released through the hydroturbines; none is discharged through the sluice or lost over the spillway.

8.6.2 Lake Retention Time (Flushing Time)

Lakes occur either as part of a river system or as isolated entities. In both cases the water is retained for periods of days, months, or years. This retention time is generally sufficient to allow the development of planktonic algae, which provides food for zooplankton and fish. Death and decay of the plankton community provides food for a benthic community (dominated by bacteria, fungi and detritus feeders) via sedimentation.

Lakes are potentially a highly productive environment and may, over a period of time, pass from barren (oligotrophic) to highly productive (eutrophic). This may occur over decades or centuries, but can be accelerated by inputs of nitrogen (N) or phosphorus (P). This process, known as eutrophication, results in a decline in water quality and a shift the dominant species of fish and plankton.

A further reason for avoiding waste discharges to lakes is that the recovery time is on the order of years or decades. Lake retention time (residence time or flushing time) is a calculated quantity expressing the mean time that water (or some dissolved substance) spends in a particular lake. At its simplest, it is the lake volume divided by either the mean rate of inflow of all tributaries or by the mean rate of outflow (ideally including evaporation and seepage). It roughly expresses the amount of time taken for a substance introduced into a lake to flow out of it again. The retention time is especially important where pollutants are concerned.

Retention time assumes that water in the lake is well-mixed rather than stratified, so that any portion of the lake water is much like any other. In reality, larger and deeper lakes are generally not well mixed. Many large lakes can be divided into distinct portions with only limited flow between them. Deep lakes are generally stratified, with deeper water mixing infrequently with surface water. These are often better modeled as several distinct sub-volumes of water.

Example 8.5 RESIDENCE TIMES FOR LAKE SUPERIOR AND LAKE ERIE

Lake Superior and Lake Erie have the longest and shortest residence times of the five Great Lakes. Lake Superior has a surface area of 82,100 km^2 and an average depth of 147 m, for a volume of 12,069 km^3.

$$T_{\text{Superior}} = \text{Volume/Outflow} = 12{,}069\ \text{km}^3/63.2\ \text{km}^3/\text{y} = 191\ \text{years}$$

Lake Erie has a surface area of 25,700 km^2 and an average depth of 19 m, for a volume of 488.3 km^3

$$T_{\text{Erie}} = 488.3\ \text{km}^3/187.8\ \text{km}^3/\text{y} = 2.6\ \text{years}$$

The other Great Lakes residence times are 99 years for Lake Michigan, 6 years for Lake Ontario, and 22 years for Lake Huron. A few other well-known lakes are Lake Geneva, Switzerland, = 11.4 years, Lake Como, Italy = 4.5 years, Lake Baikal, Russia = 330 years, and Lake Titicaca, Peru = 1343 years.

8.6.3 Phosphorus in Lakes

The active form of phosphorus in lakes is orthophosphate (PO_4^{3-}), which is readily taken up by algae and other organisms. Some of the phosphorus is flushed out of the lake, but much of it can be retained and recirculated within the lake.

In lakes, phosphorus is the nutrient in least supply relative to plant needs. The N:P ratio in plant tissue is 10:1 to 15:1. If the ratio of N:P in water is greater than 15:1 then the lake is phosphorus limited. The P will be used up before the N is used and plant growth will be limited. Eutrophication in lakes cannot be controlled only by reducing nitrogen (Schindler et al. 2008). Reducing P will reduce primary productivity of algae, as shown by the graph of chlorophyll and P concentrations and the aerial photograph in the lower half of Figure 8.10.

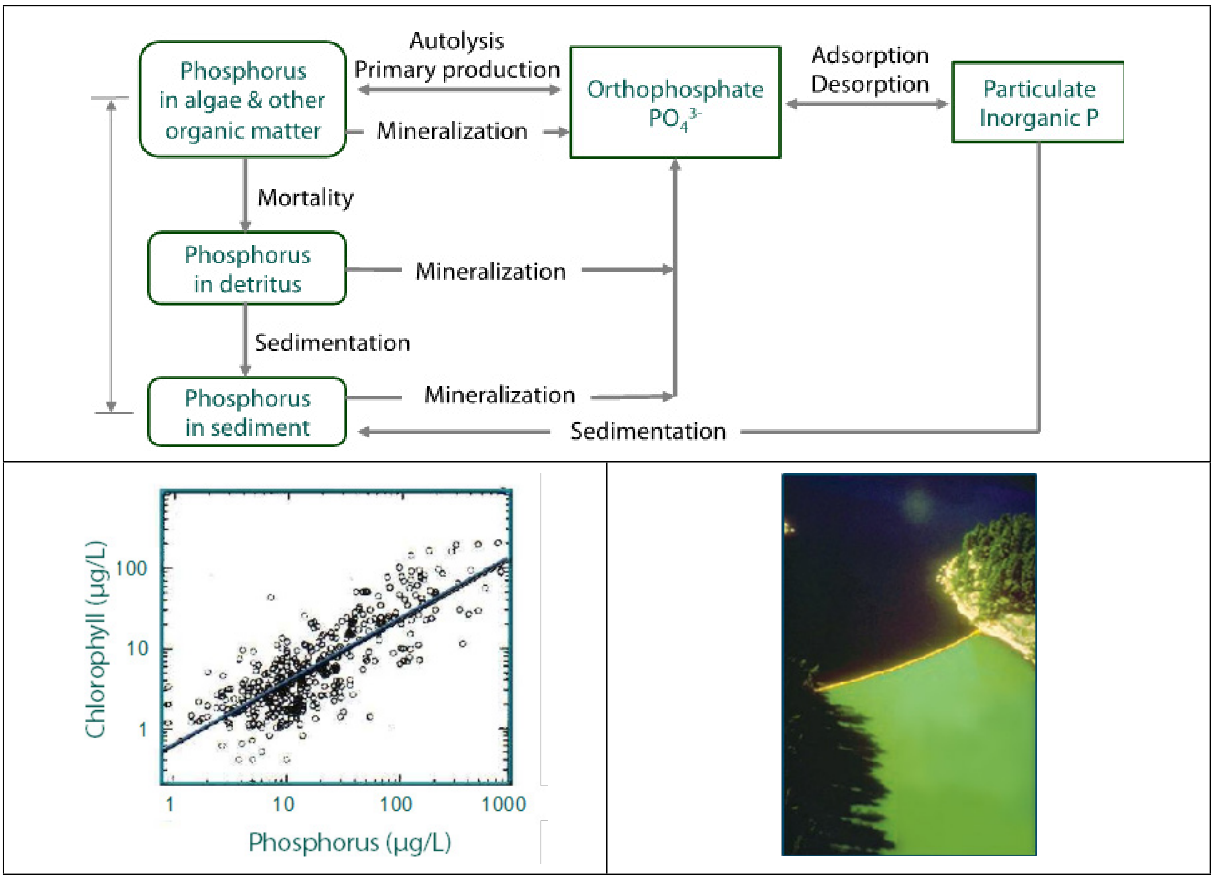


Figure 8.10 Primary productivity and eutrophication is driven by the availability of phosphorus. Phosphorus exists in water as organic matter, particulate inorganic and organic forms, and dissolved inorganic (orthophosphate). The cycle is shown in the upper block. The graph shows how the productivity of chlorophyll (algae and plants) depends on the phosphorus concentration in the water. The aerial photo on the lower right shows an experiment in a Canadian lake. C, N & P were added on one side of a curtain; C & N (no P) were added on the other. The effect of phosphorus on eutrophication is striking. (Photo used with the kind permission of Schindler 1974).

8.7 Advanced Lake Models

A conceptual model, which may also be useful for simple modeling, has hypothetical zones along the length of the reservoir and by depth, as in Figure 8.11. The riverine zones at the inlet and in tributary embayments have narrow channelized basins with relatively high flow rates. The broad deep lake basin (the lacustrine zone) has low velocities and generally is relatively clear and less eutrophic.

The water column may need to be divided into homogeneous segments or layers. This will depend on local conditions, such as the inflow of warm or cold water, changes in water temperature with season, etc.

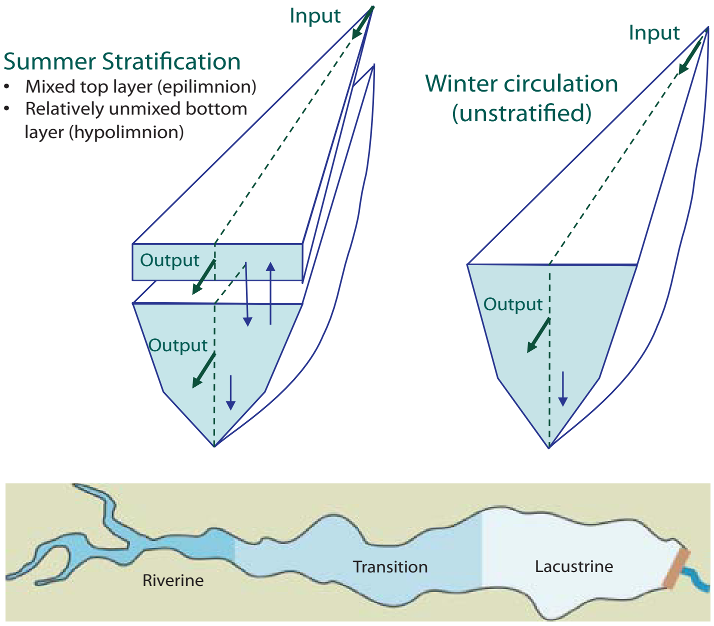
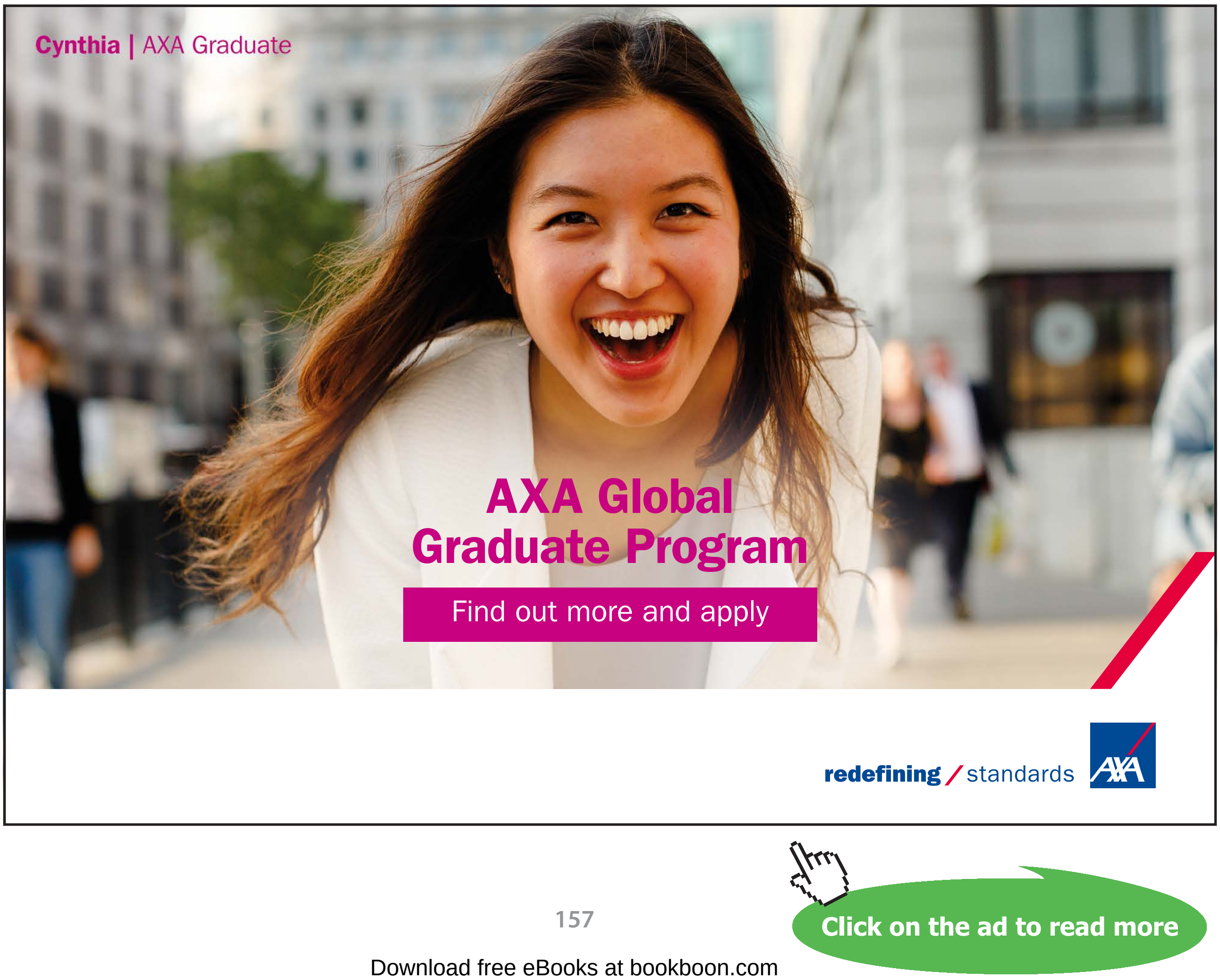


Figure 8.11 A large lake or reservoir will have zones along its length and from top to bottom, as suggested in this schematic. The riverine zone at the inlet and in tributary embayments has narrow channelized basins with relatively high flow rates. The broad deep lake basin (the lacustrine zone) has low velocities, is relatively clear, and is less eutrophic. (adapted from Loucks & van Beek 2005)



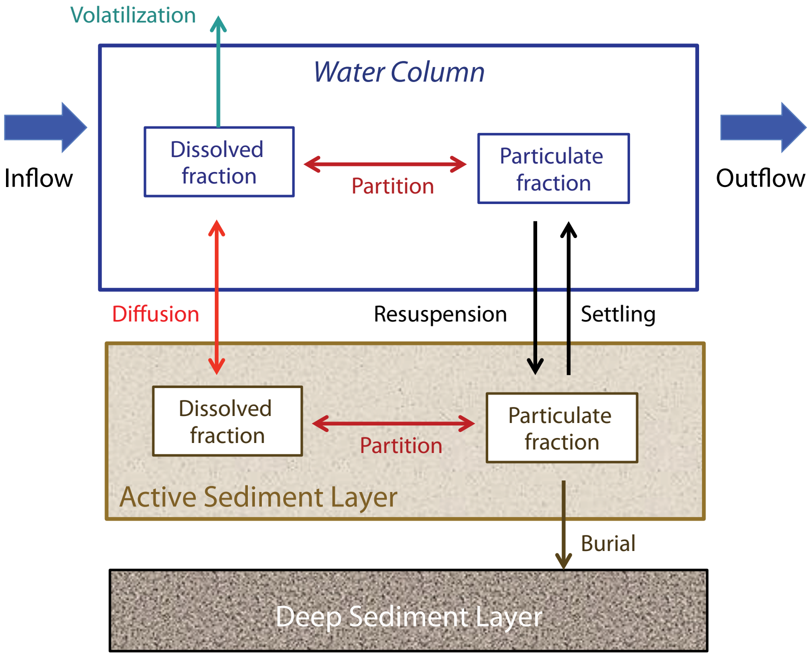


Figure 8.12 Conceptual model for a lake. Often the water column will be divided layers or segments.

Figure 8.12 is a conceptual model for a lake, showing an interchange of chemical between the sediment and the water column. The water column contains dissolved organic carbon, oxygen, nitrogen and phosphorus in various forms, carbonate compounds, and traces of many other substances. There will also be particulate matter, some living (algae, bacteria, protozoa) and some dead (detritus). The living organisms consume the dissolved nutrients and oxygen. The dead organisms decay and release nutrients and consume oxygen. Zooplankton consume other organisms and detritus.

Figure 8.13 is a hydrographic a map of Hagg Lake, Oregon, showing depths (left) and a grid (right) that was constructed to identify rather homogeneous sections for modeling. The first requirement is a hydrologic model of inflows and outflow that will predict the lake volume and surface area. Surface area data are needed to predict photosynthesis and the volume data are needed to get the residence time and correct concentrations, based on inflows and outflows. The model used was QUAL2-W2 (Ferrari 2001, Cole & Wells 2002).

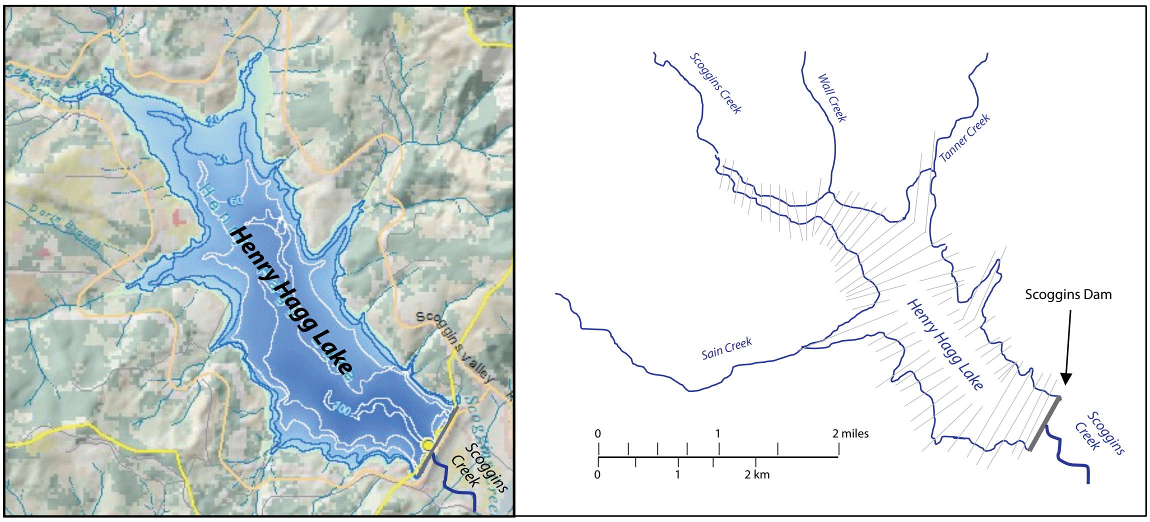


Figure 8.13 Map of Hagg Lake, Oregon, showing depth contours (left) and the grid (right) that was constructed to identify rather homogeneous sections for modeling. (Cole & Wells 2002)

8.8 Fate of Pollutants in Estuaries

8.8.1 The Tidal Cycle and Water Movement

An estuary is a narrow, semi-enclosed coastal body of water that has a free connection with the open sea and one or more rivers flowing into it, and within which the salinity of the water is measurably different than the salinity of seawater.

Estuaries were for many years regarded by large cities as a convenient location for discharging wastewaters. (Twenty-two of the world's largest cities are located on estuaries.) This resulted in major estuaries becoming seriously polluted. This situation is exacerbated by the long recovery time, which is nearer to that of lakes than of rivers.

Estuaries form a transition zone between river and ocean environments and are subject to both marine influences, such as tides, waves, and the influx of saline water; and riverine influences, such as flows of fresh water and sediment. The inflows of both seawater and fresh water provide high levels of nutrients in the water column and sediment, making estuaries among the most productive natural habitats in the world. A healthy estuary is a productive nursery and growth environment for fish, shellfish, and other aquatic organisms. Also, migratory bird populations make essential use of estuaries.

