# SULFUR IN THE ENVIRONMENT

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## Part I: The Atmospheric Cycle

Edited by

JEROME O. NRIAGU

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# SERIES PREFACE

## Environmental Science and Technology

The Environmental Science and Technology Series of Monographs, Textbooks, and Advances is devoted to the study of the quality of the environment and to the technology of its conservation. Environmental science therefore relates to the chemical, physical, and biological changes in the environment through contamination or modification, to the physical nature and biological behavior of air, water, soil, food, and waste as they are affected by man's agricultural, industrial, and social activities, and to the application of science and technology to the control and improvement of environmental quality.

The deterioration of environmental quality, which began when man first collected into villages and utilized fire, has existed as a serious problem under the ever-increasing impacts of exponentially increasing population and of industrializing society. Environmental contamination of air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of the ecosystem and may ultimately threaten the very survival of the human race.

It seems clear that if we are to preserve for future generations some semblance of the biological order of the world of the past and hope to improve on the deteriorating standards of urban public health, environmental science and technology must quickly come to play a dominant role in designing our social and industrial structure for tomorrow. Scientifically rigorous criteria of environmental quality must be developed. Based in part on these criteria, realistic standards must be established and our technological progress must be tailored to meet them. It is obvious that civilization will continue to require increasing amounts of fuel, transportation, industrial chemicals, fertilizers, pesticides, and countless other products; and that it will continue to produce waste products of all descriptions. What is urgently needed is a total systems approach to modern civilization through which the pooled talents of scientists and engineers, in cooperation with social scientists and the medical profession, can be focused on the development of order and equilibrium in the presently disparate segments of the human environment. Most of the skills and tools that are needed are already in existence. We surely have a right to hope a technology that has created such manifold environmental problems is also capable of solving them. It is our hope that this Series in Environmental Sciences and Technology will not only serve to make this challenge more explicit to the established professionals, but that it also will help to stimulate the student toward the career opportunities in this vital area.

*Robert L. Metcalf*
*James N. Pitts, Jr.*
*Werner Stumm*

# PREFACE

The energy crisis has fostered heightened interest in the effects of sulfur pollution on the environment. As the skills and techniques of many scientific disciplines are brought to bear on the problem, the difficulty of obtaining a broad picture of the various research activities has greatly increased. *Sulfur in the Environment* was conceived as a systematic endeavor to interface the biological, chemical, geological, and clinical studies on pollutant sulfur, and represents perhaps the first attempt to bring most aspects of environmental sulfur pollution together in a single work. The chapters have been contributed by experts from many scientific disciplines; indeed, the literature on sulfur pollution has become so vast that no single scientist can present a detailed account of all the recent developments.

A comprehensive coverage of the various aspects of sulfur pollution must entail a large number of pages, as indeed is the case here. Part I includes papers on the sources (Chapters 1–3), behavior (Chapters 8 and 9), and transport (Chapters 5–7) of sulfur in the atmosphere. Chapter 4 on the costs and benefits of sulfur emission controls and Chapter 10 on ambient air monitoring for pollutant sulfur compounds add further dimension to the volume. Part II contains reports on the biological (Chapters 12–14), ecological (Chapters 11, 16–21), and health (Chapters 12 and 13) significance of sulfur pollution. The division of chapters into Parts I and II is quite arbitrary in view of the supply and effect relationships for pollutant sulfur in the environment.

Inevitably, several important topics have been slighted or even omitted. For example, we have not emphasized the metabolism and homeostasis of (pollutant) sulfur in mammalian systems because there are several good volumes and review papers devoted to this topic. We have also shied away from considering specific sources of sulfur and the control technologies; to do so would have more than doubled the size of the present work. The primary focus has clearly been on the processes of change and the ecological stresses stemming from environmental sulfur pollution.

*Sulfur in the Environment* is basically the result of the combined efforts of our distinguished group of contributors. Acknowledgment is also due to Drs. A. L. W. Kemp and P. G. Sly for their generous advice and counsel.

