AIR POLLUTION

Physical and Chemical Fundamentals

John H. Seinfeld

McGRAW-HILL BOOK COMPANY
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This book was set in Times New Roman.
The editors were B. J. Clark and Matthew Cahill;
the cover was designed by Pencils Portfolio, Inc.;
the production supervisor was Leroy A. Young.
The drawings were done by J & R Services, Inc.
Kingsport Press, Inc., was printer and binder.

Library of Congress Cataloging in Publication Data

Seinfeld, John H
Air pollution: physical and chemical fundamentals.

1. Air-Pollution. I. Title.
TD883.S4 628.5′3 74-4296
ISBN 0-07-056042-0

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1 2 3 4 5 6 7 8 9 0 KPKP 7 9 8 7 6 5 4

PREFACE

This book is an outgrowth of my experience with a course on the fundamentals of air pollution for advanced undergraduates and graduate students at the California Institute of Technology. In the early stages of developing material for the course, it became apparent that a single textbook suitable for such a course did not exist. In an effort to provide a cohesive development of the study of air pollution, I prepared a set of lecture notes, from which this book has evolved.

The basic aim of the book is to present in a rigorous, quantitative manner many of the necessary fundamentals required for an analysis of the air pollution problem. There exists a number of books which treat the subject from an essentially descriptive point of view. Although such treatments can be worthwhile for the beginner and the nonscientist, they often do not answer in a satisfactory manner such questions as:

How are air pollutants formed at the source?

In what way do conventional control methods abate pollutant formation and emission?

How does one predict the concentrations of airborne pollutants?

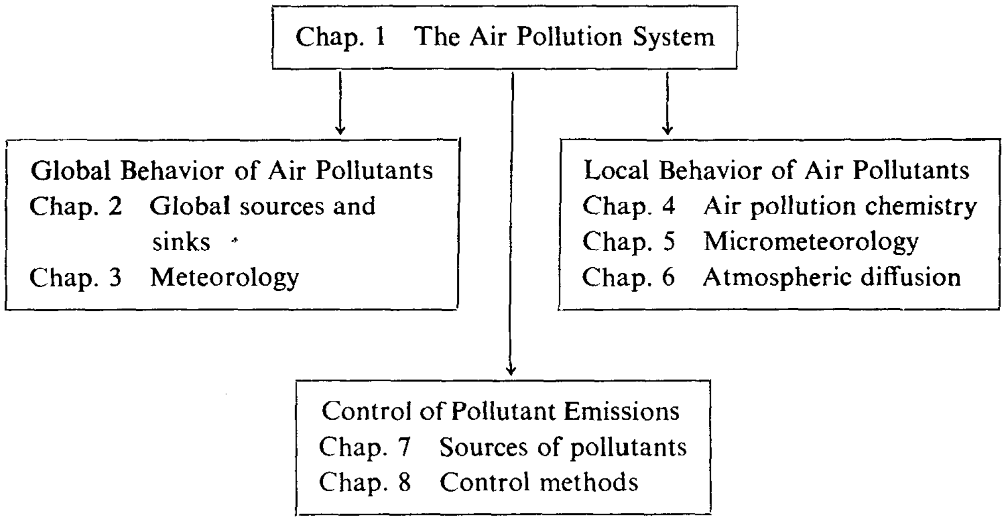
What are the chemical processes responsible for the transformation of pollutants in the atmosphere?

Because of the range of disciplines touched by the overall air pollution problem (such as meteorology, atmospheric chemistry, combustion chemistry, and medicine), it is impossible to cover all aspects of the problem in equal levels of detail in a single textbook of moderate length. In selecting material to cover a rather broad subject, an author invariably weights his choices with his own areas of interest. Thus, I have chosen to stress two subject areas in air pollution: the physical and chemical behavior of air pollutants in the atmosphere and the sources and control methods for pollutants. As a result, the disciplines which are drawn upon most heavily are atmospheric chemistry, fluid mechanics, mass transfer, and combustion. I have chosen not to treat several areas in significant detail; these include effects of air pollution (on human beings, animals, plants, and materials), analytical means for the measurement and detection of air pollutants, and legislative and regulatory measures that have been enacted. In general, then, this book has been written to provide a rigorous and in-depth treatment of the *physical* and *chemical* fundamentals of air pollution.

The level of treatment is appropriate for juniors, seniors, and graduate students in engineering, physics, and chemistry. It is assumed that the reader will have had a basic undergraduate course in transport phenomena (momentum, heat, and mass transfer). This prerequisite may make the book somewhat unsuited for those whose prime interest is air pollution chemistry, although only Chaps. 5 and 6 rely heavily on transport phenomena. Similarly, a reader without an interest in air pollution chemistry may wish to omit certain sections of Chap. 4 on first reading.

