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SECOND EDITION

GILBERT M. MASTERS

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Gilbert M. Masters
Stanford University



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To my parents, Gil and Ruth, who taught me the important things

Preface

The scope of environmental engineering and science continues to expand both in terms of the number of cities and countries of the world where water and air quality problems are in urgent need of attention, and in terms of the pollutants themselves, which now so often seem to have international and global impacts.

Due to diligent efforts of environmental engineers and scientists, great progress has been made in our understanding of the fate and transport of substances that contaminate our air, surface water, soil, and subsurface water systems. That progress has led to better technologies for controlling emissions and for cleaning up contaminated sites. With increased understanding and better technologies, it has been possible to craft more sophisticated legislation to address these problems. And, with a better sense of the enormous costs of cleaning up problems after they are created, we are beginning to focus on pollution prevention. In some parts of the developed world, the result has been air that is getting cleaner, greater areas of surface waters that allow beneficial uses such as fishing and swimming, some improvement in subsurface water quality, and, very importantly, continued access to safe drinking water. Unfortunately, the numbers of people globally who do not enjoy these environmental benefits continues to grow, some traditional environmental problems still seem intractable, the global implications of greenhouse gases and ozone-depleting substances seem even more threatening, and, in spite of the importance of the work to be done, our public will to face these challenges seems no longer assured.

It is hoped that some of the science, technology, and policy instruments that have enabled parts of the United States to approach clean air and water goals can be applied to the enormous pollution problems that are coming to light as the former Soviet Union and other eastern bloc countries transform their economies. Similarly, the continued rapid population growth and urbanization occurring in the developing countries of the world is causing unparalleled environmental health risks as people flock to cities that lack basic sanitation services and other infrastructure to control air and water contamination. Environmental engineers will play an increasingly important role as these countries attempt to improve their lot.

Since publication of the first edition of this book, there have been a number of significant studies and actions that are changing the way we think about and deal with our environmental challenges. The Clean Air Act Amendments of 1990, for example, are shifting the approach taken to emission controls from the traditional "command and control" methods, in which government dictates the use of technology, to a more market-based approach that allows major sources to buy and sell emission allowances. In the area of groundwater cleanup, which has received much of the research funding and offered a significant fraction of the professional environmental engineering work

in the last decade, a 1994 national Research Council report concluded that the most commonly used remediation technologies have little hope of ever restoring many of our contaminated aquifers to drinking water quality. Our perceptions of "how clean is clean?" are changing. The Comprehensive Environmental Response, Compensation, and Liabilities Act that created Superfund, which deals with such sites, has been only moderately successful and has been severely criticized as providing too little risk reduction for too many dollars. Partly in response, the concept of "brownfields," with more flexible cleanup goals and much more limited liability to owners who redevelop abandoned urban industrial sites, is emerging as a way to stimulate local economies while speeding cleanup of modestly polluted sites.

In the area of global atmospheric contamination, the impact of the Montreal Protocol on Substances that Deplete the Ozone Layer is beginning to be felt as the ban on production and use of ozone-depleting substances takes effect. The atmospheric concentrations of the most important chlorofluorocarbons are no longer increasing, and models suggest that the ozone layer will begin to repair itself in the early twenty-first century. The apparent success of the Montreal Protocol is serving as a model for negotiations on the other global atmospheric problem, global warming. The 1996 assessments by the Intergovernmental Panel on Climate Change (IPCC) have concluded that the current global warming trend is not entirely natural in origin. Our understanding of the implications of continued warming, how fast it will occur, and how extensive it will be is fraught with uncertainties. How we make decisions about adaptation or mitigation for such a potentially critical environmental problem, given those uncertainties, is sure to be a contentious issue in the coming years.

This second edition has been completely updated, slightly reorganized, and modestly expanded. The goal continues to be to provide an environmental textbook that can bridge the gap between the qualitative descriptions so well presented in many environmental science books and the quantitative analysis and design techniques that are the essence of most advanced environmental engineering texts. A new chapter has been added on solid waste management, which fits in well with the emerging themes of pollution prevention and product stewardship. The material on risk assessment has been expanded and separated from hazardous substance legislation and is now a complete chapter in itself. By moving risk closer to the front of the book, it now stands along with the other three introductory chapters on mass and energy balances, environmental chemistry, and mathematics of growth as a topic that is fundamental to many environmental problems. The material on regulation of hazardous substances has been added to the water quality control chapter, which has been reorganized and renamed.