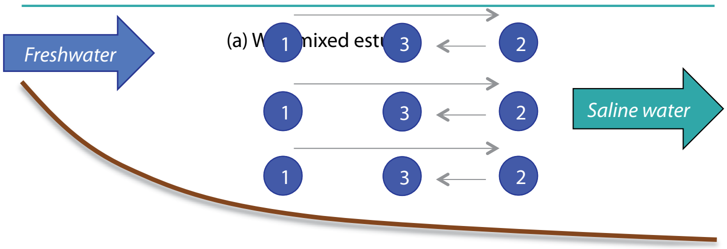
Two of the main challenges of estuarine life are the variability in salinity and sedimentation. Many species of fish and invertebrates have methods to control or conform to the shifts in salt concentrations. Many animals also burrow to avoid predation and to live in the more stable sediment environment.

Biologically estuaries can be commercially important for two reasons: (a) they are home to benthic vertebrates such as prawns and flounders, and (b) they serve as the gathering grounds for salmon (upstream) and eels (downstream). Where migration of salmon occurs, very high water quality is required to attract the fish to enter the estuary and then to move upstream successfully while undergoing the profound physiological change from sea water to fresh water.

Phytoplankton, mainly diatoms and dinoflagellates, are primary producers in estuaries. They move with the water and can be flushed in and out with the tides. Their productivity is largely dependent upon the turbidity of the water. Another primary source of food for many organisms, including bacteria, is detritus from dead organisms.

Estuaries tend to be naturally eutrophic because land runoff supplies nutrients. With urbanization and industrial growth, run-off also now includes chemicals used as fertilizers in agriculture and on lawns, waste from livestock and humans, and industrial inputs.

Water movement in estuaries is the complex result of a freshwater flow and a tidal oscillation, with additional momentum from the wind, and a density difference. The total distance travelled by a water particle from low water slack to high water slack and vice versa is referred to as the tidal excursion, as shown in Figure 8.14. This represents the maximum distance travelled by a water particle during the rising or falling limb of the tide. Tidal excursion is not to be confused with the distance travelled by the tide wave itself (e.g., high water), which propagates from the ocean to the end of the estuary each tide cycle, which may be up to 150 km.



(b) Stratified estuary

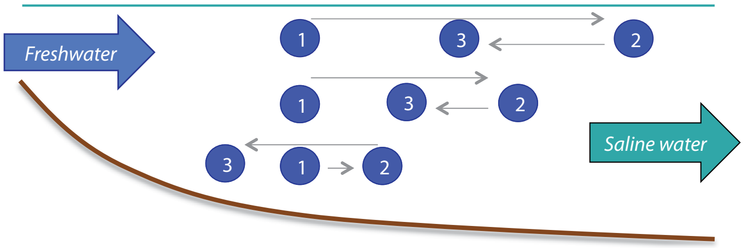
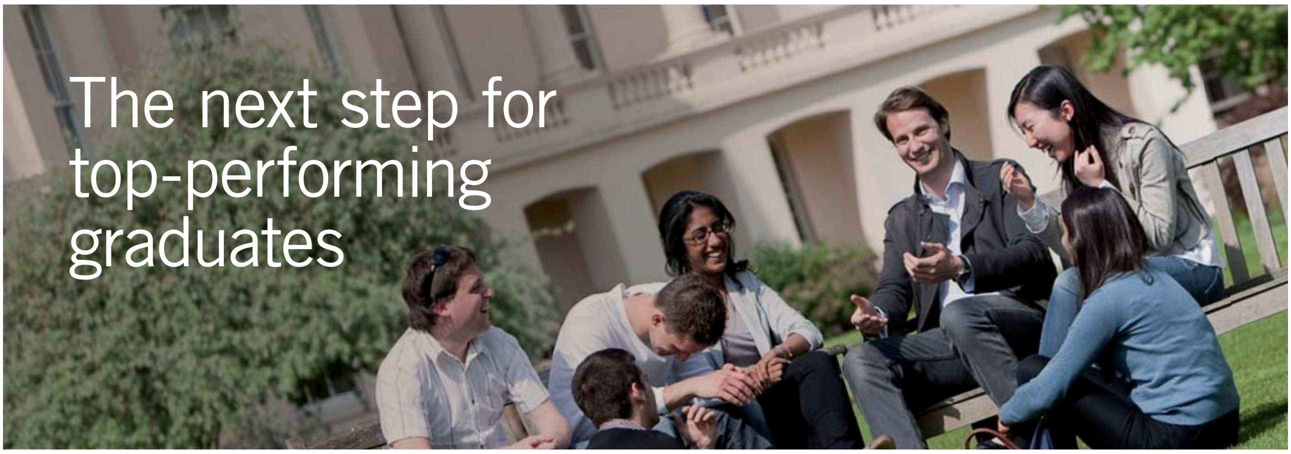


Figure 8.14 Movement of a parcel of water down an estuary. 1 is the start position. A parcel of water moves to position 2 at the end of the ebb tide and back upstream to position 3 at the end of the flood tide. The net tidal excursion is the distance between 1 and 3. This is the movement due to fresh water advection into the estuary. Several tidal cycles may pass before a parcel of water moves from the estuary inlet to the sea.

8.8.2 Salinity, Mixing and Stratification

Density differences due to temperature and salinity influence tidal mixing, Figure 8.15, shows the typical 3 percent increase in density that occurs from the freshwater inlet to the ocean. An estuary frequently has vertical gradients in salinity, depending on the mixing, as shown in Figure 8.16.

Saline coastal waters are carried into an estuary by the tides; freshwater inflows tend to wash the saltwater back out to sea. The presence of salt in an estuary produces a longitudinal density gradient, with water densities around the mouth of the estuary being greater (because of higher salt concentrations) than densities around the head of the estuary. This results in the enhancement of flood tide velocities near the bed and ebb tide velocities near the surface. When averaged over a tidal cycle, this behavior leads to residual currents, in which saline water flows upstream along the bottom of the estuary and less salty, even fresh water, flows seawards near the surface. This pattern of residual flows is referred to as gravitational circulation; it is driven by the gravitational forces resulting from density differences (see Figure 8.14b). Gravitational circulation can give rise to discharges that are 10 or 20 times greater than freshwater inflows. Gravitational circulation is an important mechanism of upstream sediment transport and the longitudinal dispersion of salt in estuaries.



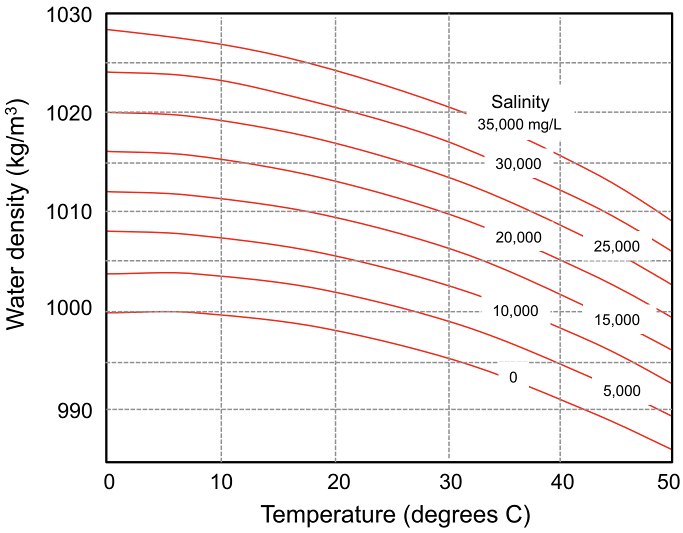


Figure 8.15 Water density as a function of temperature and salinity.

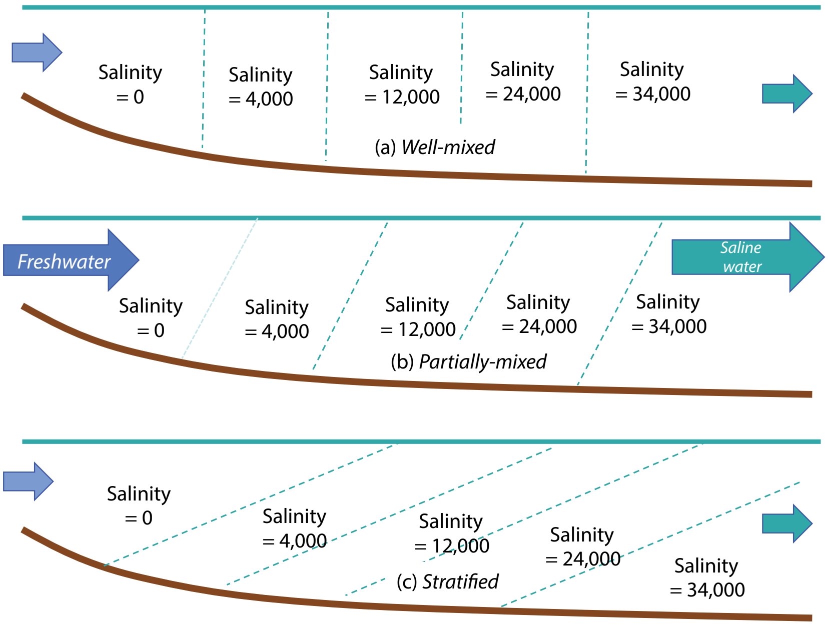


Figure 8.16 Classification of estuaries on the basis of vertical salinity gradients.

One major difference from the upstream river system is that high fresh water flows do not generate sufficient velocities on the bed of the estuary to wash out all the sediment and associated benthos. This particularly applies to stratified estuaries, where high freshwater flows cause an increased upstream movement of deep water. The biological consequences of this is the opportunity for building a much larger benthic community that depends on an adequate supply of dissolved oxygen to exist, or the accumulation of sediment which may adsorb high concentrations of toxins such as metals or organics.

The concentrations of a conservative pollutant in a well-mixed estuary are nearly the same in the surface layer and the bottom layers. In a stratified estuary the saline water flows along the bottom and is largely isolated from mixing with less dense wastewater discharges. The result is a high pollutant concentration near the surface, which is mainly seaward flowing river water, and a low concentration at the bottom.

A larger freshwater flow means a shorter residence time. A few Irish estuaries illustrate this. Galway Bay, a poorly flushed estuary, has an average residence time of from 59 days to several hundred days. The moderately-flushed Killary Harbor estuary average residence time is 40–50 days. Dublin Bay is well-flushed with a residence time of 1–2 days. Ninety percent of a conservative dye injected into Dublin Bay will be flushed away after ten tidal cycles. To reach the same dilution in Killary Harbor takes 250 tidal cycles.

8.9 Case Study – The Chesapeake Bay Watershed Model

Now we take a brief look at the complex Chesapeake Bay estuarine system. This is one of the most important estuaries in the United States. The Chesapeake Bay Phase 3 Watershed Model includes studies and models of land use, hydrology, geology, air quality, and water quality. The watershed extends into seven states and the District of Columbia. There are 24 land-use classifications and the watershed is divided into 899 sub-sections. (USEPA 2010; www.chesapeakebay.net)

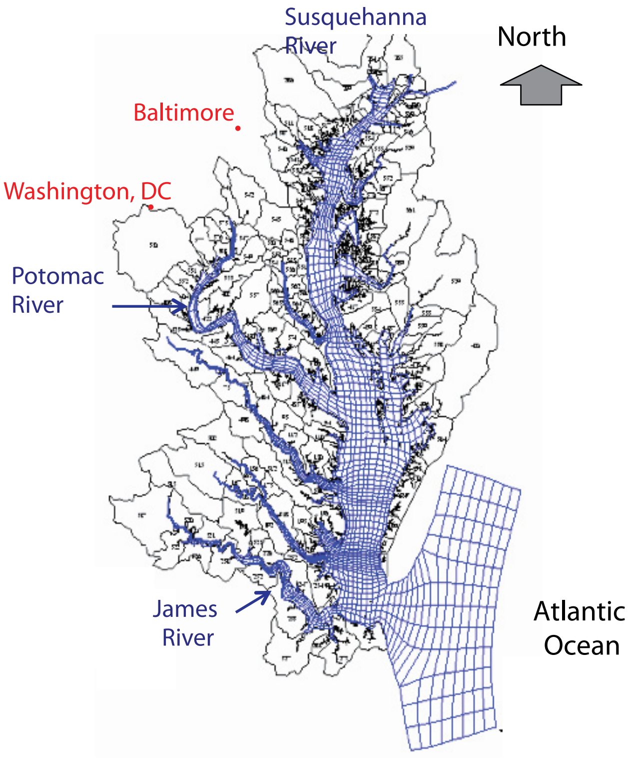


Figure 8.17 Structure of a water quality model for Chesapeake Bay, one of the most important estuaries in the United States (U.S. EPA 2010).

The water quality model has 54,000 cells, up to 15 layers deep (USEPA 2010). Figure 8.17 gives an idea of the structure of the model grid. There are 18 years of data to calibrate and test the model.

To compute algae and dissolved oxygen, 24 variables are used. A few of these are temperature, salinity, dissolved organic nitrogen, inorganic suspended solids, total phosphate, dissolved organic phosphorus, dissolved organic carbon, dissolved oxygen, ammonium, nitrate, chemical oxygen demand, diatoms, blue-green algae, micro-zooplankton and meso-zooplankton (Cerco & Noel 2004).

The predicted conditions are bottom-water hypoxia, the spring phytoplankton bloom, nutrient limitations, sediment-water interactions, and the nitrogen and phosphorus budget.

Figure 8.18 is an example of the model output that shows dissolved oxygen for June 2009. A large portion of the estuary, especially the deeper water, has zero dissolved oxygen (red). The surface water has sufficient oxygen for fish (DO > 4 mg/L) due to wind-aided aeration. The dissolved oxygen situation is better in the colder months of the year.

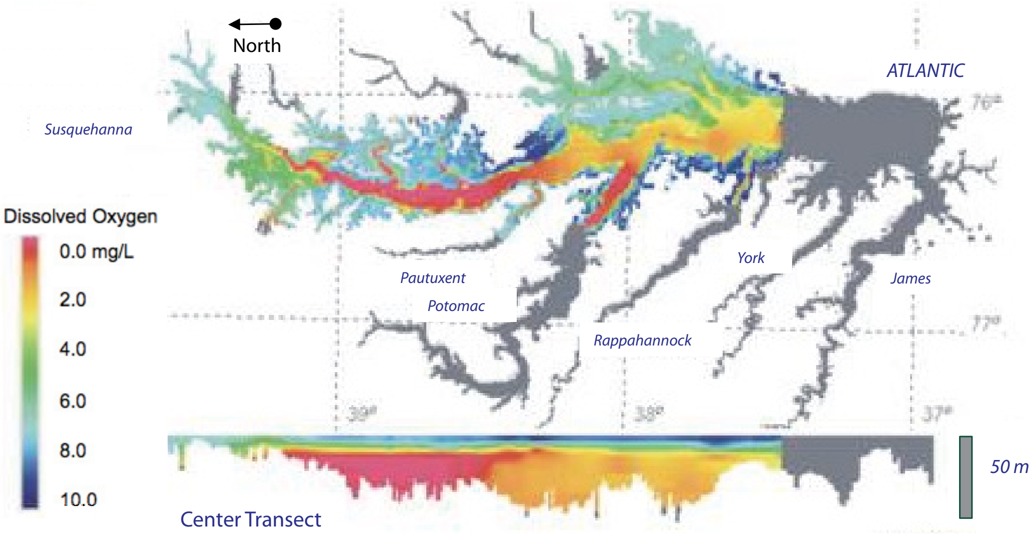


Figure 8.18 Model results for dissolved oxygen in Chesapeake Bay for June 2009. The bottom plot shows the condition along the centerline of the estuary. There is sufficient dissolved oxygen for fish (DO > 4 mg/L) in the upper layers, but a large region of deeper water is oxygen deficient. Note the map has been turned so North is to the left instead of the top as would be normal. (Maryland Eyes on the Bay web site).

8.10 Fate of Pollutants in the Sea

8.10.1 Dilution and Buoyant Jets

An ocean outfall is used to discharge an effluent some distance from the shore of large coastal cities and to achieve a high dilution factor. Because of the need to prevent deposition of material on beaches, discharge to the sea invariably occurs at some distance past the lowest low water mark.

If dilution of a pollutant is an acceptable disposal method, the dilution must be accomplished by injecting the low-density effluent below the high-density seawater. The density difference aids mixing. The effluent emerges as a jet from a diffuser and becomes buoyant due to the density difference and the momentum of the discharge. The jet entrains seawater and expands with a gradual reduction in both velocity and concentration. When the dilution factor reaches 50, the buoyancy is virtually zero.

Maximum dilution occurs when the effluent mixes all the way to the ocean surface. It is possible for a dense layer of seawater to inhibit the plume rise. This is analogous to the gaseous plume from a stack being trapped near the ground by heavy atmospheric conditions.

8.10.2 The Deer Island Boston Harbor Project

A recent and successful ocean outfall installation is part of the Boston Harbor Project, Figure 8.19. Boston treats its wastewater at the Deer Island Plant, the second largest treatment plant in the United States. With the former outfall locations, high pollutant concentrations were found within Boston Harbor and along the coastline immediately south. With the new outfall location, high concentrations are found only within a few kilometers of the outfall, concentrations are dramatically lower in Boston Harbor.

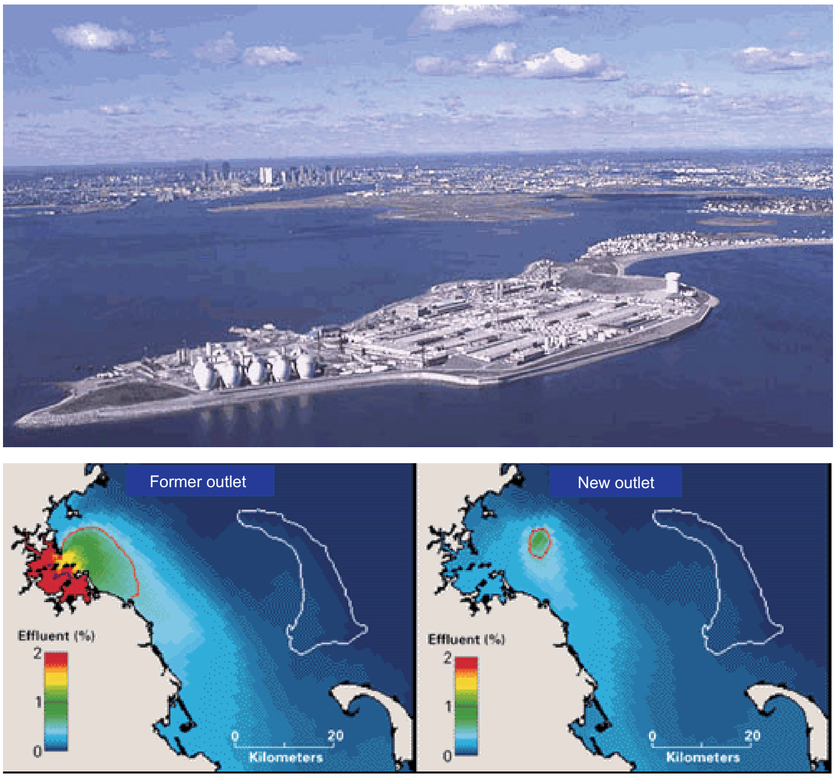


Figure 8.19 The Deer Island Boston Harbor Project. The lower pictures are computer-generated maps showing the lack of effective dispersal of effluent from the former outfall (left-hand map) and the highly effective dilution and dispersal from the new outlet. The white tip of land is the northern tip of Cape Cod. The area outlined in white is the Stellwagen Bank. The top photo shows the Deer Island Wastewater Treatment Plant, Boston, the second largest treatment plant in the United States. The egg-shaped structures in the left foreground are anaerobic sludge digesters (12 units, 64 m tall, 3 million gallon volume). (Source: Massachusetts Water Resources Authority (MWRA.com) 2009)

The outfall, Figure 8.20, has a design hydraulic capacity of 1,270 million gallons per day (4.8×10^6 m^3/day). The length is 49,624 ft (15.1 km) and the diameter is 24 ft (7.3 m). The effluent is discharged through 270 diffuser ports that have diameters of 0.49 ft (0.15 m) to 0.64 ft (0.20 m). A 400 ft (120 m) drop shaft feeds a 43,300 ft (13.2 km) outfall tunnel and a 6,600 ft (2.0 km) diffuser tunnel. The tunnels are in bedrock. The diffusers are seated on the sea floor some 250 ft (76 m) above the diffuser tunnel and 100 ft (30 m) below the water surface. [approximate metric conversions shown]

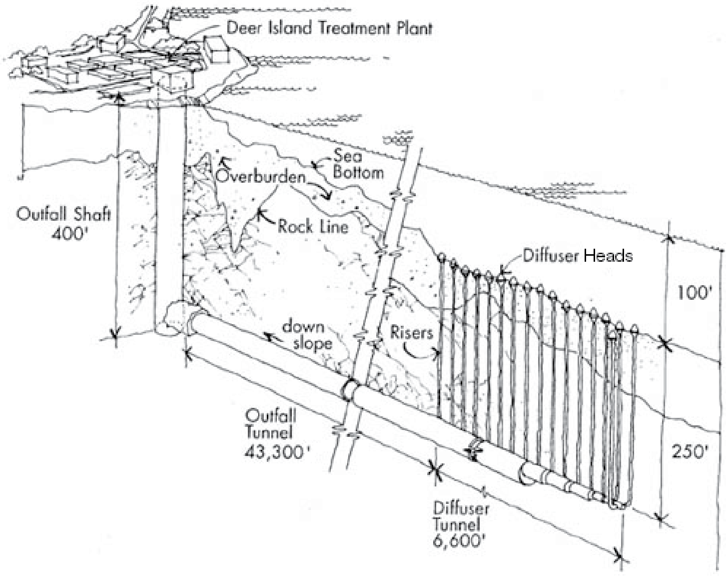


Figure 8.20 The effluent tunnel and diffusers constructed in Massachusetts Bay (Boston) to serve the Deer Island Wastewater Treatment Plant. The design discharge capacity is 1,270 x 10^6 gal/d (4.8 x 10^6 m^3/d).