The book is organized as shown on page xv. Chapter 1 presents an overview of the entire air pollution problem, including sources, atmospheric behavior, and effects. In addition, we discuss in Chap. 1 the issue of air quality standards versus emissions standards and the economic evaluation of control alternatives. In Chap. 2 the classes of air pollutants are discussed with respect to global sources and sinks. Chapters 3 to 6 are devoted to the physical and chemical behavior of air pollutants in the atmosphere. Finally, the mechanisms of pollutant formation and associated methods of control are the subjects of Chaps. 7 and 8. Appendixes elaborating on certain aspects in the main body of the text are also provided.

This book can be used for a course of one or two quarters (or one semester) in length. For courses in which there is insufficient time available to cover the entire book, the following sections may be omitted: 1.7, 4.6, 4.7, 5.5, 6.4, and 6.5. Material which constitutes detailed derivations or extensions of the general level of treatment appears in smaller print. Those desiring a deeper coverage of a subject than that prevailing in the book as a whole are encouraged to undertake these portions. Finally, the problems at the end of the chapters are intended to provide the reader with the opportunity of applying the material presented in the chapters to situations of practical interest. It is important that these problems be considered an integral part of the text and therefore be attempted.



Many people have contributed to this book. Particular acknowledgment is extended to Sheldon K. Friedlander who originally kindled my interest in air pollution and with whom I share the above-mentioned course. I am also greatly indebted to Robert G. Lamb who provided me with many insights on the problem of turbulent diffusion. Special appreciation is given Thomas A. Hecht for his contributions to Chap. 4 and Grant E. Robertson who aided in the preparation of Appendix B. Also, I wish to extend gratitude to Philip M. Roth and James Wei for reading the manuscript and providing valuable comments on its content. To Lenore Kerner I give special acknowledgment for her superb typing. Finally, to my wife Connie goes deep gratitude for her encouragement and understanding.

JOHN H. SEINFELD

CONTENTS

1

ELEMENTS OF THE AIR POLLUTION PROBLEM

1.1 AIR POLLUTION SYSTEM

Air pollution may be defined as any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation, or materials. By "substances" we mean any natural or man-made chemical elements or compounds capable of being airborne. These substances may exist in the atmosphere as gases, liquid drops, or solid particles. As stated, our definition includes any substance, whether noxious or benign; however, in using the term "measurable effect" we will generally restrict our attention to those substances which cause undesirable effects.

The air pollution problem can be simply depicted as a system consisting of three basic components:

1		2		3
Emission sources	—— Pollutants ——→	Atmosphere	—— Mixing and chemical transformation ——→	Receptors

The ultimate aim of a study of this system is to provide an answer to the question: What is the optimum way to abate air pollution? It is quite clear that the abatement of air pollution in the large urban centers of the world will require a substantial economic investment as well as, perhaps, changes in patterns of living and energy use. It is unrealistic to speak of no air pollution whatsoever; it is virtually impossible to eliminate entirely all man-made emissions of foreign gases and particles into the atmosphere. It is more sensible to aim toward the reduction of pollutant emissions to a point such that serious adverse effects associated with the presence of pollutants in the air are eliminated. Because of the great expenditure of money that will be required, social and political factors will play a major role in meeting this goal.

Efforts to formulate a coherent strategy for air pollution control have been hampered to a large extent by the inability of those who have studied the various aspects of air pollution to demonstrate clearly the relationship between emission levels and airborne concentrations and between airborne concentrations and the adverse effects (mainly to human health) of air pollutants. In short, the motivation for appropriate action by the political segment of the society will arise only if the necessity for change is clearly evident. The necessity for action must be established by a thorough, scientific analysis of all aspects of the problem.

The study of emission sources, such as the internal combustion engine and the burning of coal and oil in industrial boilers and furnaces, requires a knowledge of the chemistry of combustion as well as of the engineering aspects of the design of such equipment. The understanding of the physical and chemical behavior of pollutants in the atmosphere necessitates a knowledge of meteorology, fluid mechanics, and atmospheric chemistry, as well as of aerosol physics. Finally, the evaluation of the effects of pollutants on people, animals, and plants requires backgrounds in physiology, medicine, and plant pathology. Clearly, the scope of disciplines encompassed by the full air pollution system is too vast for one person to master effectively. Thus, in a one-volume treatment of the fundamentals of air pollution, one must elect to cover some aspects in more depth than others. Although we strive to touch upon each of the elements mentioned above, particular emphasis is given to sources and their control and the atmospheric processes involving air pollutants. It would have been desirable to devote equal space to the third link in the chain, namely the effects of air pollutants; however, considerably less is known about this link than about the other two. In fact, the lack of ability to associate health effects with air pollutant dosages in an unambiguous way has been one of the principal obstacles in gaining public support for air pollution control.