JEROME O. NRIAGU

*Burlington, Ontario*
*April 1978*

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# CONTENTS
## *PART II*

# 1

# PRODUCTION AND USES OF SULFUR

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## 1. INTRODUCTION

The key feature in the widespread industrial application and use of sulfur is that it is abundant and inexpensive. Equally important is the fact that compounds of sulfur are exceedingly numerous and varied and include both important organic and important inorganic groups of compounds. Sulfur in various forms has been produced from a wide variety of sources in over 70 countries.

Although the use of sulfur is mentioned in the earliest records of many civilizations, its classification as an element by Lavoisier in 1777 was conclusively proved by Joseph Gay-Lussac and Louis Thenard only in 1809. Historical records indicate that by 3000 B.C. man had discovered that the strange yellow rock burns with an ethereal blue flame which emits a sharp, pungent odor. High priests used sulfur (the name came from the Latin word for brimstone, or burning stone) in religious ceremonies, thus creating the belief that hellfire is fueled by brimstone. The use of fumes from burning sulfur (i.e., $SO_2$) to bleach cotton and linen was practiced by the Egyptians as early as 2000 B.C., as was the use of sulfur as a paint additive. Homer referred to its use as a disinfectant in 1000 B.C., and by A.D. 50 Pliny had reported that sulfur had 14 medical virtues. One of mankind's most important discoveries was made about 500 B.C. when the Chinese invented gunpowder, using sulfur as an essential ingredient. Nobody knows the date of the discovery of sulfuric acid, although available evidence suggests some time around A.D. 1000. Both suflur and sulfuric acid featured prominently in the alchemy of the Middle Ages, both in the phlogistic theory and in efforts to turn base metals into gold. Production of sulfur on a commercial scale began in Sicily early in the fifteenth century.

At present about 50 million tons of sulfur is produced and wasted annually in the environment. The quantity is comparable to the annual anthropogenic emission of sulfur, estimated to be in the range of 40 to 70 million tons (Moss, this volume), but is small compared to the total amount of sulfur (144 to 365 million tons) that cycles annually through the atmosphere. Although sulfur industries may not be an important factor in sulfur pollution on a global scale, their effects on local ecosystems may be quite profound, as illustrated by the chapter on sulfur in soils (Nyborg, Part II). At any rate a consideration of the production and uses of sulfur provides a good entry point for the discussion of sulfur in the environment.

## 2. OCCURRENCE

Sulfur is the tenth most abundant element in the universe and the eighth and fourteenth most abundant element in the solar atmosphere and the earth's crust, respectively (Kaplan, 1972). The average concentrations of sulfur in the various rock types and waters of the crust are shown in Table 1. Comparison of the average abundance in the crust of 260 ppm (see Krauskopf, 1967) with reliable estimates of meteoritic abundances (1.93% in chondritic meteorites, e.g.) has led to the suggestion that the earth's mantle and core are rich in metal sulfides, particularly troilite.

Sedimentary rocks constitute the largest reservoir of sulfur in the earth's crust (Table 1). The sulfate in the oceans ($1.3 \times 10^{15}$ tons) is equivalent to only about 50% of the reduced forms of sulfur in sediments. The large size of the mafic sulfur reservoir merely reflects

Table 1. Inventory of Sulfur in the Earth's Crust[a]

| | Mean Sulfur Content (ppm) | Mass of Sulfur Pool ($10^{12}$ tons) |
|---|---|---|
| Atmosphere[b] | — | ($1.8 \times 10^{6}$) |
| Fresh water[c] | 5.5 | 0.0015 |
| Ice | 0.08[e] | 0.003 |
| Sea | 900 | 1280 |
| Soils[c] | 850 | 0.26 |
| Terrestial plants[c] | 500 | ($7.6 \times 10^{8}$) |
| Aquatic biota[d] | | |
| Marine | 750 | ($7.5 \times 10^{8}$) |
| Freshwater | 250 | ($0.8 \times 10^{8}$) |
| Sedimentary rocks | | |
| Sandstone[c] | 240 | 67 |
| Shale | 2700 | 2000 |
| Limestone | 1300 | 380 |
| Evaporites | 170000 | 5100 |
| Volcanics | 400 | 50 |
| Connate water | 190 | 27 |
| Deep oceanic rocks | | |
| Sediments[c] | 1300 | 390 |
| Mafic rocks (to Moho) | 530 | 2300 |
| Continental igneous and metamorphic rocks (to Moho) | 320 | 6800 |
| Granitic | 210 | 2200 |
| Mafic | 530 | 4600 |