(Source: Massachusetts Water Resources Authority (MWRA.com) 2009)

8.11 Conclusion

Useful water quality models range from the simple input-output calculation for a mixing zone, to segmented river models with 2 to 15 water quality variables, to compartmentalized models of stratified reservoirs, to the 24-variable, 54,000 cell Chesapeake Bay model.

The range of complexity that can be formulated and calculated is astonishing. Where one works within that range is determined by the available data and the local problem. The Chesapeake Bay estuary is complex and impressive, but it could not have been developed and verified without the excellent historical data.

Use the simplest model that will answer the important questions.

9 The Fate of Pollutants in Soil and Groundwater

9.1 Groundwater Contamination

Contaminated groundwater problems often are not detected until many years after the initiating event. A chemical spilled onto the ground may slowly sink into the groundwater and then move a few meters per year until it is finally detected at a drinking water well. By then the relatively small problem of cleaning up a spill has become a large problem of cleaning a contaminated aquifer.

The largest and most serious contaminated groundwater sites were created through ignorance, carelessness, and accidents. Dangerous chemicals were dumped without much thought about their persistence and ability to disperse. Chemicals were spilled around factory loading docks. Underground storage tanks leaked. Industrial and military wastes were dumped into pits and lagoons that did not retain the materials. Landfills slowly released leachate. Table 9.1 lists the many ways that problems can originate.

Controlled applications of pesticides and herbicides can pollute groundwater and indiscriminate use has loaded aquifers and lakes with atrazine and other varieties.

The Problem Originates		
On the land surface	**In the ground above the water table**	**In the ground below the water table**
• Infiltration of polluted surface water • Land disposal of solid or liquid wastes • Stockpiles or dumps • Disposal of sewage or water-treatment plant sludge • De-icing salt usage and storage • Animal feedlots • Accidental spills • Particulate matter from airborne sources • Infiltration of polluted surface water • Land disposal of solid or liquid wastes • Stockpiles or dumps	• Septic tanks, cesspools, and privies • Holding ponds and lagoons • Sanitary landfills • Waste disposal in excavations • Leakage from underground storage tanks • Leakage from underground pipelines • Artificial recharge • Sumps and dry wells • Graveyards	• Waste disposal in well excavations • Drainage wells and canals • Well disposal of wastes • Underground storage • Mines • Exploratory wells • Abandoned wells • Water-supply wells • Ground-water development

Table 9.1 Sources of Ground-Water Quality Degradation

9.2 The Movement of Groundwater

The flow of water in a saturated aquifer is defined by Darcy's Law:

$$Q = KiA$$

where K = hydraulic conductivity (L/T), i = hydraulic gradient (L/L) and A = cross sectional area through which the flow is conducted (L^2). Note that A is the area of cross-sectional face of the soil and not the area of the pore openings in the face. These terms are defined in Figure 9.2

The apparent average velocity of the groundwater is Darcy's flux: $V = Ki$

The actual average velocity of the water through the soil pores is: $V = Ki/\theta$
where θ is the soil porosity.

K varies over many orders of magnitude, from 10^{-9} for fine clay to 100 for coarse gravel. A crude scale of hydraulic conductivity of soils is

Clayey = $10^{-9} - 10^{-6}$ cm/s
Silty = $10^{-7} - 10^{-3}$ cm/s
Sandy = $10^{-5} - 10^{-1}$ cm/s
Gravelly = $10^{-1} - 10^{2}$ cm/s

The change in hydraulic gradient provides the force to move the water. The easiest picture of this is the slope of the groundwater table below the ground surface. The flow moves in the downhill direction of the hydraulic gradient. This can be observed by installing observation wells. (There is a hydraulic gradient even when the aquifer is confined by an upper impervious layer, but it is less easy to picture.)

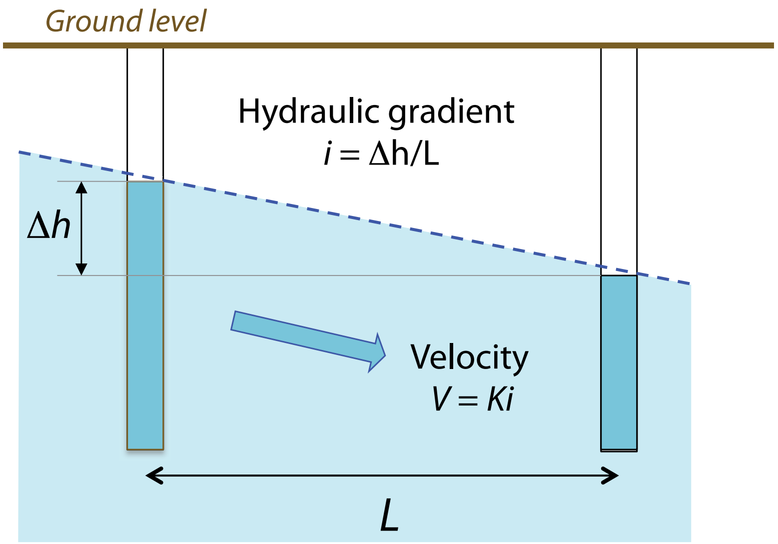


Figure 9.1 The hydraulic gradient is *Δh/L*, expressed as m/m (ft/ft)

The concentration of pollutant in the groundwater is *C*, usually expressed as mg/L or µg/L. The mass flux of contaminant is

$$QC = KiAC$$

9.3 The Movement of Chemicals in Groundwater

A contaminant plume will spread and be diluted as it moves down gradient with the groundwater. If the distance, or time of travel, between the source of contamination and a drinking water well or river is sufficient, dilution may eliminate the potential problems of toxicity and unpleasant tastes and odors. To the contrary, if the dilution is not sufficient and a problem still exists, the volume of affected groundwater has grown, perhaps to a magnitude that makes it difficult and expensive to interrupt the contaminant movement or clean up the groundwater.

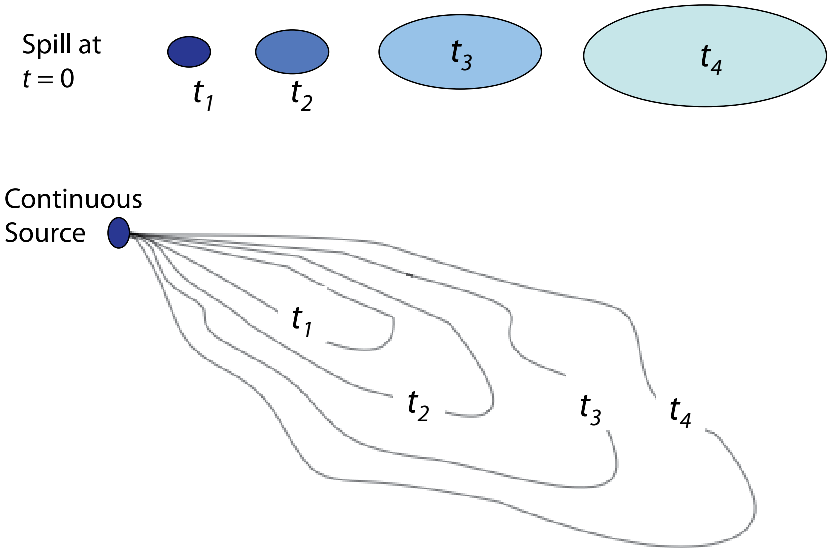


Figure 9.2 Hypothetical plumes for a spill (a one-time source) and a continuous source of contamination.

Figure 9.2 shows hypothetical plumes for of a one-time source (top), such as an accidental spill, and for a continuous source (bottom), such as a dump of leaking drums or an underground storage tank. Showing only one contour for concentration suggests a single chemical moving with the groundwater.

Most contaminated sites involve a mixture of chemicals and many chemicals do not move at the average velocity of the groundwater. They move slower due to the effect of adsorption to the soil. This is particularly true for less soluble contaminants, which can move even hundreds of times slower than water. The effect is for the more soluble (less adsorbable) species to travel faster and farther than the less soluble ones.

This phenomenon is measured by the *retardation factor,* R_d.

$$\text{Retardation factor} = R_d = \frac{\text{Velocity of water}}{\text{Velocity of chemical}}$$

$$\text{Velocity of chemical} = \frac{\text{Velocity of water}}{R_d}$$

A higher value of R_d means the chemical movement is slower relative to the groundwater movement.

Example 9.1 Movement of a non-reactive contaminant

How long will it take for a non-reactive contaminant to travel a distance of 10 m if Darcy's flux is $V = 5$ cm/day through saturated soil. The porosity of the saturated soil is $\theta = 0.5$.

$V_{\text{water}} = V/\theta = (5 \text{ cm/day})/0.5 = 10 \text{ cm/day}$

Time for the chemical to travel 10 m = (10 m)(100 cm/m)/(10 cm/day) = 100 days

Example 9.2 Movement of a reactive contaminant

How long will it take for a reactive contaminant ($R_d = 11.4$) to travel a distance of 10 m if Darcy's flux is $V = 5$ cm/day and the porosity of the saturated soil is $\theta = 0.5$.

The water is traveling at $V_{\text{water}} = (5 \text{ cm/day})/0.5 = 10 \text{ cm/day}$

The chemical is traveling at $V_R = V_{water}/R_d = (10 \text{ cm/day})/(11.4) = 0.877 \text{ cm/day}$

Time for the chemical to travel 10 m = (10 m)(100 cm/m)/(0.877 cm/hr) = 1140 days

The retardation factor is strongly related to solubility – higher solubility means a lower retardation coefficient. For example, the solubility of chloroform is 8,200 mg/L and chlorobenzene is 500 mg/L; their retardations factors are 3 and 35.

R_d also depends on the chemical nature of the aquifer and on the chemical concentration. The retardation coefficient is higher at low concentrations, and low at high concentrations. This means it becomes more difficult to extract chemical from a contaminated site as it becomes cleaner. The residual adsorbed chemical is released more slowly from the soil.

9.4 Redirecting Groundwater Flow by Pumping

A pumped well changes the local hydraulic gradient and can be used to divert a contaminated flow away from drinking water wells. The pumped well can also be used to extract contaminated groundwater for treatment. Figure 9.3 shows how pumping creates a draw down cone (in effect, a drain hole) around the well that will collect and accelerate the withdrawal of groundwater.

Figure 9.4 shows a hypothetical spill or leak of an organic chemical pollutant that is dense enough to sink. It may also exist as a vapor in the unsaturated soil zone (the zone above the groundwater table), as a dissolved molecule in the moving groundwater, and be adsorbed onto the soil. A pump-and-treat facility is proposed to extract the contaminated water before reaches the city well water water supply.

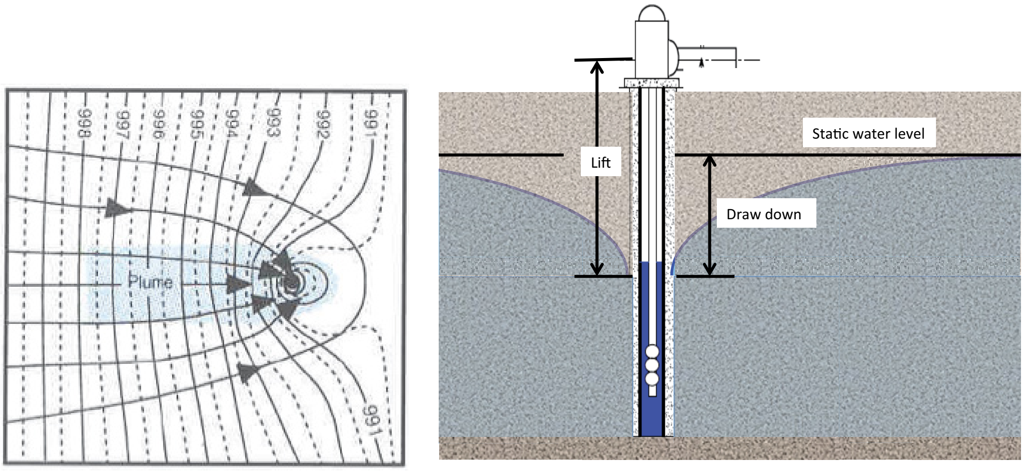


Figure 9.3 A pumped well redirects the flow of groundwater by altering the local hydraulic gradient.

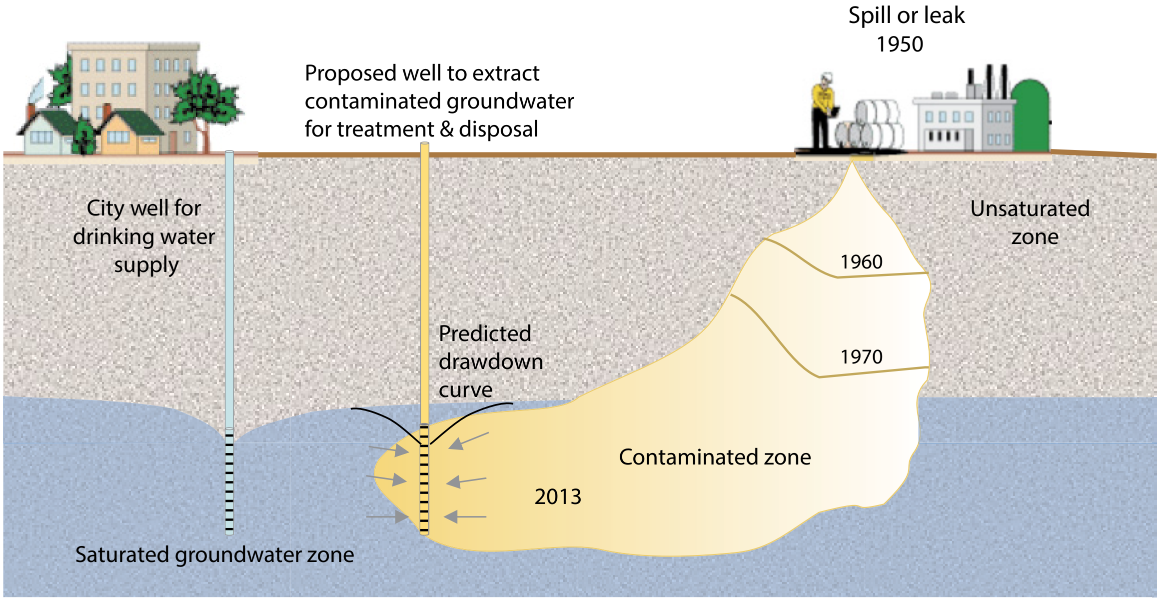


Figure 9.4 Hypothetical plume from a chemical spill in 1950 that is to be redirected and extracted by a pump-and-treat facility. There may be chemical vapor in the unsaturated zone.

9.5 Case Study: Tucson International Airport Area (TIAA) Superfund Site

Models are used to understand how a problem developed and to predict how it will unfold in the future. A model may be needed to estimate how much chemical was spilled or leaked into the groundwater, and when the material first entered the groundwater. Rarely does one find reliable records about quantities and kinds of chemical that were lost.

How quickly will the contaminant travel, and in which direction, and how will the concentrations change over time? Can the spread of the plume be contained by strategically located wells? How many wells would be needed, where should they be located, and what pumping capacity should be installed? As time goes on, and the plume changes in size and concentration, how should the containment or cleanup program be modified? Is the expected time scale of the project months or years?

There is no way to answer these questions without modeling. Monitoring data, even long records, cannot be extrapolated toward future conditions once we start containment or remediation.

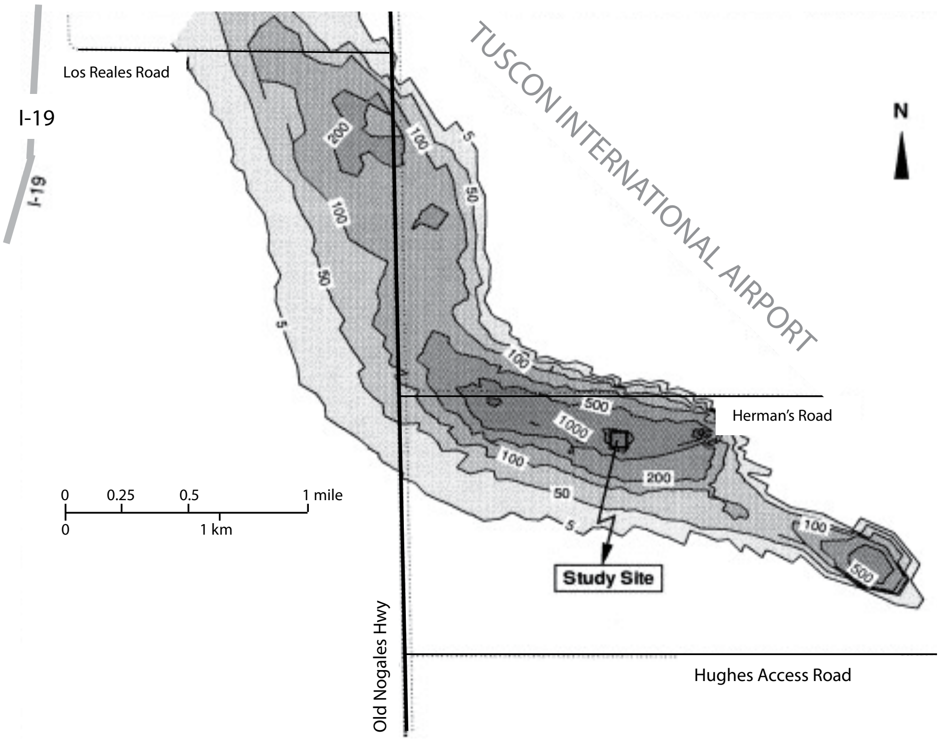


Figure 9.5 Trichloroethylene (TCE) plume at the Tucson International Airport Area (TIAA) in 1987 before the Superfund cleanup began.