This book is not the only one designed for use in entry-level technical courses on the environment, but it does offer some features that are not commonly found in other texts. This book covers the basic, traditional materials on air and water pollution that have been the backbone of many introductory environmental engineering and science courses. It provides the necessary fundamental science and engineering principles that are generally assumed to be common knowledge for an advanced undergraduate, but that may be new, or may need to be reviewed, for many students in a mixed class of upper and lower division students. What it adds to the usual engineering introduction,

though, is a basis for analyzing and understanding the newer environmental issues that have become the focus of much of the environmental attention in more recent years. Special attention is given to such topics as hazardous waste, risk assessment, groundwater contamination, indoor air quality, acid deposition, global climate change, and stratospheric ozone depletion.

The book has been organized and presented with a variety of possible courses in mind. First, it could be used, from start to finish, in a standard sophomore or juniorlevel environmental engineering class. In a more advanced undergraduate course, the first three chapters on fundamentals might be skipped or reviewed only lightly. Emphasis could them be placed on some of the more technical details provided in later chapters, supplemented with current environmental literature. I also envision the book being used as a text for a second course on the environment for less technical students, which would come after the usual general environmental science course that most colleges and universities now offer. Many of the more detailed quantitative aspects of the book can be covered lightly in such courses if necessary, while keeping the basic modeling and problem-solving techniques intact. Actually, I use the book at Stanford for a course that attracts both engineering and nontechnical students ranging from freshman to seniors. By carefully adjusting the level of presentation for the mixed classroom, and offering alternative assignments from the book for students with more intense and stronger backgrounds, it is possible to meet the needs of students with quite a range of abilities.

For most topics covered in this book, pertinent environmental legislation is described, simple engineering models are generated, and qualitative descriptions of treatment technologies are presented. The book has been designed to encourage self-teaching by providing numerous completely worked examples throughout. Virtually every topic that lends itself to quantitative analysis is illustrated with such examples. Each chapter ends with a relatively long list of problems that provide added practice for the student and should facilitate the preparation of homework assignments by the instructor.

The first four chapters use environmental problems to illustrate the application of certain key principles of engineering and science that are required for any quantitative treatment of environmental problems. The first chapter presents mass and energy transfer, the second reviews some of the essential chemistry with new material on enthalpy, and the third introduces certain mathematical functions used to model growth that are especially useful in developing future scenarios and projections. The fourth chapter introduces risk assessment and includes new material on risk perception. These four chapters provide the basic foundation needed for the more specialized topics that are the focus of subsequent chapters.

The remaining five chapters are much longer presentations of some of the major environmental problems of the day. these chapters are relatively modular and could be covered in virtually any order. My course at Stanford, for example, takes these chapters in almost reverse order, beginning with global atmospheric change. Chapters 5 and 6 cover topics that traditionally have been the essence of undergraduate civil engineering courses on the environment. In Chapter 5, an expanded introduction to water resources is followed by major sections on surface water contamination and ground-

water. The description of groundwater remediation now includes material on the challenges posed by nonaqueous-phase liquids that contaminate the subsurface along with a summary of the National Resource Council's assessment of the ability of conventional pump-and-treat remediation technologies to restore aquifer quality. Chapter 6 focuses on water and wastewater treatment systems for conventional pollutants supplemented with sections on the treatment of hazardous substances: the Toxic Substances Control Act, the Resource Conservation and Recovery Act, and the Comprehensive Environmental Response, Compensation, and Liabilities Act.

Chapter 7 presents a rather thorough introduction to traditional air pollution problems involving criteria pollutants, local meteorology, simple dispersion models, and emission controls. The material on mobil source controls has been expanded to include a description of reformulated gasoline and other alternative fuels, and new material on two-stroke engines and hybrid electric vehicles has been added. The chapter has much more coverage of the often overlooked, but serious problems of indoor air quality, with special attention paid to environmental tobacco smoke and radon.