In the broadest sense, air pollution is a global problem since pollutants ultimately become dispersed throughout the entire atmosphere. Customarily, air pollution is thought of as a phenomenon characteristic only of large urban centers and industrialized regions, wherein concentrations often reach values several orders of magnitude greater than ambient background levels. For this reason we will consider primarily air pollution within so-called airsheds, regions of hundreds to tens of thousands of square kilometers which by virtue of meteorology and topography have common air pollution problems.

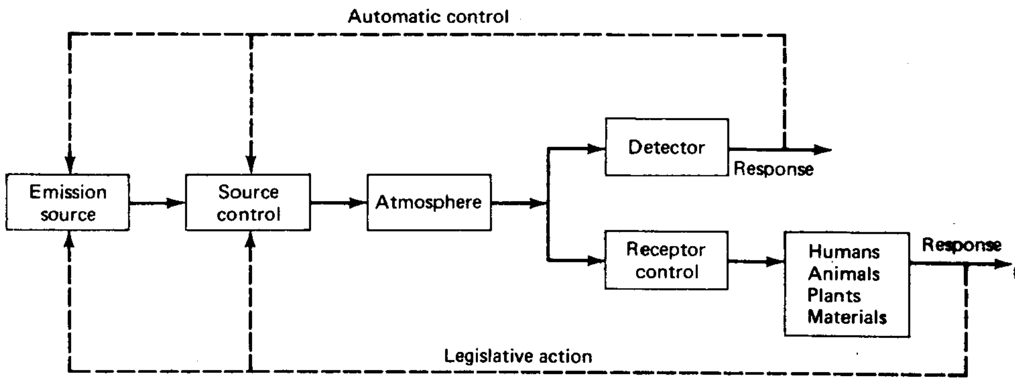


FIGURE 1.1
Air pollution system. Each block represents a given process in the chain of events from the formation of pollutants at the source to the detection of airborne pollutants by receptors. The dashed lines illustrate means by which responses become a basis for the regulation of emission sources and their controls.

Let us consider in slightly more detail the elements of an air pollution problem for a particular airshed. Figure 1.1 summarizes in block-diagram form the components of the air pollution system.

The genesis of air pollution is an *emission source.* Major emission sources are (1) transportation, (2) electric power generation, (3) refuse burning, (4) industrial and domestic fuel burning, and (5) industrial processes. Associated with emission sources are *source controls* which are devices or operating procedures that prevent some of the pollutants produced by the emission source from reaching the atmosphere. Typical source controls include the use of gas-cleaning devices, substitution of a fuel which results in less emissions for one which results in greater emissions, and modifications of the process itself. Pollutants are emitted to the *atmosphere* which acts as a medium for transport, dilution, and physical and chemical transformation. Pollutants may subsequently be detected by instruments or by human beings, animals, plants, or materials. Detection by these various "sensors" is manifested by some response, such as an irritation. Finally, as a result of these responses, emission sources and their controls can be modified either through automatic remote sensing of airborne concentrations or through public pressure and subsequent legislation.

In Fig. 1.1 we have indicated controls at both the sources and the receptors. Three points in the air pollution system are amenable, at least in principle, to control action. First, as we have mentioned, control can be exercised at the source of emission, resulting in lower quantities or a different distribution of effluents reaching the atmosphere or an alteration of the spatial and temporal distribution of emissions. Second, control could be directed to the atmosphere, for example by diverting wind flows or by discharging huge quantities of heat to alter the temperature structure of the atmosphere. Finally, control could be reserved for receptors, for example by extensive use of filtered air conditioning systems or, in the limit, use of gas masks. Of the three, control at the emission source is not only the most feasible but also the most practical. In short, the best way to control air pollution is to prevent contaminants from entering the atmosphere in the first place. Therefore, when we consider air pollution control measures, we will restrict our attention to source controls.

The study of air pollution follows the components shown in Fig. 1.1. The major categories are:

Sources of air pollutants
Control methods
Atmospheric behavior of air pollutants
Effects of air pollutants
Legislative and regulatory measures

In this first chapter we shall discuss briefly each of these five components so as to provide an overview of the air pollution problem. We shall spend somewhat more time in this chapter on those aspects which will not be covered subsequently, namely effects of air pollutants and legislative and regulatory measures.

1.2 AIR POLLUTANTS

The variety of airborne matter is so great that it is difficult to construct tidy classifications. Nevertheless, we begin by placing air pollutants in two general categories:

1 *Primary pollutants:* those emitted directly from sources
2 *Secondary pollutants:* those formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents

Sampling of effluent streams from various sources provides the types and quantities of primary pollutants emitted from sources, usually in terms of the chemical nature and the physical state (gas, liquid drops, solid particles), and atmospheric measurements serve to identify secondary pollutants.