Figure 9.5 is a 1987 map of a trichloroethylene (TCE) plume at the Tucson International Airport Area (TIAA). At least twenty separate facilities have operated at the TIAA since 1942, including aircraft and electronics facilities that discharged waste liquids directly into the soil in the World War II era.

Trichloroethylene does not occur naturally in the environment. It is used as a metal degreaser, and may be found in paint and cleaning fluids. It evaporates easily, but if released onto soil it readily enters the groundwater. The state and Federal drinking water standards for TCE are 5 µg/L and 3 µg/L for 1,4-Dioxane. Drinking water with these contaminates may cause kidney, liver, and lung damage, and lymphoma.

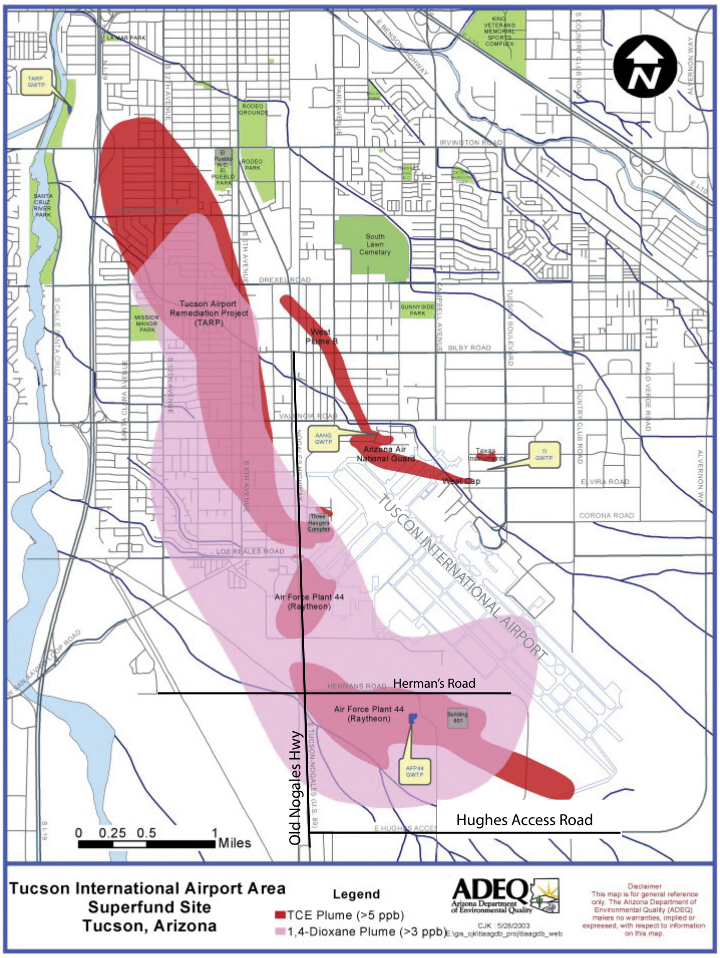


Figure 9.6 TCE plume in groundwater at the Tucson International Airport Area Superfund Site in 2010. TCE = 5 µg/L in drinking water. The dark red areas are where the TCE plume was above 5 µg/L TCE. The light red areas is where the 1,4-Dioxane plume was above 3 µg/L.The highest TCE concentrations were about 300 µg/L. Source: Arizona Dept. of Environmental Quallity. (More detailed maps of the TCE and 1,4-Dioxane plumes, that can be found by searching for TCE Plume, TIAA CERCLA Site, Tucson.)

The area was named a Superfund site in 1982 and subsequent sampling identified a main plume of contaminated groundwater approximately 0.5 miles (0.8 km) wide and 5 miles (8 km) long. In 1982, when cleanup started, the contaminants were found 25 to 30 meters below ground surface in an aquifer that is 20 to 30 meters thick. Additional smaller plumes of contamination north and northwest of the airport have been found. The plumes are moving west toward the river.

Figure 9.6 shows the TCE and 1,4-Dioxane plumes in 2010, after a 20-year, $20 million cleanup. More than 100 million cubic meters of groundwater have been extracted and treated to remove more than 60,000 kg of volatile organic chemicals. The dark red areas are where the TCE plume was above 5 µg/L TCE. The light red areas are where the 1,4-Dioxane plume was above 3 µg/L. It may take another 20 years of cleaning to meet the drinking water standard.

Figure 9.7 shows the model predictions for TCE mass removed by remediation (solid line) and without remediation (dotted line). The concentrations observed over the first eight years are shown with dots.

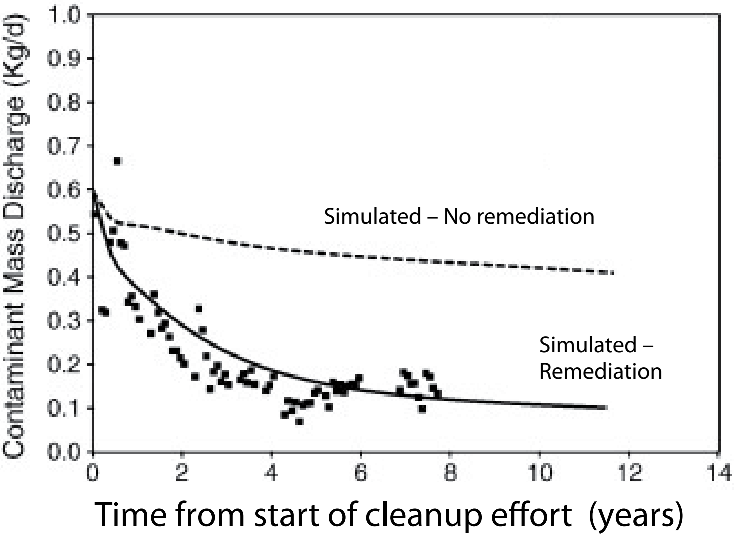


Figure 9.7 Model predictions for TCE at the Tucson airport site with remediation (solid line) and without remediation (dotted line). The mass of TCE removed over the first eight years are shown with dots. Time = 0 is the start of the cleanup effort.

9.6 Conclusion

Groundwater modeling is a challenge because there typically is not a lot of data when the project begins. Air pollution modeling generally will have the most dense data sets and groundwater will be the most sparse. Monitoring wells need to be installed. Analyzing the water samples for toxic organic chemicals requires special methods. The groundwater moves slowly so doing repeated sampling over a short time does not provide a great deal of new information. The slow rates of movement and change dampen the sudden changes and seasonality that can complicate air and surface water quality modeling.

10 Guidelines for Environmental Protection

10.1 Introduction

Investments in water supply and sanitation usually yield economic benefits. The reductions in adverse health effects and health care costs outweigh the cost of intervention. Nevertheless, environmental protection often comes after the development of schools, hospitals, telecommunications, transportation and other national needs. This was true in the United States and in Europe. And it usually comes under pressure from a collection of laws that protect environmental quality and public health.

Every pollution control project has a legal component. The laws are complicated. It is difficult, but necessary, to learn the applicable rules and regulations and work within the legal constraints they impose. They will dictate which chemicals and substances are to be controlled, and they constrain the quantities and concentrations that may be released into the environment. Some laws specify pollution control technology. Some prescribe analytical methods and how remedial investigations are to be done. They establish requirements for getting permits to discharge effluents and gaseous emissions, and to transport and store solid wastes.

The laws have been developed with an understanding of the natural cycles of carbon, nitrogen and phosphorus. They are based on the science of toxicology and bioassays, and on the engineering methods of risk assessment and calculating the fate of pollutants in the environment. These are the subjects in the previous chapters.

In this chapter we undertake a brief survey of the most important World Health Organization guidelines, European Union directives, and United States federal laws. This is necessarily superficial, but those who are not familiar with environmental law may find the material helpful as a guide to finding more details, if they should be desired. Fortunately, vast amounts of information are readily available on web sites of the USEPA, the European Union, and the World Health Organization. The USEPA has delegated implementation of the laws to the states, as the European Union has done for its members, and this creates another second level of accessible information. Wikipedia is also an excellent source of information.

10.2 International Environmental Agreements

The *Rio Declaration on Environment and Development*, produced at the 1992 Earth Summit, consisted of 27 principles for future sustainable development around the world (Wikipedia). Three of these are:

- In order to achieve sustainable development, environmental protection shall constitute an integral part of the development process chain and cannot be considered in isolation from it.
- States shall enact effective environmental legislation. Environmental standards, management objectives and priorities should reflect the environmental and developmental context to which they apply. Standards applied by some countries may be inappropriate and of unwarranted economic and social cost to other countries, in particular developing countries.
- Peace, development and environmental protection are interdependent and indivisible."

The *Kyoto Protocol* is an international treaty that sets binding obligations on industrialized countries to reduce emissions of greenhouse gases. The goal is to prevent "dangerous" human-induced interference of the climate system.

Many developed countries have agreed in two commitments periods. The first period applied to greenhouse gas emissions between 2008–2012. Developed countries may use emissions trading until late 2014 or 2015 to meet their first-round targets. The second commitment period applies to emissions between 2013–2020, but this amendment has (as of January 2013) not entered into legal force.

The 37 countries with binding targets in the second commitment period are Australia, all members of the European Union, Belarus, Croatia, Iceland, Kazakhstan, Norway, Switzerland, and Ukraine. Japan, New Zealand, and Russia participated in Kyoto's first round but have not taken on new targets in the second commitment period. The United States signed but did not ratify the Protocol and Canada withdrew from it in 2011.

The *Vienna Convention for the Protection of the Ozone Layer* of 1985 is a multilateral environmental agreement that was ratified by 196 states, including all United Nations members and the European Union. It acts as a framework for international efforts to protect the ozone layer, but it does not include legally binding reduction goals for the use of CFCs, the main chemical agents causing ozone depletion. These are laid out in the accompanying *Montreal Protocol*.

10.3 World Health Organization Guidelines

10.3.1 Drinking Water

The WHO Guidelines for Drinking-water Quality (WHO 2011) explain the science and risk assessment methods behind the WHO chemical and microbiological standards. The guidelines provide toxicity data and explain how the guidelines were established for the toxic metals and organic chemicals listed in Table 10.1. Guidelines are also given for agricultural chemicals (nitrate and pesticides) and radionuclides.

The use of 'guidelines', as opposed to standards or mandatory limits, is in recognition that the minimum requirements for safety are universal, but the nature and form of drinking water standards may vary among countries.

Metals	**Guideline Values (mg/L)**	**Organic Chemicals**	**Guideline Values (µg/L)**
Arsenic	0.01 (P)	Benzene	10[b]
Barium	0.7	Carbon tetrachloride	4
Boron	0.5 (T)	Di(2-ethylhexyl)phthalate	8
Cadmium	0.003	1,2-Dichlorobenzene	1000 (C)
Chromium (total)	0.05 (P)	1,4-Dichlorobenzene	300 (C)
Cyanide	0.07	1,2-Dichloroethane	30[b]
Fluoride	1.5	1,2-Dichloroethene	50
Manganese	0.4 (C)	Dichloromethane	20
Mercury (inorganic)	0.006	1,4-Dioxane	50[b]
Molybdenum	0.07	Hexachlorobutadiene	0.6
Selenium	0.01	Nitrilotriacetic acid (NTA)	200
Uranium[a]	0.015 (P, T)	Pentachlorophenol	9[b] (P)
		Styrene	20 (C)
		Tetrachloroethene	40
		Toluene	700 (C)
		Trichloroethene	20 (P)
		Xylenes	500 (C)

Table 10.1 Guideline values for chemicals that are of health significance in drinking water (WHO 2011).

[a] Only chemical aspects of uranium addressed; radiation risk not included.

[b] For non-threshold substances, the guideline value is the concentration in drinking-water associated with an upper bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking water containing the substance at the guideline value for 70 years). Concentrations associated with estimated upper-bound excess lifetime cancer risks of 10-4 and 10-6 can be calculated by multiplying and dividing, respectively, the guideline value by 10.

P = provisional guideline value based on evidence of a hazard, but the available information on health effects is limited.

T = guideline value set at the practical treatment limit, source protection, etc.

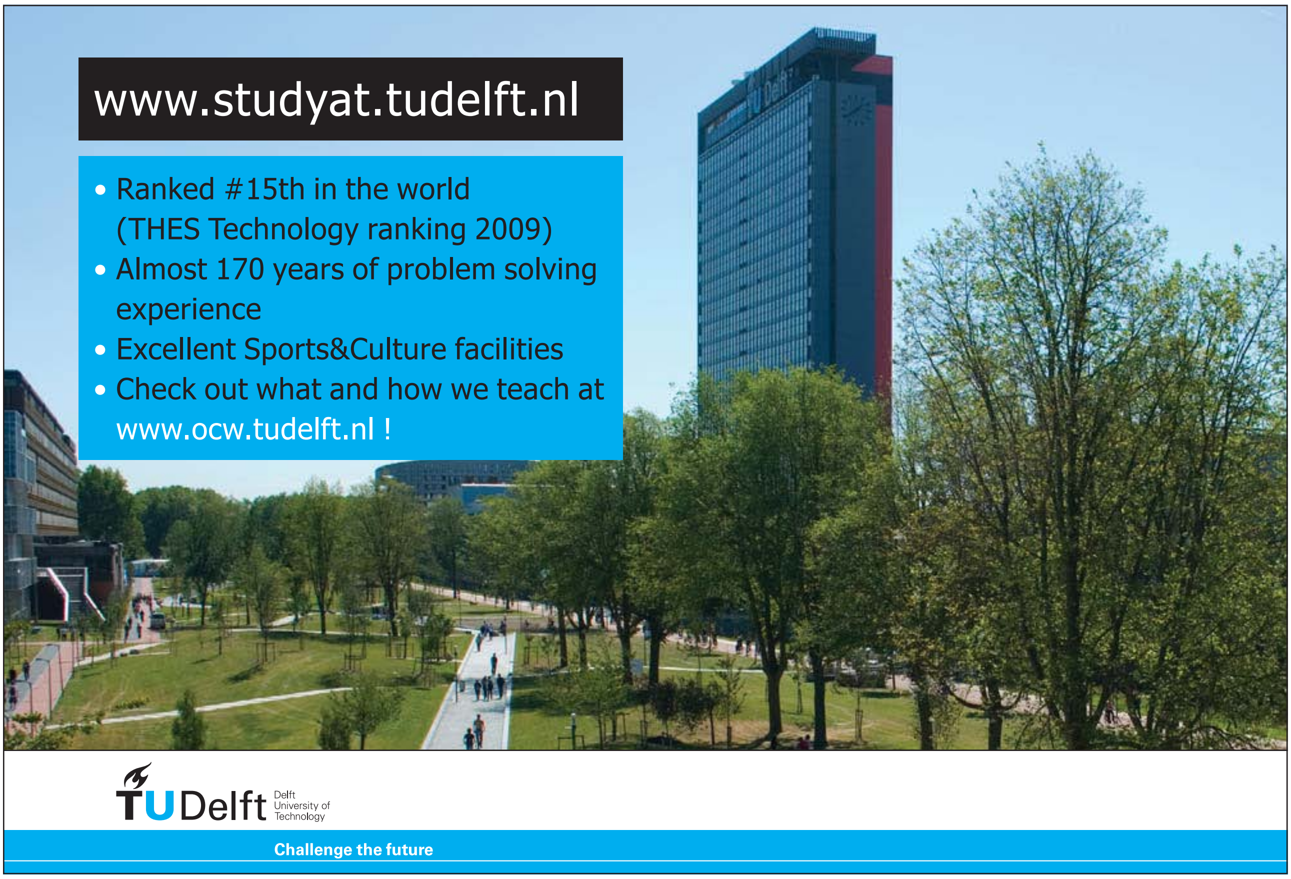
C = concentrations at or below the health-based guideline value may affect the appearance, taste or odor of the water.

10.3.2 Air Quality

WHO (2011) states these basic facts about air pollution:

- Air pollution is a major environmental risk to health.
- By reducing air pollution levels, we can help countries reduce the global burden of disease from respiratory infections, heart disease, and lung cancer.
- Exposure to air pollutants is largely beyond the control of individuals and requires action by public authorities at the national, regional and even international levels.
- The lower the levels of air pollution in a city, the better respiratory and cardiovascular health of the population will be.
- Urban outdoor air pollution is estimated to cause 1.3 million deaths worldwide per year. Those living in middle-income countries disproportionately experience this burden.
- Indoor air pollution is estimated to cause approximately 2 million premature deaths mostly in developing countries. Almost half of these deaths are due to pneumonia in children under 5 years of age.

The WHO Air Quality Guidelines (2009) represent the most widely agreed upon and up-to-date assessment of health effects of air pollution, recommending targets for air quality at which the health risks are significantly reduced. Table 10.2 summarizes the WHO air quality guidelines (2006).



Contaminant	Guideline Value
$PM_{2.5}$	10 μg/m^{3}annual mean 25 μg/m^3 24-hour mean
PM_{10}	20 μg/m^3 annual mean 50 μg/m^3 hourly mean
Ozone	100 μg/m^3 8-hour mean
NO_2	40 μg/m^3 annual mean 200 μg/m^3 1-hour mean
SO_2	20 μg/m^3 24-hour mean 500 μg/m^{3}10-minute mean
VOCs (benzene)	5 μg/m^3

Table 10.2 WHO Air Quality Guidelines (2006).

Outdoor urban air pollution, much of it generated by vehicles, is associated with higher rates of cardiovascular and respiratory diseases. Exhaust from gasoline and diesel engines contains irritating and toxic chemicals. Sulfur dioxide is corrosive. Ozone is dangerous to persons with breathing disorders (e.g., asthma). In general, particles emitted by fuel combustion processes may contain or carry more toxic compounds (e.g. metals) than particles from natural sources such as dust storms. SO_2 emissions are contributed mainly by thermal power generation and NO_2 is an indicator of vehicular pollution, although it is produced in almost all combustion reactions. Particulate matter (PM) is the most general indicator of pollution because it receives key contributions from fossil fuel burning, industrial processes, and vehicular exhaust.

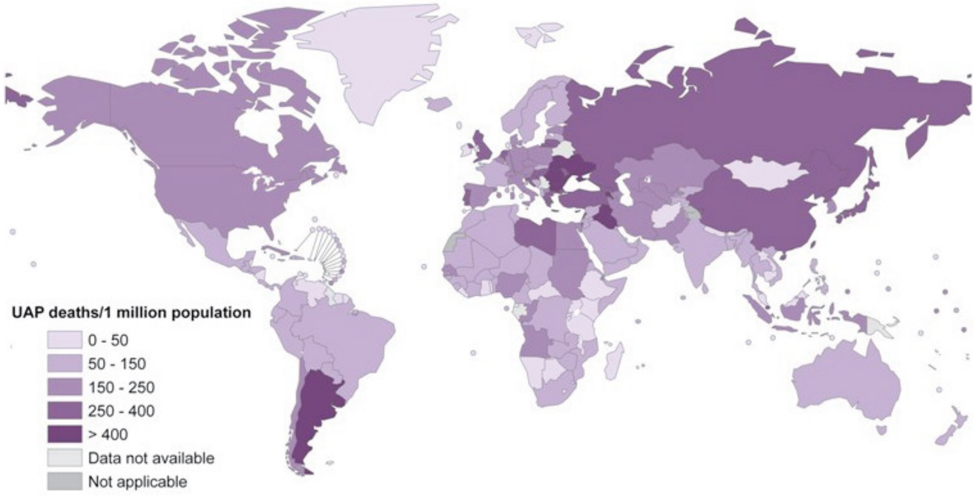


Figure 10.1 is a World Health Organization map of deaths attributable to urban air pollution (WHO 2009).