Chapter 8, on global atmospheric change, has been completely revised to match the perspectives, terminology, and approaches that have become the standard methods of addressing the problem of global warming as presented in the IPCC Scientific Assessments. The IPCC reports are lengthy, detailed documents that are periodically updated to present the latest summary of the technical literature on climate change. They assume a working knowledge of the basic attributes of radiatively active gases and how they affect the global energy balance, which Chapter 8 has been specifically rewritten to provide. The chapter has also been updated to include more extensive coverage of the status of ozone-depleting substances.

Chapter 9, on solid waste management and resource recovery, is a new addition to this book. The conventional topics of collection and transfer operations and municipal solid-waste landfills are briefly introduced, but the emphasis here is on the hierarchy of solid-waste management priorities, including source reduction, recycling, composting, and waste-to-energy combustion.

Obviously, for a single author to write a text that covers the range of topics introduced here is a challenging task. I have found it to be remarkably rewarding to continue to learn new things as I struggle to keep abreast of these fields, but I am always concerned about getting it right and rely heavily on the reviews and criticisms of my colleagues, who are much more focused in their work. Fortunately, the experts who have helped by providing suggestions, corrections, and criticisms have done so with generosity and gentle humor, and I am greatly in their debt. In particular, I would like to thank Professors Lynn Hildemann of Stanford; Susan Masten, Michigan State University; Brian J. Savilonis, Worcester Polytechnic Institute; and John T. Pfeffer, University of Illinois for their many helpful suggestions. Special thanks go to Kiersten West for her extensive help in gathering material for the new chapter on solid waste management, and to Professor John Ferguson from the University of Washington for offering his special spot on Orcas Island as a quiet place to write. Finally, I wish to acknowledge my wife, Mary, whose writing skills and expertise in hazardous waste management have made the book better, and whose encouragement and patience have been essential to its completion.

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Mass and Energy Transfer

- 1.1 INTRODUCTION
- 1.2 UNITS OF MEASUREMENT
- 1.3 MATERIALS BALANCE
- 1.4 ENERGY FUNDAMENTALS PROBLEMS

When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science.

—William Thomson, Lord Kelvin (1891)

1.1 INTRODUCTION

While most of the chapters in this book focus on specific environmental problems, such as pollution in surface waters or degradation of air quality, there are a number of important concepts that find application throughout the study of environmental engineering and science.

This chapter begins with a section on units of measurement. Engineers need to be familiar with both the American units of feet, pounds, hours, and degrees Fahrenheit as well as the more recommended International System of units. Both are used in the practice of environmental engineering and both will be used throughout this book.

Next, two fundamental topics, which should be familiar from the study of elementary physics, are presented: the *law of conservation of mass* and the *law of conservation of energy*. These laws tell us that within any environmental system we theoretically should be able to account for the flow of energy and materials into, and out of, that system. The law of conservation of mass, besides giving us an important tool for quantitatively tracking pollutants as they disperse in the environment, reminds us that pollutants have to go somewhere, and that we should be wary of approaches that merely transport them from one medium to another.

In a similar way, the law of conservation of energy is also an essential accounting tool with special environmental implications. When coupled with other thermodynamic

2 Chapter 1 Mass and Energy Transfer

principles, it will be useful in a number of applications, including the study of global climate change, thermal pollution, and the dispersion of air pollutants.

1.2 UNITS OF MEASUREMENT

In the Unites States, environmental quantities are measured and reported in both the *U.S. Customary System* (USCS) and the *International System of Units* (SI) and so it is important to be familiar with both. In this book, preference is given to SI units, though the American system will be used in some circumstances. Table 1.1 gives conversion factors between the SI and USCS systems for some of the most basic units that will be encountered. A more extensive table of conversions is given in the appendix at the end of the book.

In the study of environmental engineering, it is quite common to encounter both extremely large quantities and extremely small ones. The concentration of some toxic substance may be measured in parts per billion (ppb), for example, while a country's rate of energy use may be measured in thousands of billions of watts (terawatts). To describe quantities that may take on such extreme values, it is useful to have a system of prefixes that accompany the units. Some of the most important prefixes are presented in Table 1.2.