[a] From Holzer and Kaplan (1966) unless noted otherwise.
[b] Friend (1973).
[c] Krauskopf (1967).
[d] Estimates based on published information.
[e] Weiss et al. (1975).

the fact that these rock types comprise the bulk of the crust. Fresh water and the atmosphere contain small but very active sulfur reservoirs.

Sulfur is a common minor constituent of soils and organic matter. Chemically, sulfur displays 2−, 0, 4+, and 6+ oxidation states and thus is widely distributed as a constituent of a large number of minerals formed under diverse geological environments. The principal sulfur-bearing minerals (see Nriagu and Hem, Part II) may conveniently be grouped into two classes: the sulfides, including the sulfosalts, and the sulfates. In meteorites and igneous and metamorphic rocks, sulfur commonly occurs as a sulfide. Because of the chalcophile nature of sulfur, the sulfide melts generally serve as a scavenger for the transition elements, a phenomenon that has given rise to the formation of many economic deposits of base, precious and ferroalloy metals. Hydrothermal processes often concentrate both the sulfides and the transition elements into exploitable mineral deposits. Sulfates are characteristically associated with near-surface and sedimentary environments. Native sulfur is usually found where there is an incomplete oxidation of sulfides of volcanic, magmatic, or biogenic origin.

## 3. SULFUR DEPOSITS

The principal types of minable deposits include (*a*) native sulfur, associated with salt domes, volcanic deposits, or bedded anhydrite; (*b*) sulfides, associated with metal ores; (*c*) sour gases from natural and refinery sources; (*d*) sulfates, associated with calcite, gypsum, and anhydrite deposits and in seawater; (*e*) metal sulfides (mostly pyrite) in coals; and (*f*) organic sulfur in coal, crude oil, and tar sands. It should be emphasized that sulfur-bearing minerals are widely dispersed in the lithosphere, implying that the sulfur recovery from a given source is largely controlled by the economics of production.

Although salt domes occur in many parts of the world, only those in the Gulf Coast of the United States and in Mexico are overlain by minable sulfur-bearing cap rocks. When fully developed, the cap rock consists of three mineralogically distinct units: anhydrite (bottom layer), gypsum, and calcite (top layer). The native sulfur usually is found as well-developed crystal aggregates or disseminated particles in the porous gypsum or calcite units of the cap rock, at depths which vary between 150 and 800 m. Carbon and sulfur isotope studies suggest that the native sulfur was derived by partial oxidation of hydrogen sulfide generated from the bacterial reduction of cap rock sulfates (see Thode, 1963). Before 1913 Sicily was the leading producer of sulfur. The development of the Frasch process in 1894 for profitable extraction of sulfur from salt domes completely changed the status of the world's principal sources of sulfur. In 1975 production from the Frasch mines of the Gulf Coast was about 7.5 million tons or about 65% of the total sulfur production in the United States. Sulfur production from the salt domes of Mexico stood at 2.3 million tons in 1974 and 1975.

A modified Frasch process has also been successfully used to mine evaporitic anhydrite deposits in Sicily, Poland, the USSR, and western Texas and other areas of the United States. Anhydrite deposits with estimated reserves in excess of 100 million tons have been found in Iraq; unevaluated prospects have also been reported in Angola and northern Alberta, Canada. As in cap rock deposits, the sulfur occurs in porous or vuggy limestone. In 1974 production of sulfur from anhydrite deposits amounted to 2.4 million tons in western Texas and about 4 million tons in Poland. The worldwide supply of sulfur from sulfate minerals has declined from 2.6% in 1965 to 0.9% in 1973.