Figure 10.1 maps the WHO estimates of premature deaths caused by urban air pollution. The 2008 estimate was some 1.3 million deaths around the world (WHO 2009) and that more than 1 million deaths could be avoided if the mean annual Air Quality Guideline values of PM_{10} = 20µg/m^3 and $PM_{2.5}$ =10 µg/m^3 were implemented. At present, total PM_{10} or $PM_{2.5}$ mass concentrations per volume of ambient air are considered to be the best indicators of potentially health-damaging exposures for risk reduction purposes.

10.3.3 Particulate Matter

Particulate matter (PM) affects more people than any other pollutant. The major components of PM are sulfate, nitrates, ammonia, sodium chloride, carbon, mineral dust and water. It consists of a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air.

The particles are identified according to their aerodynamic diameter, as either PM_{10} (particles with an aerodynamic diameter ≤ 10 µm) or $PM_{2.5}$ (aerodynamic diameter ≤ 2.5 µm). Particle shape and chemical composition as well as size are thought to influence their harmfulness, as do the metals or adsorbed organic chemical that adsorb to their surface. The $PM_{2.5}$ fraction has also been measured for several years in the U.S. The EU has started to measure $PM_{2.5}$, although the present standards only apply to PM_{10}. Some measurements have also been initiated to study the very smallest particles, such as PM_1 and $PM_{0.1}$.

The very fine particles are considered the most harmful because they may be inhaled deep into the bronchioles, and interfere with gas exchange inside the lungs. Studies made in the U.S. and in Europe have shown that a rise in the concentration of small particles, even from low levels, causes a rise in mortalities from respiratory, cardiac and circulatory diseases, and more people seek hospital care for bronchitis and asthma. Even exposure to low levels for long periods is considered harmful. The Guidelines indicate that reducing particulate matter (PM_{10}) pollution from 70 to 20 micrograms per cubic meter can cut air quality related deaths by around 15%.

The mortality in cities with high levels of pollution exceeds that observed in relatively cleaner cities by 15–20%. Average life expectancy in the EU is reduced by 8.6 months due to exposure to $PM_{2.5}$ produced by human activities. Calculations for Austria, Switzerland, and France indicate that PM_{10} particles at current levels cause 40,000 premature deaths a year, and the average life expectancy of people living in an urban environment is reduced by 18 months. A recent study on 19 European cities with a total population of 32 million concluded that reducing the levels of PM_{10} by just 5 µg/m^3 would prevent more than 5,500 premature deaths annually in those cities. Furthermore, these particles trigger half a million asthma attacks each year and lead to a total of 16 million lost person-days of activity.

In response to the growing body of evidence regarding the health impacts of particulates, the 2006 WHO Air Quality guidelines for the first time set guideline values for $PM_{2.5}$ and PM_{10}. The guidelines are

$PM_{2.5}$	10 µg/m^3 annual mean	25 µg/m^3 24-hour mean
PM_{10}	20 µg/m^3 annual mean	50 µg/m^3 hourly mean

The United States Environmental Protection Agency (USEPA) has a standard of 50 µg/m^3 annual mean for PM_{10} ambient air levels, and the annual mean limit value set by a European Union directive is 40 µg/m^3.

As a reference point, New York City has an average PM_{10} = 13 µg/m^3. The cleanest city in the world, as measured by air particulates, is Santa Fe, New Mexico, USA, with PM_{10} = 6 µg/m^3; the dirtiest was Ahvaz, Iran with PM_{10} = 372 µg/m^3 (WHO 2011).

10.3.4 Ozone (O_3)

Ozone at ground level (not to be confused with the ozone layer in the stratosphere) is one of the major constituents of photochemical smog. It is formed by the reaction with sunlight (photochemical reaction) of pollutants such as nitrogen oxides (NO_x) from vehicle and industry emissions and volatile organic compounds (VOCs) emitted by vehicles, solvents and industry. The highest levels of ozone pollution occur during periods of sunny weather.

Excessive ozone can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases. In Europe it is currently one of the air pollutants of most concern. Several European studies have reported that every 10 µg/m^3 increase in ozone exposure increases the daily mortality by 0.3%.

The previously recommended limit, which was fixed at 120 µg/m^3 8-hour mean, has been reduced to 100 µg/m^3, based on recent conclusive associations between daily mortality and ozone levels occurring at ozone concentrations below 120 µg/m^3.

10.3.5 Nitrogen Dioxide (NO_2)

The major sources of anthropogenic emissions of NO_2 are combustion processes (heating, power generation, and engines in vehicles and ships). NO_2 is the main source of nitrate aerosols, which form an important fraction of $PM_{2.5}$ and, in the presence of ultraviolet light, of ozone. At short-term concentrations exceeding 200 µg/m^3, it is a toxic gas that causes significant inflammation of the airways. The guideline values are 40 µg/m^{3}annual mean and 200 µg/m^{3}1-hour mean.

10.3.6 Sulfur Dioxide (SO_2)

The main anthropogenic source of SO_2, a colorless gas with a sharp odor, is the burning of sulfur-containing fossil fuels (coal and oil) for domestic heating, power generation, operating motor vehicles, and the smelting of mineral ores that contain sulfur.

SO_2 can affect the function of the lungs and cause irritation of the eyes. Inflammation of the respiratory tract causes coughing, aggravates asthma and chronic bronchitis, and makes people more prone to respiratory tract infections. Mortality and hospital admissions for cardiac disease increase on days with higher SO_2 levels. A proportion of people with asthma experience change in pulmonary function and respiratory symptoms after periods of exposure to SO_2 as short as 10 minutes. The guideline values are 24-hour mean = 20 µg/m^{3}and 10-minute mean = 500 µg/m^3.

10.3.7 Volatile Organic Compounds (VOCs)

A large group of pollutants is known collectively as volatile organic compounds (VOCs). They can occur either as gases or bound to particles. Several of the substances in this group contribute to the formation of ground-level ozone – which probably is the most significant health effect of this group as a whole.

The group includes known carcinogens such as benzene and various aromatic hydrocarbons. The nitrated polyaromatic hydrocarbons (nitro-PAH), several of which are present in diesel exhaust fumes, are some of the most carcinogenic substances known. At present the EU has a limit only for benzene, which is 5 µg/m^3.

10.4 European Union (EU Directives)

10.4.1 Background

The European Union (EU) is a relatively new entity, but it rapidly assumed a leadership role in international environmental policy, starting in the late 1980s and strengthening thereafter. The EU Environmental Policy Handbook gives the history and explains the EU Directives (Scheur 2005).

10.4.2 REACH Regulations – Registration, Evaluation, Authorization and Restriction of Chemicals

The REACH regulations took seven years to pass. It has been described as the most complex legislation in EU history and the most important in 20 years. It is the strictest law to date regulating chemical substances and will affect industries throughout the world.

REACH entered into force in 2007, with a phased implementation over the next decade. When it is fully in force, REACH will require all companies manufacturing or importing chemical substances into the EU in quantities of one tonne or more per year to register these substances with a new European Chemicals Agency (ECHA). Since REACH applies to some substances that are contained in objects, any company importing goods into Europe could be affected.

Bringing substances to the European market that have not been pre-registered or registered is illegal (known in REACH as "no data, no market"). Chemicals manufactured or imported in amounts of 1000 tonnes were required to be registered by December 2010. The deadlines were June 2013 for 100 tonnes and June 2018 for 1 tonne. About 143,000 chemical substances marketed in the European Union were pre-registered by December 2008.

Substance Information Exchange Forums (SIEFs) were formed to allow all manufacturers, importers, and data holders who are dealing with the same substance to join forces and finances to create one registration dossier. A SIEF requires cooperation between many legal entities, which must find each other, communicate openly and honestly, share data, and share costs in a fair and transparent way.

There are special requirements for chemical *substances of very high concern* (SVHC). As of June 2012, there were 84 SVHCs. The European Chemicals Agency must be notified if the total quantity used is more than one tonne per year and the SVHC is present at more than 0.1% of the mass of the object. Applicants for authorization must include plans to replace the SVHC with a safer alternative (if no safer alternative exists, the applicant must work to find one).

10.4.3 Air Quality and Air Emissions

Air pollution has been a priority since the early days of EU environmental protection. In 2005 the EC adopted a thematic strategy on air pollution, and the Clean Air for Europe Programme (CAFÉ) provides technical analysis and policy development. The European Pollutant Emission Register, the first European-wide register of industrial emissions into air and water, has been extended to include more emitting facilities, require more substances to be reported, encourage wider coverage and public participation, and require annual instead of triennial reporting.

The EU Limit Values (LV) and Target Values (TV) for ambient air quality are given in Table 10.3. The LV is fixed with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained. The TV is fixed with the aim of avoiding more long-term harmful effects on human health and/or the environment as a whole, to be attained where possible over a given period.

Pollutant	**Human Health Criteria**				**Vegetation & Ecosystem**
	1-hr Ave	**24-hr Ave.**	**Annual Ave.**	**8-hr Mean**	
Limit Values					
Sulfur dioxide (SO_2)	350 µg/m^3	125 µg/m^3			20 µg/m^3
Nitrogen dioxide (NO_2)	200 µg/m^3		40 µg/m^3		30 µg/m^3
PM_{10}		50 µg/m^3 (a)	20 µg/m^3		
Lead (Pb)			0.5 µg/m^3		
Benzene (C_6H_6)			5 µg/m^3		
Carbon monoxide (CO)				10 µg/m^3	
Ozone (O_3)	180/240 µg/m^3 (b)			120 µg/m^3 (c)	AOT_{40} (d) = 18,000 µg/m^3 hours
Target Values (For 2012)					
PAH				1 ng/m^3	
Cadmium (Cd)				5 ng/m^3	
Arsenic (As)				6 ng/m^3	
Nickel (Ni)				20 ng/m^3	

Table 10.3 Limit Values (LV) and Target Values (TV) in the EU Air Quality Directives.

(a) Not to be exceeded more than 7 times a calendar year.
(b) At 180 µg/m^3, the information threshold, the population should be informed, and at 240 µg/m^3, the alert threshold, short-term action should be taken.
(c) Not to be exceeded more than 25 times per year.
(d) AOT_{40} = Accumulated exposure over the threshold 40 ppb.

The climate change levy seeks to reduce emissions in energy-intensive industry sectors (such as brewing, cement, printing, and animal feed). Emissions trading (cap-and-trade) offers economic incentives for achieving reductions in emissions of greenhouse gases (especially carbon dioxide). Companies that emit the pollutant are given credits or allowances which represent a right to emit a specific amount, and if they exceed their allowances they must buy credits from those who pollute less than their allowances. In theory, the more firms that need to buy credits, the higher the price of credits becomes, which makes reducing emissions cost-effective in comparison.

This is a simplified hypothetical example of how a cap-and-trade system might work. Two emissions sources, A and B, both emit 100,000 tonnes of CO_2 per year. The government gives each of them 95,000 emission allowances with one allowance representing the right to emit 1 tonne of CO_2. Both installations A and B are, therefore, 5,000 allowances short (5%) of covering their annual CO_2 output. The plant owners face the same choice: either reduce their emissions by 5,000 tonnes, or purchase 5,000 allowances on the market. In order to decide which option to pursue, they will compare the costs of reducing their emissions by 5,000 tonnes with the projected market price for allowances. And, as permits become more limited and their prices rise, A and/or B might decide to invest in CO_2 reduction strategies instead.

10.4.4 Water

Water resources are limited and supply and sanitation systems are under pressure from urbanization and climate change. The water policy of the EU is primarily codified in three directives:

- The 1991 Urban Waste Water Treatment Directive concerning discharges of municipal and some industrial waste waters;
- The 1998 Drinking Water Directive concerning potable water quality;
- The 2000 Water Framework Directive concerning water resources management.

The framework for water management aims to improve water quality, reduce risks from drought or flooding, and stop the deterioration of wetlands and other ecological habitats. The key concept is river basin management, which requires closer co-operation between competent authorities, often across boundaries. A River Basin Management Plan should set out how inland and coastal waters can achieve 'good status' by the year 2015.

EU member states have enacted national legislation in accordance with these directives. The institutional organization of public water supply and sanitation remains the responsibility of each member state, not the EU.

10.4.5 Waste

The EU defines waste as that which the holder discards or intends to discard, or is required to discard, a definition which aims to be as inclusive as possible. Sub-categories of waste include: municipal solid waste, hazardous waste, special waste, hospital and clinical waste, ash and slag from combustion processes, agricultural waste, sludge from waste water treatment, and mining waste.

The European Union produces 1.3 billion tonnes of waste each year, including manufacturing and construction and demolition waste but excluding mining and agricultural and forestry wastes. This amounts to about 3.5 tonnes of solid waste for every person (European Environment Agency 2002). The five major waste streams are manufacturing (26%), mining and quarrying (29%), construction and demolition (22%) and municipal solid waste (14%), and a large but not precisely known quantity of agricultural and forestry waste. About 27 million tones, or 2%, of this waste is hazardous waste (Eurostat 2000). (Eurostat, the statistical office of the European Union, provides on-line access to economic and environmental data.).

A measure of the complexity and importance of waste management is that it has the longest section in the Handbook for Implementation of EU Environmental Legislation. The aim is to ensure recovery or disposal without pollution risk. The waste management hierarchy prioritizes (in descending order) re-use, recycling and recovery, use as a source of energy, incineration without energy, recovery, and landfilling (the least desirable option).

The key principles are:

- *Proximity Principle*. Waste should be disposed of as closely as possible to its place of generation, following the principle that environmental damage should, if possible, be rectified at the source.
- *Producer Liability (Polluter pays)*. Liability rules ensure that any environmental damage is restored and the cost of cleanup work will be born by the person that generated the waste and not by the average taxpayer. Producers of waste must bear the costs of having licensed transporters and managers of waste handle their waste, especially hazardous waste. The owner of the land where waste is deposited, legally or illegally, also can be considered to be the holder of the waste and thereby responsible for ensuring its safe treatment or disposal (Eunomia 2003).
- *Producer responsibility*. Producer responsibility is different from producer liability. Producer liability deals with damage that is caused by a product that has to be compensated. Producer responsibility creates an obligation to recover products or to collect waste, to establish funds or schemes for recovery or recycling, to organize recycling or recovery, or consider product disposal during design and manufacture of the product.

10.5 India and China

There is no umbrella of environmental regulations for Asia, but many countries have well codified environmental protection plans. Implementation and enforcement are increasing in proportion to economic growth and stability.

India and China are the two most important countries because of their large populations and their rapid industrialization. Since most of the growth in greenhouse gas emissions is projected to occur in developing countries, such as India and China, their successful enactment and enforcement of environmental regulations will contribute greatly to the well being of our planet.

India has a rich history of environmental regulations. The Constitution of India states that it is the duty of the state to 'protect and improve the environment and to safeguard the forests and wildlife of the country'. It imposes a duty on every citizen 'to protect and improve the natural environment including forests, lakes, rivers, and wildlife'. Three important laws are:

- The Water Prevention and Control of Pollution Act (1974) established standards for water quality and effluents, and required polluting industries to seek permission to discharge waste into effluent bodies.
- The Air Prevention and Control of Pollution Act (1981) provides for the control and abatement of air pollution.
- The Environment Protection Act (1986) filled many gaps in other laws. It authorizes the central government to protect and improve environmental quality, control and reduce pollution from all sources, and lay down procedures for setting standards of emission or discharge of environmental pollutants.

Actual enforcement of environmental regulations is done at the state level.

China has been one of the top performing countries in terms of GDP growth (9.64% annually over the past ten years). The high economic growth has put immense pressure on its environment and the environmental challenges that China faces are greater than in most countries. In 1983, China implemented a sustainable development strategy outlined in Table 10.4.

Command-and-control	Economic incentives	Voluntary instruments	Public participation
Concentration-based pollution discharge controls	Pollution levy fee	Environmental labeling system	Clean-up campaign
Mass-based controls on total provincial discharge	Non-compliance fines	ISO 14000 system	Environmental awareness campaign
Environmental impact assessments (EIA)	Discharge permit system	Cleaner production	Air pollution index
Centralized pollution control	Sulfur emission fee	Non-governmental organizations	Water quality disclosure
Environmental compensation fee	Sulfur emission trading		Administrative permission hearing
	Subsidies for energy saving products		
	Regulation on refuse credit to high-polluting firms		

Table 10.4 Pollution control instruments in China (Wikipedia; Chunmei & Zhaolan, 2010)

China has taken several initiatives to increase its protection of the environment and combat environmental degradation:

- China's investment in renewable energy grew 18% in 2007 to $15.6 billion, accounting for approximately 10% of the global investment in this area.
- In 2008, spending on the environment was 1.49% of GDP, up 3.4 times from 2000.
- The discharge of CO (carbon monoxide) and SO_2 (sulfur dioxide) decreased by 6.61% and 8.95% in 2008 compared with that in 2005.
- China's protected nature reserves have increased substantially. In 1978 there were only 34 compared with 2,538 in 2010. The protected nature reserve system now occupies 15.5% of the country's land area; this is higher than the world average.

10.6 The United States

10.6.1 History

Until the 1970s the amount of pollution put into the environment in the U.S. grew along with the population and industrial productivity. In the 1960s and early 1970s there was great emphasis on wastewater treatment, with new laws and financial assistance from the government to cities to build treatment plants. In the late 1970s serious efforts and investments began to reduce air pollution, to improve the disposal of solid wastes, and to remediate sites where hazardous and toxic wastes had been improperly handled. This history and the general reduction in pollutant discharges and emissions are shown in Figure 10.2.

The 1990s emphasized clean manufacturing, green manufacturing, waste minimization and design for environment. These ideas have been well known and widely used by engineers from the 1940s, although with the less emotional names of water conservation, water recycling, water reuse, energy conservation, waste segregation, and material reclamation.

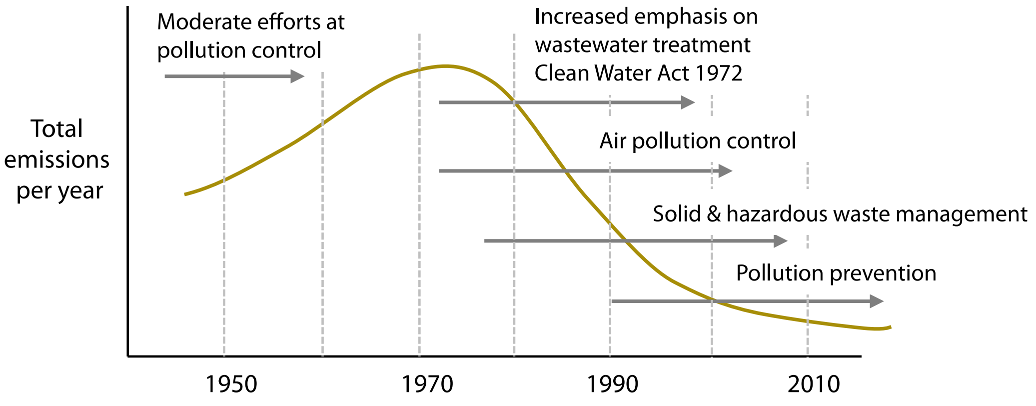


Figure 10.2 The progress of pollution control as a result of new legislation and serious financial investments starting in the late 1960s has been impressive.