The composition of dry air at sea level in units of parts per million (ppm) by volume is shown in Table 1.1. There are, of course, several other constituents present at very low background levels, including those species normally classed as air pollutants. Some of these other constituents exhibit significant spatial or temporal variations. For example, background levels of water vapor and ozone are

Water vapor	H_2O	0 to 3% by volume (0 to 30,000 ppm)
Ozone	O_3	0 to 0.07 ppm (ground level)

Depending on the water vapor concentration, the other components of Table 1.1 have lower fractions than shown, although still in the same proportions.

There are two ways in which the concentration of air pollutants is normally expressed. The first, used in Table 1.1, is employed for gaseous pollutants, namely parts per million by volume (volume fraction $\times 10^6$), abbreviated ppm. For example, from Table 1.1 we see that N_2 present at 78.084 percent by volume is 780,840 ppm. By contrast, typical concentrations of gaseous air pollutants are 0.0001 percent by volume, or 1 ppm. To avoid the clumsiness associated with such low percentages, a ppm measure is used. Concentrations are sometimes also expressed in parts per hundred million (pphm) or parts per billion (ppb).

The second common concentration measure is based on the weight of pollutant per volume of air in micrograms per cubic meter, abbreviated $\mu g/m^3$. This measure is generally employed for particulate matter and also sometimes for gases. Conversion between ppm and $\mu g/m^3$ depends on the molecular weight and the volume occupied by a mole of the substance. At standard temperature (25°C) and pressure (1 atm), the relation is

$$1 \mu g/m^3 = \frac{\text{ppm} \times 24{,}500}{\text{molecular weight}} \times 10^{-6}$$

Those substances usually considered air pollutants can be classified as follows:

1 Sulfur-containing compounds
2 Nitrogen-containing compounds
3 Carbon-containing compounds (excluding carbon monoxide and carbon dioxide)
4 Carbon monoxide and carbon dioxide
5 Halogen compounds
6 Particulate matter
7 Radioactive compounds

Table 1.1 COMPOSITION OF DRY AIR AT SEA LEVEL

Gas	Concentration, ppm
Nitrogen N_2	780,840
Oxygen O_2	209,460
Argon Ar	9340
Carbon dioxide CO_2	315
Neon Ne	18
Helium He	5.2
Methane CH_4	1.0–1.5
Krypton Kr	1.1
Nitrous oxide N_2O	0.5
Hydrogen H_2	0.5
Xenon Xe	0.08

The first point to note about the above list is that classifications are on both a chemical and physical basis, since particulate matter refers to the physical state whereas the other categories refer to the chemical state. This conforms with the standard air pollutant classifications that are used in virtually all publications on the subject. Particulate matter may, in fact, contain sulfur, carbon, and nitrogen compounds, etc. Therefore, we will assume categories 1 to 5 above to refer to gaseous compounds.

Table 1.2 summarizes the classifications of gaseous air pollutants. We shall study the global sources and sinks of these compounds in Chap. 2 and the mechanisms by which they are formed at the source in Chap. 7. As we shall see, in several cases, global natural emissions (but not local emissions in an urban area) of a particular pollutant far exceed man-made (anthropogenic) emissions. This is the case for ammonia (NH_3), the nitrogen oxides (NO and NO_2), and methane (CH_4). Often when referring to the oxides of nitrogen, NO and NO_2, the compact designation NO_X is used. (Sometimes the oxides of sulfur, SO_2 and SO_3, are given a similar designation SO_X.)

Both CO and CO_2 are products of the combustion of carbonaceous fuels, from incomplete and complete combustion, respectively. Actually, CO_2 (together with water, the other product of complete combustion of hydrocarbon fuels) is not normally considered a pollutant. Nevertheless, the global background concentration of CO_2 has been steadily increasing, leading to concern about its possible effect on global meteorology.

Certain halogen compounds such as HF and HCl are produced in metallurgical and other operations. Fluoride compounds are harmful and irritating to human beings, animals, and plants, even when they are present at very low concentrations.

Table 1.2 CLASSIFICATION OF GASEOUS AIR POLLUTANTS

Class	Primary pollutants	Secondary pollutants	Man-made sources
Sulfur-containing compounds	SO_2, H_2S	SO_3, H_2SO_4, MSO_4†	Combustion of sulfur-containing fuels
Nitrogen-containing compounds	NO, NH_3	NO_2, MNO_3†	Combination of N_2 and O_2 during high-temperature combustion
Carbon-containing compounds	C_1–C_5 compounds	Aldehydes, ketones, acids	Combustion of fuels; petroleum refining; solvent use
Oxides of carbon	CO, CO_2	None	Combustion
Halogen compounds	HF, HCl	None	Metallurgical operations

† MSO_4 and MNO_3 denote general sulfate and nitrate compounds, respectively.