Metal sulfides, which are widely distributed throughout the world and encountered in every rock type, rank second to brimstone as a major source of sulfur. The economically important sulfides include pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$), sphalerite ($ZnS$), galena ($PbS$), arsenopyrite ($FeS_2 \cdot FeAs_2$), and pentlandite [$(Fe, Ni)_9S_8$]. Quantitatively, the pyrite deposits are the most important and are being mined in more than 40 countries. The world's largest deposits of pyrite, however, are in the Alentejo region of Portugal and the Huelva Province of Spain; other major deposits are located in Canada, Cyprus, France, West Germany, Italy, Japan, Norway, and the United States. Pyrite and pyrrhotite concentrates are also recovered as by-products of base metal mining operations. The sulfur in pyrites is commonly used for the direct manufacture of sulfuric acid. The decomposition of the sulfide minerals has been accomplished on an industrial scale by the Orkla, Noranda, or Outokumpu process. The production of sulfur from pyrite declined from well over 50% of the total world supply during the first half of this century to just over 20% of total production in 1975.

The recent worldwide campaign against environmental pollution by sulfur dioxide has engendered technological development aimed at removing $SO_2$ from smelter and power plant waste gases. Meisel (1972) has reviewed 30 potential processes for the recovery of sulfur from metallurgical flue gases. The various sytems for $SO_2$ removal have been classified into five main groups: (1) sorption (on active metal oxides or activated carbon), (2) liquefaction, (3) direct dissolution and reaction with, for example, limestones and dolomites, (4) reduction, and (5) oxidation. The technology for the removal and/or recovery of sulfur from waste gases is the subject of many memoirs and numerous review articles (e.g., see Slack, 1971; Beinstock et al., 1958; Barrekette, 1973; Sax, 1974); a discussion of the topic exceeds the scope of the present chapter.

The recovery of sulfur from nonferrous metal sulfide ores showed only a modest increase from 10% of total world supply in 1965 to about 13% of total output in 1974. Coals potentially represent the world's largest reservoir of sulfur. Coke oven gases invariably contain some hydrogen sulfide with the quantity dependent upon the sulfur content of the coal being carbonized. As a result of the stricter air-pollution-control laws, numerous research projects were initiated to desulfurize the coal before its use, chiefly in utility plants, and to remove $SO_2$ from the gaseous effluents. Annual sulfur recovery from coals has not made a significant impact on the supply inventory; production from this source (mostly in the United States) maintained a relatively constant share (1 to 2%) of the total world output between 1965 and 1974.

The past decade has witnessed a massive increase in supplies of "involuntary" sulfur from desulfurization of sour natural gases and fuel oils. These hydrocarbons generally contain sulfur in quantities that vary from 1.0 to over 90 wt %. When the sulfur content exceeds the level recommended in the pollution abatement guidelines, it must be removed, usually by the Claus process or one of its variants (see Kohl and Riesenfeld, 1960). The quantity of involutary sulfur from oil and gas increased from 18% of the total world sulfur production in 1965 to over 30% of the total supply in 1975. Recovery of sulfur from sour natural gas is presently the most important source in Canada and accounted for over 80% of the total sulfur produced in the country during 1975 (Pearse, 1975).

The Athabasca oil sands have been estimated to contain some 300 billion barrels of recoverable oil and about 2 billion tons of sulfur. Ancilliary sulfur recovery plants are generally designed to accompany the oil extraction programs. Sulfur production from the tar sands increased from 47,000 tons in 1970 to about 95,000 tons in 1974. It has been estimated that the annual output may reach 3 million tons by the year 2000 (Pearse, 1975).

The production of sulfur according to ore type during the past decade or so is shown in Figure 1.