Table 10.5 lists the major federal legislation related to environmental protection. Mechanisms for the control of toxic pollutants are contained in several federal regulations, such as the Toxic Substance Control Act (PL 94-469), Comprehensive Environmental Response, Compensation, and Liability Act (PL 96-510), Resource Conservation and Recovery Act (PL 95-580), Clean Water Act (PL 95-217), Clean Air Act (PL 95-95), and the Safe Drinking Water Act (PL 93-523). PL indicates Public Law. CFR is Code of Federal Regulations. Appendix 4 explains how Federal laws and regulations are developed.

National Environmental Policy Act	40 CFR Parts 1500 to 1517
Federal Clean Air Act (PL 95-95) and 1990 Amendments (PL 101-549)	40 CFR Parts 50–85
Federal Clean Water Act (PL 95-217)	40 CFR Parts 100–140, 400–501
Federal Resources Conservation and Recovery Act (PL 95-580)	40 CFR Parts 240 to 281
Comprehensive Environmental Response, Compensation, and Liability Act (PL 96-510)	40 CFR Parts 300 to 31142 CFR Part 9601
Federal Safe Drinking Water Act (PL 93-523)	40 CFR Parts 141–143
Pollution Prevention Act of 1990	42 CFR Part 133
Occupational Safety and Health Act	29 CFR Parts 1900 to 1990
Toxic Substance Control Act (PL 94-469)	40 CFR Parts 700–766
Emergency Planning and Right-to-Know Act	40 CFR Parts 350 to 372
Rivers and Harbors Act	33 CFR Part 322
Federal Coastal Zone Management Act	15 CFR Part 930

Table 10.5 The Major U.S. Federal Laws on Environmental Protection

The Clean Water Act (CWA) lists 148 pollutants, the Resource Conservation & Recovery Act (RCRA) lists 502, the Clean Air Act (CAA) lists 189, the Occupational Safety & Health Act (OSHA) lists 450, and the Emergency Planning & Community Right-to-Know Act (EPCRA) lists 599. Only 49 chemicals are regulated under all five of these acts, 119 are regulated under 4 acts, and 768 are regulated under only one. Each list omits pollutants that are on all four other lists, and each list includes pollutants that are not on any other list. The Clean Water Act and the Clean Air Act list a total of 269 pollutants and only 68 (25.3%) are common to both laws; all other two-way pairings of laws have a lower percentage of common pollutants with the lowest being 13% for CWA and OSHA (Dernbach 1977).

This is the result of each law having been formulated in isolation of the others and of Congress separately adopting the lists of pollutants for the statutes. It is also, in part, due to the USEPA having to develop the lists when less was known about the toxic properties of the chemicals and their behavior in the environment. We now have better scientific knowledge and years of experience. This means that the engineer may be able to negotiate terms of a discharge permit or cleanup regulation that take into account special features of a local problem.

Pollution prevention is one way for a discharger to avoid this snarl of regulations. Do not bring a listed chemical or substance into the factory as a raw material or raw material contaminant. Capture regulated pollutants at the source within the manufacturing process in as pure a form as possible to facilitate reuse or safe disposal. Do not burn substances that will cause a toxic emission, or burn them at such a high temperature that the substances are completely destroyed.

10.6.2 The Safe Drinking Water Act

The Safe Drinking Water Act (SDWA) of 1974 is not a pollution control law, but it does directly protect human health by setting maximum contaminant levels (MCLs) on a list of inorganic chemicals and ions, organic substances, radioactive substances, and pathogenic microorganisms. The public water utility is responsible for maintaining these levels until the water arrives at the consumer's tap. The MCL levels, the health effect, and the recommended treatment methods for each parameter are given in Appendix 1. The best and most economical way to keep these chemicals out of drinking water is to control them in effluents and emissions.

10.6.3 The Clean Water Act (CWA)

The Federal Water Pollution Control Act of 1972, as amended by the Clean Water Act of 1977 and the Water Quality Act of 1987, established the National Pollutant Discharge Elimination System (NPDES). The federal government has delegated NPDES authority to all 50 states.

Every point source discharge of wastewater, such as municipal treatment plants, industries, animal feedlots, aquatic animal production facilities, and mining operations, is required to have a NPDES permit. The permit specifies effluent limits, a compliance schedule, monitoring and reporting requirements, and any other terms and conditions necessary to protect water quality. Permits are renewed every five years, at which time the allowable effluent concentrations, mass discharge rates, or the specific compounds that must be monitored may be changed.

The categories of pollutants are listed in Table 10.6.

Conventional Pollutants	All dischargers must submit information on biochemical oxygen demand, chemical oxygen demand, total organic carbon, total suspended solids, and ammonia.
Conventional Pollutants, Radioactivity and Certain Inorganic Pollutants.	Effluent limits for fecal coliforms, oil and grease, fluoride, nitrate and nitrite, phosphorus, sulfate, and bromide are established only if they are expected to be present.
Toxic or "Priority" Pollutants (129 pollutants listed).	All discharges are analyzed for cyanide, phenol, and heavy metals. Monitoring for other chemicals may be required if the effluent contains industrial process water (as opposed to storm water runoff).
Hazardous Substances and Asbestos	Monitoring will be required for additional toxic substances that are expected to be present.

Table 10.6 Categories of Pollutants used in the NPDES permit application.

The CWA sets forth water quality criteria for surface waters that protect human health from the harmful effects of pollutants in the water and from the consumption of fish. The criteria are based solely on data and scientific judgments: they do not consider economic or social impacts. The human health water quality criteria for the priority and non-priority pollutants are given in Appendix 2.

The act also sets aquatic life criteria for acute toxicity and chronic toxicity in freshwater and saltwater (see Appendix 3). These national guidelines are intended to protect the vast majority of the aquatic communities in the United States.

10.6.4 Biosolids Management

Biosolids are the concentrated solid residue of wastewater that has been processed by biological treatment. This residue may be a slurry (3% to 8% solids by weight) or a semi-dry cake (18% or more solids by weight). The beneficial use of biosolids, which usually means recycling the biosolids as a soil conditioner or fertilizer on farms is encouraged, but it is also strictly regulated. Obviously, beneficial use can occur only if the biosolids present no unacceptable risk to humans or the environment. The USEPA's '503 regulations' control risk by setting limits on nine metals, bacterial quality, and insect and vector control.

The risk assessment guidelines are more flexible than those used in Superfund and the Clean

Water Act. Superfund risk assessment protects the most exposed individual (MEI). The 503 regulations protect a highly exposed individual (HEI), who lives in nearly normal conditions. The numerical standards and a discussion of the risk assessment methods were given in Chapter 5.

10.6.5 Industrial Pretreatment Regulations

Amendments to the original Clean Water Act (PL 92-500) deal specifically with the difficulties caused by industries putting toxic or hazardous substances into municipal sewers or treatment plants. The pretreatment rules prohibited the discharge of:

- Substances that create a fire or explosive hazard.
- Corrosive materials and discharges with a pH of less than 5.
- Solid or viscous materials in amounts that will obstruct flow or interfere with operation of a municipal wastewater treatment plant.
- Heated discharges that will inhibit, interfere with, or damage biological wastewater treatment processes, or which will create temperatures which exceed 65°C (150°F) in the wastewater collection system and 40°C (104°F) at the treatment plant unless other temperature limits have been approved.

10.6.6 The Clean Air Act

Air pollution is the release of unwanted particles (dusts and solid particles), gases (vapors or fumes), or aerosols (minute particles) into the air by either “natural” or “human” sources. An air pollution source can be stationary (industries) or mobile (automobiles). In the U.S. mobile sources contribute at least as much or more toxic compounds to the atmosphere than stationary sources.

Significant reductions have been made in outdoor air pollution in the United States. Between 1970 and 2004, total emissions of the six major air pollutants regulated by the Environmental Protection Agency (EPA) dropped by 54 percent. This is particularly impressive when noted that the gross domestic product increased 187 percent, energy consumption increased 47 percent, and U.S. population grew by 40 percent during the same time, which shows that economic growth and environmental protection can go hand in hand.

There are two types of National Ambient Air Quality Standards (NAAQS). Primary standards are designed to protect the public health. Secondary standards are designed to protect the public welfare (e.g., vegetation and building materials). The NAAQS summarized in Table 10.7, specify the concentration (μg/m^3) of a pollutant in ambient air above which humans or the environment may experience some adverse effects. The NAAQS differentiate between long-term and short-term exposure: some are based on short-term averages, while others are based on an annual average.

Criteria Pollutant	**Averaging Time**	**Primary standard[1]**		**Secondary Standard**	**Public Health Concern**
		μg/m^3	**ppmv**		
Particulate matter (PM_{10})	24-hr	150		same	respiratory problems, visibility
Particulate matter ($PM_{2.5}$)	Annual	12		15 μg/m^3	
	24-hr	35		same	
Sulfur dioxide (SO_2)	1 hour	214	0.075	none	acid rain
	3 hour	none	none	0.5 ppmv	
Nitrogen dioxide (NO_2)	1-hour	134	0.100	none	
	Annual	71	0.053	same	acid rain and smog
Ozone (ground level)	8 hour	161	0.075	same	smog, breathing
Carbon monoxide (CO)	8 hour	11,200	9	none	global warming potential
	1 hour	43,700	35	none	
Lead	3 months	0.15		same	toxicity

Notes: ppmv = concentration in parts per million by volume at 25°C and 1 atm
PM_{10} indicates particles 10 μm or less in diameter

Table 10.7 Summary of the National Ambient Air Quality Standards (NAAQS) (http://www.epa.gov/air/criteria.html)

Outdoor urban air pollution, much of it generated by vehicles, is associated with higher rates of cardiovascular and respiratory diseases. Very fine particles, less than 10 μm diameter, inhaled into the lungs are irritants and the particles may carry metals or adsorbed organic chemicals that are dangerous.

Ozone itself is not emitted. It is formed in the presence of sunlight, through a series of complex reactions involving volatile organic compounds. In extreme ozone non-attainment areas, sources with the potential to emit 10 tons of VOCs per year are considered "major." In less seriously affected areas a major source may be defined as one that emits 50 ton/yr or even 100 ton/yr.

The 1990 Amendments established the Hazardous Air Pollutant (HAP) program that regulates an additional 189 specific toxic compounds. A major HAP facility is one that emits, or has the potential to emit, 10 or more tons per year of any single HAP or 25 ton/yr of a combination of HAPs. Major HAP source categories must install Maximum Achievable Control Technology (MACT) to achieve emission standards. Industrial facilities may be required to develop control technology on the basis of risk assessment. Emission rates in permits are specified as mass rates (e.g. lb/hr or tons/yr).

10.6.7 Resource Conservation and Recovery Act (RCRA)

The Solid Waste Disposal Act (SWDA) of 1965, Resource Conservation and Recovery Act (RCRA) in 1976, and the Hazardous and Solid Waste Amendments (HSWA) of 1984 are collectively known as RCRA. RCRA controls hazardous waste generators, transporters, and treatment and disposal facilities and applies to wastes that were disposed of after November 1980. Appendix 5 is an expanded version of this summary of RCRA.

RCRA regulates hazardous wastes 'from the cradle to the grave'. Any person, company, transporter, or previous waste disposal facility owner that ever had contact with any waste now located at a problem site is liable for problems arising from disposal of the waste. In the language of RCRA, they are a *responsible party*. In short, there is no way to contract away one's liability for hazardous waste management. Thus, generators and waste handlers are forced to consider the long-term risks associated with disposal as well as the short-term costs.

RCRA, despite its name, does not require resource conservation and recovery, but it does encourage these practices by imposing standards for managing hazardous wastes today to prevent future problems. Actual recycling is unregulated (except waste burned as fuel), but generation, transportation, and storage of solid waste prior to recycling are regulated. In most cases, waste generated from treatment and storage of a hazardous waste remains a hazardous waste.

Solid waste is a regulatory term that does not refer to a material's physical state. A solid waste is any discarded material that is not excluded or delisted. Delisting is the process by which a generator petitions on a case-by-case basis to have a hazardous waste reclassified as a nonhazardous waste.

A discarded material is any material that is (1) disposed, stored, or treated before its disposal; (2) burned as a fuel, treated, recycled, abandoned, considered inherently waste-like; or (3) stored or accumulated before recycling. If the material does not fit this definition it is not a RCRA hazardous waste, but it may be regulated under others laws.

Hazardous waste is a subset of solid waste. For the material to be a hazardous waste it must first be a solid waste. A solid waste may be classified as hazardous because it is a listed hazardous waste or because it has characteristics that make it hazardous. The characteristics that make a waste hazardous are ignitability, corrosivity, reactivity, and toxicity.

A special concern is the leaching of toxic components into groundwater and the potential for this to occur is measured using the Toxicity Characteristics Leaching Procedure (TCLP).

10.6.8 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

"Superfund" is the nickname for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Superfund provides the mechanisms for investigation, assessment, and remediation of past mistakes, in particular abandoned and contaminated sites that were not operating under a RCRA permit or where contamination is found and there is no responsible party willing or financially able to undertake cleanup. Appendix 6 is an expanded version of this summary of CERCLA.

The Superfund Amendments and Reauthorization Act of 1986 (SARA) required EPA to involve the states in hazardous waste identification and cleanup activities. The states regulate many more uncontrolled hazardous waste sites than the USEPA. State-regulated sites do not have access to the Superfund Trust, but many states have similar programs for managing abandoned or underfunded sites.

A site under Superfund must be cleaned to specified levels using any technically and economically feasible means. Superfund activities conducted completely on a site do not require federal, state, or local permits, but must comply with any applicable regulations. RCRA, in contrast, specifies cleanup levels and cleanup technology, regardless of cost-effectiveness, and in addition the site must obtain the appropriate permits. RCRA corrective actions often require a facility to follow CERCLA guidance.

Under Superfund, hazardous substances are governed under strict liability, that is, liability even when there has been no negligence. This means that anyone who handles hazardous wastes is liable for all resulting injuries regardless of how much care has been exercised. This principle also holds under RCRA.

Hazardous waste sites are examined and rated with respect to the substances involved, their tendency to migrate from the site, their toxicity, and other factors related to environmental health and safety. Sites with high scores are placed on the National Priorities List (NPL). Listing does not mean that the site is an immediate threat to public health, but it is considered to have some significant, long-term threat to public health.

Each site on the NPL that is targeted for remedial action must conduct a remedial investigation (RI) and feasibility study (FS). Risk assessment is an important part of this process and it is done on each remedial option, including the ‘no action’ option. The final remedial action plan, known as the record of decision, or ROD, outlines the remediation goals and procedures. It will provide a public history of the site, the RI/FS, the risk assessment, the alternative cleanup methods considered, and the rationale behind the remedy selected.

10.6.9 Toxic Substances Control Act (TSCA)

The 1976 Toxic Substances Control Act (TSCA) is focused mainly on controlling chemical manufacturing and processing, and less on the treatment and disposal of wastes. TSCA regulates individual chemicals whereas RCRA regulates waste streams that may contain multiple chemical substances. EPA may regulate a chemical under TSCA only if that chemical is found to ‘present an unreasonable risk of injury to human health or the environment’. To determine unreasonable risk, EPA must conduct an economic cost/benefit analysis. RCRA does not require economic factors to be considered in its rulemaking.

10.6.10 Occupational Safety and Health Act (OSHA)

The 1970 Occupational Safety and Health Act (OSHA) created the Occupational Safety and Health Administration (OSHA), which was given the authority both to set and enforce workplace health and safety standards. The Act also established the National Institute of Occupational Safety and Health (NIOSH), an independent research institute.

The 'general duty clause' requires employers to

- Maintain conditions or adopt practices reasonably necessary and appropriate to protect workers on the job;
- Be familiar with and comply with standards applicable to their establishments; and
- Ensure that employees have and use personal protective equipment when required for safety and health·

OSHA may act under the 'general duty clause' when four criteria are met:

- There must be a hazard
- The hazard must be a recognized hazard (e.g., the employer knew or should have known about the hazard, the hazard is obvious, or the hazard is a recognized one within the industry)
- The hazard could cause or is likely to cause serious harm or death and
- The hazard must be correctable (OSHA recognizes not all hazards are correctable).

This is theoretically a powerful tool against workplace hazards, but it is difficult to meet all four criteria. Therefore, OSHA has focused on basic mechanical and chemical hazards rather than procedures. Major areas which its standards currently cover are: toxic substances, harmful physical agents, electrical hazards, fall hazards, hazards associated with trenches and digging, hazardous waste, infectious disease, fire and explosion dangers, dangerous atmospheres, machine hazards, and confined spaces.

Employers must keep a record of every non-consumer chemical product used in the workplace. Detailed technical bulletins called material safety data sheets (MSDSs) must be posted and available for employees to read and use to avoid chemical hazards. OSHA also requires employers to report on every injury or job-related illness requiring medical treatment.

10.7 ISO 14000 Standards for Environmental Quality Management

The Organization de Standards International (ISO) sets standards for a wide range of products and management operations. They are internal standards (as opposed to government regulations) that guide a company to integrate environmental quality management systems within its business operations. The standards have no force of law. Compliance is voluntary.

The ISO 14000 family of standards pertains to how a product is produced, rather than to the product itself. The goal is to help companies (1) minimize operations that cause adverse changes to air, water, or land; (2) comply with applicable laws and regulations, and (3) continually improve pollution minimization and compliance.

Five areas are addressed in the ISO 14000 standard:

- Environmental Management Systems (EMS) comprises a written program; education and training; and knowledge of relevant local and federal environmental regulations.
- Environmental Performance Evaluations measure the impact a business is having on the environment by an inventory of air emissions and wastewater discharges.

- Environmental Auditing is a routine evaluation of a company's environmental controls that defines the inputs (raw materials, energy) and outputs (waste streams, emissions), and identifies inefficiencies that have an environmental impact. Management is expected to implement changes as needed to reduce those impacts.
- Life Cycle Assessment evaluates the environmental consequences of a manufactured item from the time it is born (manufactured), during its life (use or operation), and death (disposal). The life cycle assessment usually covers the activities of suppliers, transporters, component manufacturers, and the final manufacturer, whereas the environmental audit covers just one company.
- Environmental Labeling allows an industry to identify environmentally friendly products.

The reasons for a company to seek ISO 14000 certification include greater efficiency and reduced operational costs, reduced environmental impacts, more favorable insurance rates, a competitive advantage with environmentally aware customers, and a positive image with its shareholders and customers. Third-party organizations, rather than ISO, award the certification.

10.8 Conclusion

Knowledge of environmental laws is essential in understanding which pollutants are critical targets for elimination by pollution prevention and which may be discharged because they are harmless or easy to treat.

The World Health Organization has expanded and refined its methods for evaluating conditions that may be dangerous to human health. It used a risk assessment approach for setting drinking water guidelines and air quality guidelines. It also collects extensive data on the state of world health, which is available in the World Health Report.

The European Union takes a leading role in international environmental policy. The member states have supported strict standards and enhanced their commitments to international environmental cooperation. The EU directives cover all aspects of environmental protection. Implementation is the responsibility of the member states.

A collection of U.S. Federal laws has developed to protect drinking water and to establish environmental limits on hundreds of specific chemicals and substances, including the priority pollutants in water and hazardous air pollutants. Enforcement of the laws has been delegated to the 50 states, which also handle the granting of permits. The laws are voluminous and complex and engineers frequently will consult with state environmental protection agencies about details.