Quite often, it is the concentration of some substance in air or water that is of interest. In either medium, concentrations may be based on mass, volume, or a combination of the two, which can lead to some confusion.

Liquids

Concentrations of substances dissolved in water are usually expressed in terms of mass of substance per unit volume of mixture. Most often the units are milligrams (mg) or micrograms (μ g) of substance per liter (L) of mixture. At times they may be expressed in grams per cubic meter (g/m^3).

Alternatively, concentrations in liquids are expressed as mass of substance per mass of mixture, with the most common units being parts per million (ppm), or parts

Quantity	SI Units	SI Symbol × C	onversion Factor =	= USCS Units
Length	Meter	m	3.2808	ft
Mass	Kilogram	kg	2.2046	Ib
Temperature	Celsius	°C	$1.8 (^{\circ}C) + 32$	°F
Area	Square meter	m^2	10.7639	ft^2
Volume	Cubic meter	m^3	35.3147	ft^3
Energy	Kilojoule	kJ	0.9478	Btu
Power	Watt	W	3.4121	Btu/hr
Velocity	Meter/sec	m/s	2.2369	mi/hr
Flow rate	Meter ³ /sec	m^3/s	35.3147	ft ³ /s
Density	Kilogram/meter	3 kg/m 3	0.06243	lb/ft ³

[&]quot;See the appendix for a more complete list.

TABLE 1.2 Common Prefixes

Quantity	Prefix	Symbol
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deka	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^9	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zetta	Z
10^{24}	yotta	Y

per billion (ppb). To help put these units in perspective, 1 ppm is about the same as 1 drop of vermouth added to 15 gallons of gin, while 1 ppb is about the same as one drop of pollutant in a fairly large (70 m³) backyard swimming pool. Since most concentrations of pollutants are very small, 1 L of mixture has a mass that is essentially 1000 g, so for all practical purposes we can write

$$1 \text{ mg/L} = 1 \text{ g/m}^3 = 1 \text{ ppm (by weight)}$$
 (1.1)

$$1 \mu g/L = 1 mg/m^3 = 1 ppb (by weight)$$
 (1.2)

In unusual circumstances, the concentration of liquid wastes may be so high that the specific gravity of the mixture is affected, in which case a correction to (1.1) and (1.2) may be required:

$$mg/L = ppm (by weight) \times specific gravity of mixture$$
 (1.3)

Gases

For most air pollution work, it is customary to express pollutant concentrations in volumetric terms. For example, the concentration of a gaseous pollutant in parts per million is the volume of pollutant per million volumes of the air mixture:

$$\frac{1 \text{ volume of gaseous pollutant}}{10^6 \text{ volumes of air}} = 1 \text{ ppm (by volume)} = 1 \text{ ppmv}$$
 (1.4)

To help remind us that this fraction is based on volume, it is common to add a "v" to the ppm; giving ppmv, as suggested in (1.4).

At times, concentrations are expressed as mass per unit volume, such as $\mu g/m^3$ or mg/m^3 . The relationship between ppmv and mg/m^3 depends on the pressure,

4 Chapter 1 Mass and Energy Transfer

temperature, and molecular weight of the pollutant. The ideal gas law helps us establish that relationship:

$$PV = nRt (1.5)$$

where

P = absolute pressure (atm)

 $V = \text{volume (m}^3)$

n = mass (mol)

 $R = ideal gas constant = 0.082056 L \cdot atm \cdot K^{-1} \cdot mol^{-1}$

T = absolute temperature (K)

The mass in (1.5) is expressed as moles of gas. Recall from chemistry that one mole of any gas has Avogadro's number of molecules in it $(6.02 \times 10^{23} \text{ molecules/mol})$ and has a mass equal to its molecular weight. Also note the temperature is expressed in kelvins (K), where

$$K = {^{\circ}C} + 273.15 \tag{1.6}$$

There are a number of ways to express pressure; in (1.5) we have used atmospheres. One atmosphere of pressure equals 101.325 kPa (Pa is the abbreviation for Pascals). One atmosphere is also equal to 14.7 pounds per square inch (psi), so 1 psi = 6.89 kPa. Finally, 100 kPa is called a bar and 100 Pa is a millibar, which is the unit of pressure often used in meteorology.