## 4. SECONDARY SOURCES AND RECOVERY

Because exploiting the apparently limitless reserves of sulfur in the earth's crust is economically profitable, little emphasis has been placed on recovering sulfur from secondary sources. At present, most of the calcium and iron sulfates produced during fertilizer manufacture are wasted because there is no economical process to recover the sulfur from these wastes.

A very effective policy of sulfur conservation, however, has been practiced in the oil refinery, where most of the spent sulfuric acid is

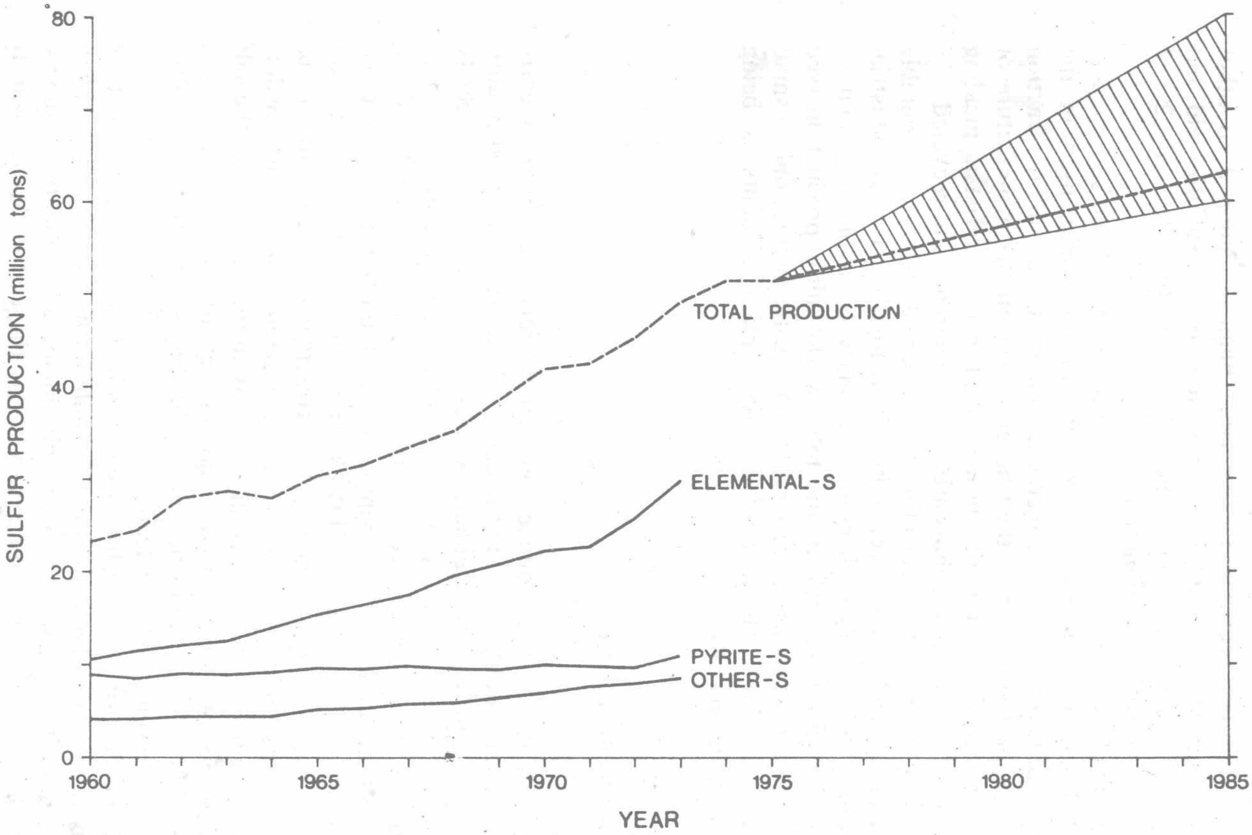

**Figure 1.** Production of sulfur from various sources since 1960. The projected worldwide production of sulfur in the coming decade is expected to lie within the hatched area; the historical trend line is shown as the broken curve.