Following an environmental ethic and making a noble effort toward environmental responsibility does not need to destroy profits. Many industries have voluntarily gone beyond the legal requirements, so it is clear that impressive results are not always explained by fear of fines and criminal prosecution.

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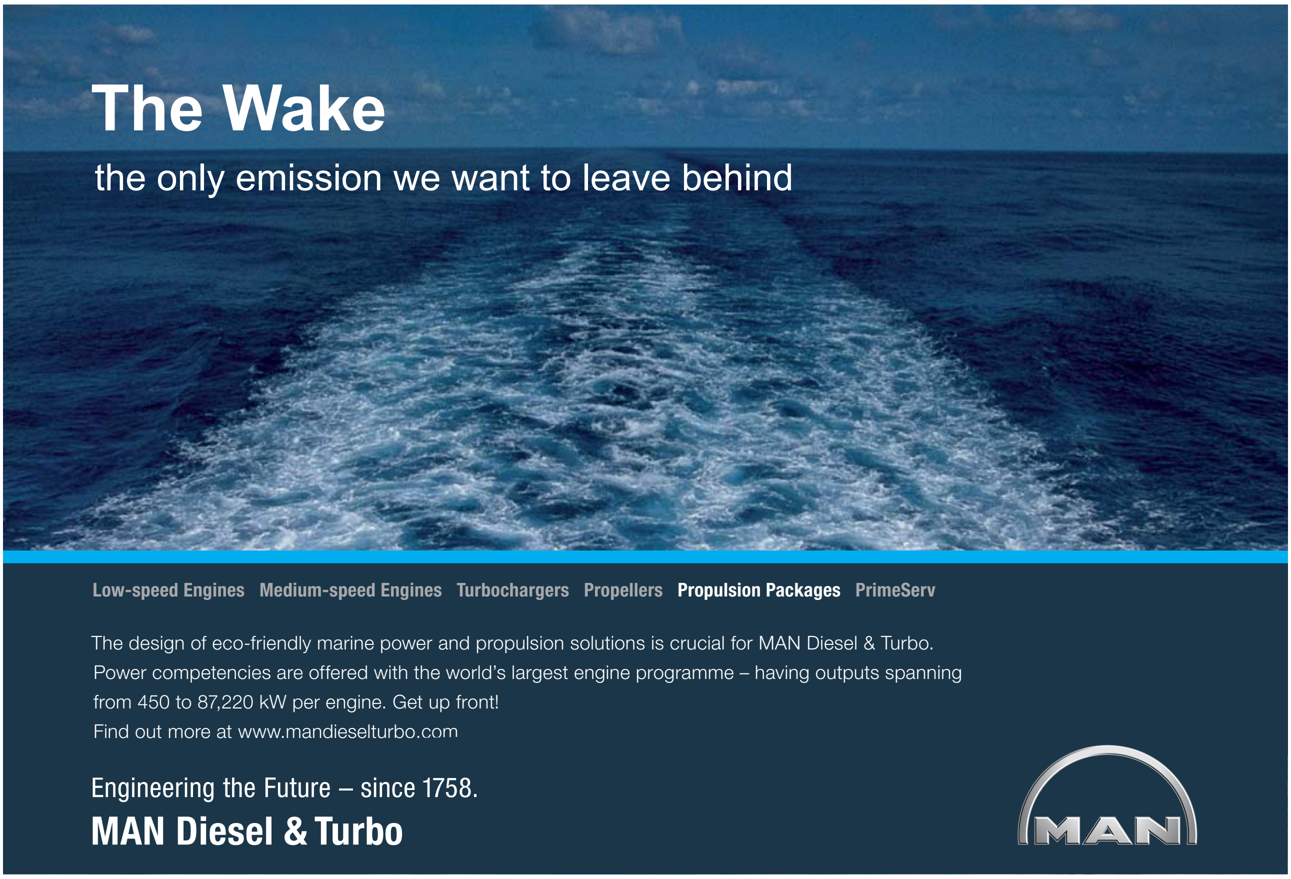

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12 Appendix 1 – Drinking Water Criteria (Safe Drinking Water Act)

Contaminant	MCL (mg/L)	Health Effect	Treatment Methods
Antimony	0.006	Alters cholesterol and glucose levels	CF, RO
Arsenic	0.01	Dermal and nervous system affects	IX, RO
Asbestos (1)	7 MFL	Benign tumors	CF, DF, DEF, CC
Barium	2.0	Circulatory system effects, high blood pressure	LS, IX, RO
Beryllium	0.004	Cancer risk and intestinal lesions	CF, LS, AA, IX, RO
Cadmium	0.005	Concentrates in liver, kidney, pancreas, thyroid	CF, LS, IX, RO
Chromium (Total)	0.1	Skin sensitization, liver, and kidney effects	CF, LS, IX, RO
Copper (2)	1.3	Gastrointestinal distress and kidney effects	CC
Cyanide	0.2	Spleen, liver and brain effects	Chlorination, IX, RO
Fluoride	4.0	Skeletal damage	AA, RO
Lead (2)	0.015	Nervous system damage and kidney effects	CC
Mercury	0.002	Nervous system damage and kidney effects	CF, LS, IX, RO
Nitrate (as N)	10.0	Methemoglobinemia	IX, RO
Nitrite (as N)	1.0	Methemoglobinemia	IX, RO
Selenium	0.05	Nervous system damage, circulatory problems	CF, LS, AA, RO

Contaminant	MCL (mg/L)	Health Effect	Treatment Methods
Thallium	0.002	Hair loss, blood, kidney, intestinal problems	AA, IX
Organic Chemicals – Pesticides			
Alachlor	0.002	Cancer risk	GAC
Atrazine	0.003	Reproductive and cardiac effects	GAC
Carbofuran	0.04	Nervous system and reproductive system	GAC
Chlordane	0.002	Cancer risk	GAC
Dalapon	0.2	Liver and kidney effects	GAC
Dibromochloropropane	0.0002	Cancer risk	GAC, PTA
Dinoseb	0.007	Thyroid and reproductive effects	GAC
Diquat	0.02	Kidney, gastrointestinal effects, cataract risk	GAC
Endothall	0.1	Liver, kidney, gastrointestinal, reproduction	GAC
Endrin	0.002	Kidney and nervous system	GAC
Ethylene dibromide	0.00005	Cancer risk	GAC
Glyphosate	0.7	Liver and kidney effects	GAC
Heptachlor	0.0004	Cancer risk	GAC
Heptachlor epoxide	0.0002	Cancer risk	GAC
Lindane	0.0002	Nervous system, kidney, and liver effects	GAC
Methoxychlor	0.04	Nervous system, kidney, and liver effects	GAC
Oxamyl (Vydate)	0.2	Kidney effects	GAC
Pentachlorophenol	0.001	Cancer risk	GAC
Picloram	0.5	Liver and kidney effects	GAC
Simazine	0.004	Cancer risk	GAC
Toxaphene	0.003	Cancer risk	GAC
2,4,5-TP (Silvex)	0.05	Nervous system, kidney, and liver effects	GAC
2,4-D	0.07	Nervous system, kidney, and liver effects	GAC
Organic Chemicals – Volatile			
Benzene	0.005	Cancer risk	GAC, PTA
Carbon tetrachloride	0.005	Cancer risk	GAC, PTA
p-Dichlorobenzene	0.075	Cancer risk	GAC, PTA
o-Dichlorobenzene	0.6	Kidney and liver effects	GAC, PTA
1,2-Dichloroethane	0.005	Cancer risk	GAC, PTA
1,1-Dichloroethylene	0.007	Kidney and liver effects	GAC, PTA
cis-1,2-Dichloroethylene	0.07	Nervous system and liver effects	GAC, PTA
trans-1,2-Dichloroethylene	0.1	Nervous system and liver effects	GAC, PTA
Dichloromethane	0.005	Cancer risk	PTA
1,2-Dichloropropane	0.005	Cancer risk	GAC, PTA
Ethylbenzene	0.7	Kidney and liver effects	GAC, PTA
Monochlorobenzene	0.1	Kidney and liver effects	GAC, PTA
Styrene	0.1	Nervous system and liver effects	GAC, PTA
Tetrachloroethylene	0.005	Cancer risk	GAC, PTA
Toluene	1	Nervous system and kidney effects	GAC, PTA
1,2,4-Trichlorobenzene	0.07	Kidney and liver effects	GAC, PTA

Contaminant	MCL (mg/L)	Health Effect	Treatment Methods
1,1,1-Trichloroethane	0.2	Nervous system	GAC, PTA
1,1,2-Trichloroethane	0.005	Kidney and liver effects	GAC, PTA
Trichloroethylene	0.005	Cancer risk	GAC, PTA
Vinyl chloride	0.002	Cancer risk	PTA
Xylenes	10	Liver and kidney effects	GAC, PTA
Organic Chemicals – Synthetic			
Acrylamide (3)	TT	Cancer risk, nervous system	GAC, PTA
Benzo(a)pyrene	0.0002	Cancer risk	GAC
Di (2-ethylehexyl) adipate	0.4	Liver and reproductive effects	GAC, PTA
Di (2-ethylehexyl) phthalate	0.006	Cancer risk	GAC, PTA
Epichlorohydrin (3)	TT	Cancer risk	
Hexachlorobenzene	0.001	Cancer risk	GAC
Hexachlorocyclopentadiene	0.05	Kidney and stomach effects	GAC, PTA
PCBs	0.0005	Cancer risk	
2,3,7,8 Tetrachloro- dibenzo-p-dioxin	3×10^{-8}	Cancer risk	GAC
Disinfection By-Products			
Bromate	0.01	Cancer risk	AD, PR
Chlorite	1.0	Anemia, cancer risk	AD, PR
Haloacetic acids-HAA5 (4)	0.08	Cancer risk	AD, PR
Total trihalomethanes-TTHMs (5)	0.06	Cancer risk, liver, kidney, nervous system	AD, PR
Turbidity			
Turbidity (6)	TT	Interferes with disinfection	CF, SSF, DEF, DF, D
Microbiological Contaminants			
Cryptosporidium (7)	TT	Gastrointestinal infections	
Giardia lambia (8)	TT	Giardiasis (parasitic infection)	CF, SSF, DEF, DF, D
Heterotrophic Plate Count HPC (9)	TT	Gastrointestinal infections	
Legionella (3)	TT	Legionnaire’s Disease	
Total coliform (10)	TT	Indicates possible presence of pathogens	D
Viruses (11)	TT	Gastrointestinal and other viral infections	CF, SSF, DEF, DF, D
Radionuclides			
Gross alpha (12)	15 pCi/L	Cancer risk	CF, RO
Gross beta (13)	4 mrem/yr	Cancer risk	CF, IX, RO
Radium 226 + Ra 228	5 pCi/L	Bone cancer risk	LS, IX, RO
Uranium	30 µg/L		CF, LS, AX, LS

Table A1.1 Drinking Water Criteria and Best Available Treatment Technology. The Maximum Contaminant Limit (MCL) is the level in drinking water that has been established to protect human health. Footnotes identify treatment methods. (Compiled from Pontius 1992, 1993 and EPA website http://water.epa.gov/drink/contaminants/index.cfm).

Notes on Water Quality Criteria:

1. MFL = million fibers per liter longer than 10 microns.
2. Action levels at the tap have been set instead of MCLs. Action levels are: Lead ≤ 0.015 mg/L and Copper ≤ 1.3 mg/L. Both must be met in at least 90% of samples.
3. Defined on basis of treatment technology.
4. Haloacetic acids: dichloroacetic acid (zero); trichloroacetic acid (0.02 mg/L); monochloroacetic acid (0.07 mg/L). Bromoacetic acid and dibromoacetic acid are regulated with this group but have no MCLGs.
5. Trihalomethanes: bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L); chloroform (0.07 mg/L)
6. For conventional or direct filtration, at no time can turbidity exceed 1 NTU, and samples for turbidity must be less than or equal to 0.3 NTUs in at least 95 percent of the samples in any month. Systems that use filtration other than the conventional or direct filtration must follow state limits, which must include turbidity at no time exceeding 5 NTUs.
7. Unfiltered systems are required to include *Cryptosporidium* in their existing watershed control provisions.
8. Minimum of 3 log removal (99.9%), MCLG = 0.
9. No more than 500 bacterial colonies per milliliter.

10. Less than 40 samples/month, no more than 1 positive. 40 samples or more per month, not more than 5% positive. Minimum contaminant level goal (MCLG) = 0 for total coliform, fecal coliform, and E. coli.
11. Minimum of 4 log (99.99%) reduction, MCLG = 0.
12. pCu/L = picocuries per liter.
13. mrem/yr = millirem per year.

TT Treatment technology

Abbreviations used to identify treatment technologies (TT)

AA =Activated alumina
AD = Alternative disinfection
AX = Anion exchange
CC =Corrosion control
CF = Coagulation–Filtration
D = Disinfection
DEF = Diatomaceous earth filtration
DF =Direct filtration
GAC =Granular activated carbon
IX = Ion exchange
LS = Lime softening
PR = Precursor removal
PTA = Packed tower aeration
RO = Reverse osmosis
SSF = Slow Sand filtration

13 Appendix 2 – Clean Water Act – Human Health Water Quality Criteria

The human health water quality criteria for the priority and non-priority pollutants shown in Table A2.1 are based on carcinogenicity of 10^{-6} risk. Alternate risk levels may be obtained by moving the decimal point (e.g., for a risk level of 10^{-5}, move the decimal point in the criterion one place to the right).

Pollutant	(µg/L)	Pollutant	(µg/L)
Metals		**Organic Chemicals**	
Antimony	5.6	1,1,2-Trichloroethane	0.59
Arsenic	0.018	1,1,2,2-Tetrachloroethane	0.17
Asbestos	7 $x10^6$ fibers/L	1,2,4-Trichlorobenzene	35
Barium	1,000	1,3-Dichloropropene	0.34
Copper	1,300	1,4-Dichlorobenzene	63
Cyanide	140	2-Chlorophenol	81
Manganese	50	2,3,7,8-TCDD (Dioxin)	5 $x10^{-9}$
Mercury		Acenaphthene	670
Nickel	610	Acrolein	6
Selenium	170	Acrylonitrile	0.051
Thallium	0.24	Anthracene	8,300
Zinc	7,400	Benzene	2.2
		Benzo(a) Anthracene	0.0038
Organic Chemicals – Pesticides		Benzo(a) Pyrene	0.0038
Aldrin	0.000049	Bis(2-Chloroethyl) Ether	0.03
Chlordane	0.0008	Carbon Tetrachloride	0.23
Dieldrin	0.000052	Chlorobenzene	130
Endrin	0.059	Chlorodibromomethane	0.4
Endrin Aldehyde	0.29	Chloroform	5.7
Heptachlor	0.000079	Chrysene	0.0038
Heptachlor Epoxide	0.000039	Dibenzo(a,h)Anthracene	0.0038
Methoxychlor	100	Dichlorobromomethane	0.55
Toxaphene	0.00028	Ether, Bis(Chloromethyl)	0.0001
4,4'-DDD	0.00031	Hexachlorobenzene	0.00028
4,4'-DDE	0.00022	Hexachloroethane	1.4
4,4'-DDT	0.00022	Methylene Chloride	4.6
gamma-BHC (Lindane)	0.98	Nitrobenzene	17
Chlorophenoxy Herbicide (2,4-D)	100	Nitrosamines	0.0008
		Pentachlorobenzene	1.4
		Pentachlorophenol	0.27
		Phenol	10,000
		Polychlorinatediphenyls (PCBs)	0.000064
		Pyrene	830
		Tetrachlorobenzene,1,2,4,5-	0.97
		Tetrachloroethylene	0.69
		Toluene	1,300
		Trichloroethylene	2.5

Table A2.1 Partial list of Human Health Water Quality Criteria for the consumption of water & organism (USEPA 2009) For complete information go to EPA National Recommended Water Quality Criteria (http://water.epa.gov/scitech/swguidance/ standards/criteria/current/upload/nrwqc-2009.pdf).

14 Appendix 3 – USEPA Aquatic Life Criteria for Freshwater and Saltwater

The CWA sets aquatic life criteria for freshwater and saltwater which are given in Table A3.1. These national guidelines are intended to be protective of the vast majority of the aquatic communities in the United States.

The Criteria Maximum Concentration (CMC) applies to acute toxicity and the Criterion Continuous Concentration (CCC) applies to chronic toxicity. The CMC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an adverse effect. The CCC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an adverse effect.

Pollutant	**Freshwater**		**Saltwater**	
	CMC (acute) (μg/L)	CCC (chronic) (μg/L)	CMC (acute) (μg/L)	CCC (chronic) (μg/L)
Metals				
Aluminum (pH 6.5–9.0)	750	87		
Arsenic	340	150	69	36
Cadmium	2.0	0.25	40	8.8
Chromium (III)	570	74		
Chromium (VI)	16	11	1,100	50
Copper			4.8	3.1
Iron		1000		
Lead	65	2.5	210	8.1
Mercury	1.4	0.77	1.8	0.94
Nickel	470	52	74	8.2
Selenium		5	290	71
Silver	3.2		1.9	
Zinc	120	120	90	81
Other Common Substances				
Chlorine	19	11	13	7.5
Cyanide	22	5.2	1	1
pH		6.5 – 9		6.5 – 8.5
Sulfide-Hydrogen Sulfide		2.0		2.0

Pollutant	Freshwater		Saltwater	
	CMC (acute)	CCC (chronic)	CMC (acute)	CCC (chronic)
	(µg/L)	(µg/L)	(µg/L)	(µg/L)
Organic Chemicals				
Acrolein	3ug/L	3ug/L		
Carbaryl	2.1	2.1	1.6	
Chlordane	2.4	0.0043	0.09	0.004
Chloropyrifos	0.083	0.041	0.011	0.0056
Diazinon	0.17	0.17	0.82	0.82
Dieldrin	0.24	0.056	0.71	0.0019
Endrin	0.086	0.036	0.037	0.0023
gamma-BHC (Lindane)	0.95		0.16	
Guthion		0.01		0.01
Heptachlor	0.52	0.0038	0.053	0.0036
Heptachlor Epoxide	0.52	0.0038	0.053	0.0036
Malathion		0.1		0.1
Methoxychlor		0.03		0.03
Parathion	0.065	0.013		
Pentachlorophenol	19	15	13	7.9
Polychlorinated Biphenyls (PCBs)		0.014		0.03
Toxaphene	0.73	0.0002	0.21	0.0002
4,4′-DDT	1.1	0.001	0.13	0.001

Table A3.1 Partial list of the EPA Aquatic Life Criteria for Freshwater and Saltwater. CMC = Criteria Maximum Concentration = highest concentration to which an aquatic community can be exposed briefly without an unacceptable effect. CCC = Criterion Continuous Concentration = highest concentration to which an aquatic community can be exposed indefinitely without an unacceptable effect. (USEPA 2009) For complete information go to EPA National Recommended Water Quality Criteria (http://water.epa.gov/scitech/swguidance/standards/criteria/current/upload/nrwqc-2009.pdf).

Footnote: See the EPA's narrative statements for criteria on Aesthetic Qualities and these characteristics: Ammonia, Bacteria, Boron, Color, Copper, Gases, Hardness, Nutrients, Oil & grease, Dissolved Oxygen, Suspended solids, Turbidity, Tainting substances, and Temperature.

15 Appendix 4 – Creation of U.S. Federal Law

All major industries and consulting companies employ some people whose responsibility includes being up to date on all relevant proposed, pending, and active rules. Current law must be known to secure compliance and avoid civil or criminal penalties, and to protect the discharger's organization from unfavorable publicity. Proposed and pending regulations must be known in order to offer comments and advice that will influence the final regulation, and to be able to make orderly plans for compliance.