EXAMPLE 1.1 Volume of an Ideal Gas

Find the volume that 1 mol of an ideal gas would occupy at standard temperature and pressure (STP) conditions of 1 atm of pressure and 0 °C temperature. Repeat the calculation for 1 atm and 25 °C.

Solution Using (1.5) at a temperature of 0 °C (273.15 K) gives

$$V = \frac{1 \text{ mol} \times 0.02056 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273.15 \text{ K}}{1 \text{ atm}} = 22.414 \text{ L}$$

and at 25 °C (298.15 K)

$$V = \frac{1 \text{ mol } \times 0.082056 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298.15 \text{ K}}{1 \text{ atm}} = 24.465 \text{ L}$$

From Example 1.1, 1 mol of an ideal gas at 0 °C and 1 atm occupies a volume of 22.414 L (22.414 \times 10⁻³ m³). Thus we can write

$$mg/m^3 = ppm \times \frac{1 \text{ m}^3 \text{ pollutant/}10^6 \text{ m}^3 \text{ air}}{ppm} \times \frac{mol \text{ wt (g/mol)}}{22.414 \times 10^{-3} \text{ m}^3/mol} \times 10^3 \text{ mg/g}$$
 or, more simply,

$$mg/m^3 = \frac{ppm \times mol \ wt}{22.414} \qquad (at \ 0 \ ^{\circ}C \ and \ 1 \ atm)$$
 (1.7)

Similarly, at 25 °C and 1 atm, which are the conditions that are assumed when air quality standards are specified in the United States,

$$mg/m^3 = \frac{ppm \times mol wt}{24.465} \qquad (at 25 ^{\circ}C \text{ and } 1 \text{ atm})$$
 (1.8)

In general, the conversion from ppm to mg/m³ is given by

$$mg/m^3 = \frac{ppm \times mol \text{ wt}}{22.414} \times \frac{273.15 \text{ K}}{T(\text{K})} \times \frac{P(\text{atm})}{1 \text{ atm}}$$
(1.9)

EXAMPLE 1.2 Converting ppm to $\mu g/m^3$

The federal Air Quality Standard for carbon monoxide (based on an 8-hour measurement) is 9.0 ppm. Express this standard as a percent by volume as well as in mg/m³ at 1 atm and 25 °C.

Solution Within a million volumes of this air there are 9.0 volumes of CO, no matter what the temperature or pressure (this is the advantage of the ppm units). Hence, the percentage by volume is simply

percent CO =
$$\frac{9.0}{1 \times 10^6} \times 100 = 0.0009$$
 percent

To find the concentration in mg/m^3 , we need the molecular weight of CO, which is 28 (the atomic weights of C and O are 12 and 16, respectively). Using (1.8) gives

$$CO = \frac{9.0 \times 28}{24.465} = 10.3 \text{ mg/m}^3$$

Actually, it is usually rounded and listed as 10 mg/m³.

The fact that 1 mol of every ideal gas occupies the same volume (under the same temperature and pressure condition) provides several other interpretations of volumetric concentrations expressed as ppmv. For example, 1 ppmv is one volume of pollutant per million volumes of air, which is equivalent to saying 1 mol of pollutant per million moles of air. Similarly, since each mole contains the same number of molecules, 1 ppmv also corresponds to 1 molecule of pollutant per million molecules of air.

$$1 \text{ ppmv} = \frac{1 \text{ mol of pollutant}}{10^6 \text{ mol of air}} = \frac{1 \text{ molecule of pollutant}}{10^6 \text{ molecules of air}}$$
(1.10)

1.3 MATERIALS BALANCE

"Everything has to go somewhere" is a simple way to express one of the most fundamental engineering principles. More precisely, the *law of conservation of mass* says that when chemical reactions take place, matter is neither created nor destroyed (though in nuclear reactions mass can be converted to energy). What this concept