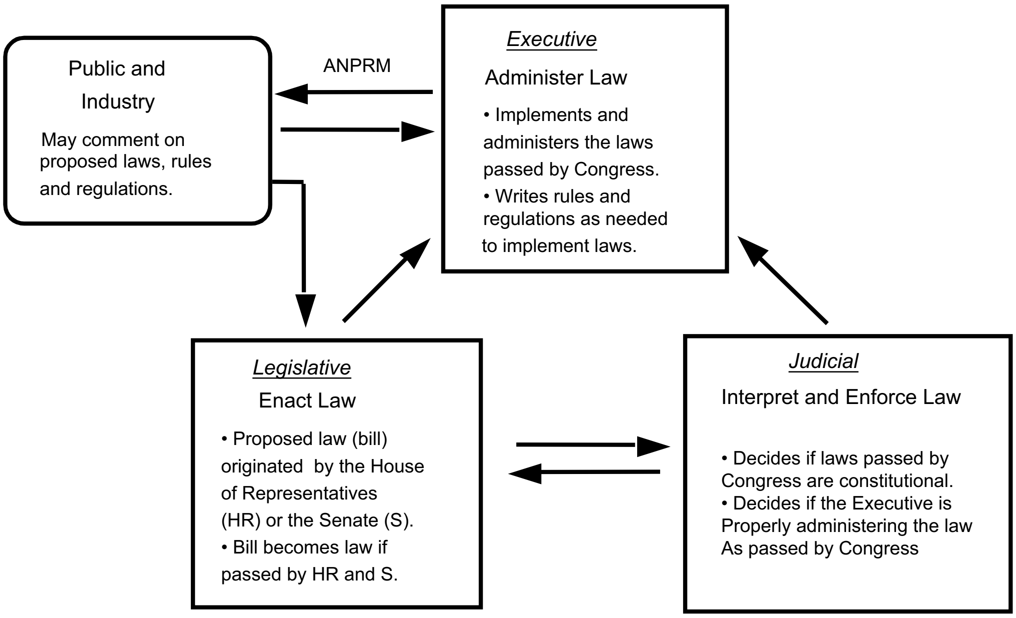


Figure A4.1 Relation of three branches of the U. S. government in making and enforcing environmental laws.

The process of creating a new law or regulation offers engineers, scientists, municipalities, and industries an opportunity to influence the scope and content of the law. In fact, the development process requires the solicitation of advice through written submissions and public hearings. All three branches of Federal Government – the Legislative, Executive, and Judicial – are active in environmental regulation. The relation of the three branches of government and the opportunity for public input are shown in Figure A4.1.

The Legislative branch enacts laws. The Executive branch – the President, the departments (Interior, Defense, etc.) and agencies within departments (e.g., Environmental Protection Agency) – develops the many details that are not specified by Congress by writing of rules and regulations. The Executive branch implements the laws, rules, and regulations.

Courts are asked from time to time to decide whether a law is constitutional. They may also deal with questions such as: Is an agency developing rules in timely fashion? Do the developed rules follow Congressional intent? Is the rule being enforced according to the spirit and the intent of the law?

A proposed law is called a Bill. Bills may originate in either the House of Representatives or in the Senate. Bills originating in the Senate have an identifying number beginning with S. Bills originating in the House of Representatives are identified with HR. As an example, the Resource Conservation and Recovery Act (RCRA) began as bill HR 14496. It was passed to become Public Law 94-580 (PL 94-580). RCRA was later amended by HR 2867 and became PL 98-616.

A law can create a new agency or give an agency a new mission. Typically, several in-house versions of proposed rules are developed. When the agency director, the Office of Management and Budget, and U.S. President agree on a version, the rule is published for state agency officials to review and comment. Revisions are made based on comments received and the agency announces an advance notice of proposed rule making (ANPRM) and requests public input. This is the opportunity for the public and industry to question, comment, and advise. Then there are hearings and a proposed rule is put out for more public comment. After more hearings, the Final Rule will be published with background, and later, the Final Rule will be published with text only.

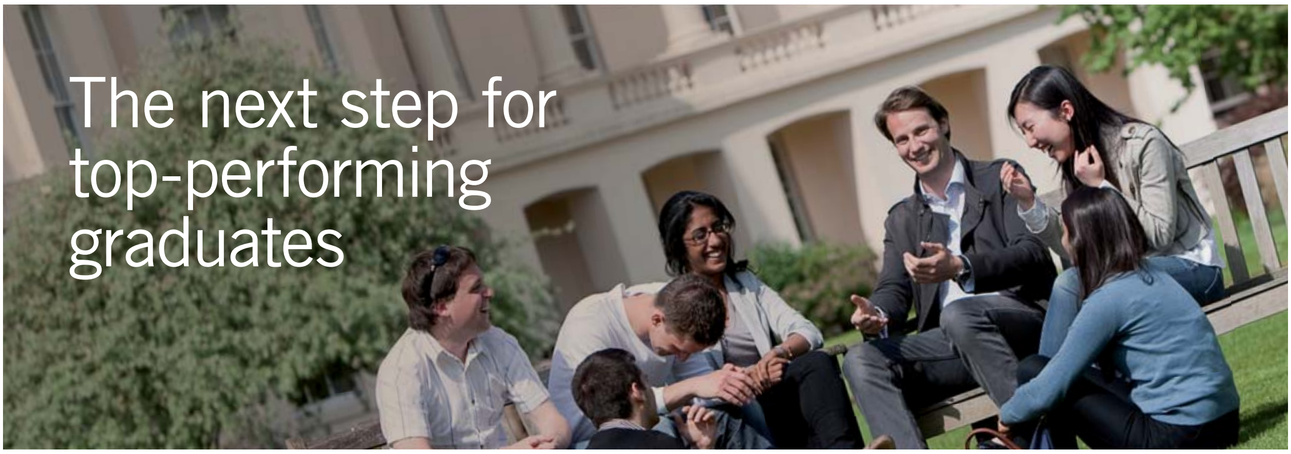
The Federal Register (FR) is published every business day. It covers only the Executive Branch. It contains in this order: Presidential Orders, [Final] rules and regulations, Proposed rules, Notices, and Special parts. All contents have background information. To use the Federal Register you need to know the annual volume number and the page number. For example, volume 50, page 614 is cited as 50 FR 614 (January 4, 1985). Giving the date of publication is optional.

The Code of Federal Regulations (CFR) is published annually. It contains the Final rules and regulations. The CFR is divided into approximately 50 Titles that group similar topics and/or agencies. The hierarchical arrangement in a title is: Title, Subtitle, Chapter, and maybe even more specific subdivisions. The Environmental Protection Agency is in 40 CFR Parts 1–799, which is 799 parts in 9 volumes. The Occupational Health and Safety Act (OSHA) is in 29 CFR 1910, which is one volume that has one part and many sections and subsections.

16 Appendix 5 – Resource Conservation and Recovery Act (RCRA)

The Solid Waste Disposal Act (SWDA) of 1965 was amended by the Resource Conservation and Recovery Act (RCRA) in 1976 and the Hazardous and Solid Waste Amendments of 1984 (HSWA). These three acts, collectively known as RCRA, regulate hazardous wastes 'from the cradle to the grave'. They affect hazardous waste generators, transporters, and treatment and disposal facilities and apply to wastes that were disposed of after November 19, 1980.

The law imposes a "cradle to grave" obligation on waste generators. Any person or company (including transporters or previous waste disposal facility owners) that ever had contact with any waste now located at a problem site is liable to be held as a *responsible party*. Waste generators who may have contracted in good faith with a disposal firm many years ago, can find themselves held responsible for unacceptable consequences. This legal principle, along with the principle of "joint and several" liability, holds all parties equally responsible for hazardous waste cleanup. This means that waste generators, transporters, and operators of treatment, storage and disposal facilities are forced to consider the long-term risks associated with disposal as well as the short-term costs.



RCRA requires all generators of hazardous wastes to apply for a permit prior to disposing of the waste. Generators can be classified as Large Quantity Generators, Small Quantity Generators, and Very Small Quantity Generators depending on the amount of waste that they produce. Generators can have Part A or Part B permits. Under Part A, a generator can store waste onsite for no more than 90 days and must contract with a licensed transporter. Part B permits allow generators to store waste for longer than 90 days and require them to have specially designed collection areas that have secondary containment. Most large industries operate under Part B.

The only exception is for household generators (motor oil, pesticides, etc.) who bring wastes to municipal collection sites. The municipality is allowed to contract with a company that holds a permit to take responsibility for the household hazardous wastes.

If an operating disposal facility is found to be out of compliance or has a release of hazardous materials to the air, ground water, surface water, or land, the facility must undertake RCRA Corrective Actions in order to continue operating. If the facility is no longer operating and releases to the environment are discovered, the facility will be regulated under CERCLA and must undertake cleanup.

RCRA, despite its name, does not require resource conservation and recovery, but it does encourage these practices by imposing design and operating standards for proper management of hazardous wastes today so as to prevent future problems. And, it regulates the handling of materials that are to be recycled if they are classified as solid wastes.

Many recycling practices cause materials to be regulated under RCRA. The actual recycling process is unregulated (except waste burned as fuel), but generation, transportation, and storage prior to recycling are regulated if the waste is a solid waste. In most cases, waste generated from treatment and storage of a hazardous waste remains a hazardous waste. Determining whether a material is a RCRA solid waste is fairly straightforward unless it is to be recycled.

If the intent is to recycle a waste, it must be known what the waste is and how it is to be recycled in order to decide whether it is a solid waste according to RCRA.

RCRA does not specifically disallow any type of treatment or disposal technology but it does impose significant requirements (e.g. groundwater monitoring, leachate collection and treatment, and double liner construction) on land-based management methods (e.g. landfarming, ponds, and landfills), making these alternatives less attractive financially than in the past. As an example, the ban on disposing of liquids in landfills forces one to treat liquids that in the past could have been buried directly.

The important first step is to determine whether a waste is a RCRA hazardous waste. Hazardous waste is a subset of solid waste. For the material to be a hazardous waste it must first be a solid waste.

Under RCRA, solid waste is a regulatory term that does not refer to a material's physical state. This makes it possible, under certain conditions, for industrial wastewater to be classified as a solid hazardous waste. A solid waste is any discarded material that is not excluded by 40 CFR 261.4(a) or that has not been delisted. Delisting is the process by which a generator petitions on a case-by-case basis to have a hazardous waste reclassified as a nonhazardous waste.

A discarded material is any material that is (1) disposed, stored, or treated before its disposal; (2) burned as a fuel, treated, recycled, abandoned, considered inherently waste-like; or (3) stored or accumulated before recycling. If the material does not fit this definition it is not a RCRA hazardous waste, but it may still be regulated under others laws. The most important exclusion is sludge from municipal wastewater treatment plants.

These materials are excluded from the statutory definition of solid waste:

1) Domestic sewage, which is regulated under the Clean Water Act.
2) Any mixture of domestic sewage and any other waste that passes through a sewer system to a publicly owned treatment works. Under RCRA, one may legally dispose of a hazardous waste into a POTW system, but POTWs are subject to pretreatment standards under the Clean Water Act and they have local jurisdiction to legally prohibit discharges that may interfere with their system or that may cause them to violate their NPDES permit.
3) Industrial wastewater discharges that are point source discharges are subject to the Clean Water Act. This does not exclude wastewaters while they are being collected, stored, or treated prior to discharge, nor does it exclude sludges that are generated by industrial wastewater treatment.
4) Pulping liquors used in the production of paper in the Kraft process.
5) Spent sulfuric acid used to produce virgin sulfuric acid.
6) Secondary materials that are reclaimed and returned to the original process in which they were generated, provided that only tank storage is used, the material is not burned, the material is not used to produce a fuel, and the material is not accumulated for more than 12 months prior to reclamation.

Materials that are classified as solid wastes, but excluded from the definition of hazardous wastes:

1) All household wastes and resource recovery facilities that burn only household wastes.
2) Manure and crops returned to the soil as fertilizers.
3) Fly ash, bottom ash waste, slag waste, a flue gas emission control waste generated primarily from the combustion of coal and other fossil fuels.
4) Drilling fluids, produced waters, and other wastes associated with the exploration, development, or production of crude oil, natural gas, or geothermal energy.

5) Waste containing primarily trivalent chromium and specified wastes from the tannery industry.
6) Specified solid wastes from the extraction and beneficiation or ores and minerals.
7) Cement kiln dust.

A solid waste may be classified as hazardous because it is a listed hazardous waste or because it has characteristics that make it hazardous. The characteristics that make a waste hazardous, separate from the listed hazardous wastes, are ignitability, corrosivity, reactivity, and toxicity. These characteristics are measured using standard available testing protocols. The responsibility for making these determinations falls on the waste generator.

One of the most significant concerns arising from hazardous wastes is the leaching of toxic components into groundwater. Because of this, the toxicity characteristic (TC) is measured using the Toxicity Characteristics Leaching Procedure test (TCLP). The waste is classified as a TC hazardous waste if the concentration of any contaminant in the leachate extracted from the TCLP exceeds the toxicity characteristic limits given in Table A5.1.

Chemical	TCL	Chemical	TCL	Chemical	TCL
Arsenic	5.0	Barium	100.0	Benzene	0.5
Chlorobenzene	100.0	Chloroform	6.0	Chromium	5.0
o –Cresol	200.0	m -Cresol	200.0	p -Cresol	200.0
Cresol	200.0	2,4-D	10.0	1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5	1,1-Dichloroethylene	0.7	2,4-Dinitrotoluene	0.13
Endrin	0.02	Heptachlor	0.008	Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5	Hexachloroethane	3.0	Lead	5.0
Lindane	0.4	Mercury	0.2	Methoxychlor	10.0
Methyl ethyl ketone	200.0	Nitrobenzene	2.0	Pentachlorophenol	100.0
Pyridine	5.0	Selenium	1.0	Silver	5.0
Tetrachloroethylene	0.7	Toxaphene	0.5	Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0	2,4,6-Trichlorophenol	2.0	2,4,5-TP Silvex	1.0
Vinyl chloride	0.2				

Table A5.1 Toxicity Characteristic Limits (µg/L) for hazardous wastes.

17 Appendix 6 – Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) is also known as Superfund. Superfund was enacted to correct past mistakes in hazardous waste management by giving the EPA authority that did not exist under RCRA. It is designed to provide mechanisms for investigation, assessment, and remediation of abandoned or uncontrolled sites, or areas that have environmental contamination that were not operating under a RCRA permit. An example is contamination detected at large federal facilities, such as military or Department of Energy facilities. Some well-known Superfund sites include Love Canal in Niagara Falls, NY and the Savannah River DOE site in South Carolina.

The Superfund Amendments and Reauthorization Act of 1986 (SARA) provided $8.5 billion over the next five years for Superfund response activities and $500 million for Underground Tank program activities. It includes provision for citizens' suits against anyone who violates any standard, regulation, condition, requirement, or order under the Act.

There is no clear line to distinguish when Superfund or RCRA applies because many provisions of the statutes overlap. In general, RCRA applies if an operating facility intends to continue its operations, or if the original owner intends to work with EPA under its permit and perform corrective action. CERCLA applies if the facility is not currently operating, if contamination from a past operation is detected at an operating facility, or if contamination is found in the environment and there is no Responsible Party willing or financially able to undertake cleanup. RCRA Corrective Actions often require a facility to follow CERCLA guidance.

A Responsible Party is defined in RCRA as any person or company, including transporters or previous waste disposal facility owners, that ever had contact with any waste now located at a problem site and has liability for problems arising from the past waster management practice. Under Superfund, hazardous substances are governed under strict liability. In tort law, strict liability is liability without fault. Therefore, one who engages in an activity that has an inherent risk of injury is liable for all injuries proximately caused by those activities, even without showing negligence. This means that anyone who handles hazardous wastes is liable for all resulting injuries regardless of how much care has been exercised. This principle also holds under RCRA.

Most Superfund actions are undertaken in cooperation with State environmental agencies, but Superfund activities conducted completely on a site, and not on any surrounding property, do not require federal, state, or local permits, but must comply with any applicable regulations. RCRA, in contrast, specifies cleanup levels and cleanup technology, regardless of cost-effectiveness, and in addition the site must obtain the appropriate permits.

Reporting spills of hazardous wastes is required under CERCLA, the Hazardous Materials Transportation Act, and the Clean Water Act. Under CERCLA, hazardous substances are simply a compilation of substances regulated under other federal statutes (CAA, RCRA, CWA, TSCA). The reporting requirement is triggered when the amount spilled reaches the reportable quantity (RQ), which may be 1, 10, 100, 1000 or 5000 lb, depending on the intrinsic physical, chemical, and toxicological properties of the substance.

Hazardous waste sites are rated with respect to the substances involved, their tendency to migrate from the site, their toxicity, and other factors related to environmental health and safety. A site that scores high enough is placed on the National Priorities List (NPL). Sites on this list are considered to pose the most significant threat to human health or the environment. This does not mean that the site is an immediate threat to public health, but listing means that a site is considered to represent some significant, long-term threat to public health.

Investigation, assessment, and remediation activities under CERCLA are financed in one of three ways.

- A Responsible Party may agree to undertake all activities, hire its own consultants, and pay all expenses. In this case, EPA would monitor activities.
- A Responsible Party accepts a settlement agreement with EPA and contributes money for current and foreseeable future activities. EPA puts this money into a Superfund Special Account and manages the account and the cleanup activities.
- If there is no Responsible Party or if the Responsible party is financially unwilling or unable to undertake activities, EPA makes use of the Superfund Trust Fund, which is appropriated by Congress.

Prior to 2003, the Trust Fund was funded by a value-added tax on chemicals, but the tax was not re-appropriated. The Fund cannot be used for actions at Federal facilities; cleanup of these facilities must be funded out of each agency's operating funds.

State-regulated sites do not have access to the Superfund Trust Fund, but many states have similar programs for managing abandoned or underfunded sites.

The National Oil and Hazardous Substance Pollution Contingency Plan (NCP) contains the regulations for implementing both CERCLA and the Oil Pollution Act. The NCP provides the blueprint for responding to both oil spills and hazardous substances releases.

The NCP requires that a remedial investigation (RI) and feasibility study (FS) be conducted for each site on the NPL that is targeted for remedial action. This is the mechanism established to characterize the risks posed by the uncontrolled waste site and the site-specific potential remedial options. Risk assessment is an important part of this process and it is done on each alternative remedial action, including the 'No Action' option.

After selection of the preferred alternative, the proposed plan is issued, and following a public comment period, the selected alternative is documented in the record of decision (ROD). The ROD is the final remedial action plan. It serves the legal function of certifying that the remedy was selected according to the requirements of Superfund and the NCP. It is also the technical document that outlines the engineering components and remediation goals. It provides a public history of the site, the RI/FS, the risks posed by conditions at the site, the alternative cleanup methods considered, and the rationale behind the remedy selected.

The Superfund Amendments and Reauthorization Act of 1986 (SARA) required EPA to involve the states in hazardous waste identification and cleanup activities. Most uncontrolled hazardous waste sites are not regulated directly by EPA but through state programs. As of 2010, all 50 states, the District of Columbia, and the Commonwealth of Puerto Rico had programs comparable to Superfund for managing sites within their jurisdictions.

As of May 2013, 1,320 uncontrolled hazardous waste sites are listed on the NPL (Federal Register, May 23, 2013). More sites are regulated under state regulations than directly under EPA. For example, there are 2,354 sites on the New York list. Many of these are gasoline stations with leaking underground storage tanks and minor spills and releases, but some include major sites that have not been added to the NPL.

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