

SULFUR IN THE ENVIRONMENT

Part II: Ecological Impacts

Edited by

JEROME O. NRIAGU

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Canada Centre for Inland Waters
Burlington, Ontario, Canada

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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.

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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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DETERIORATIVE EFFECTS OF SULFUR POLLUTION ON MATERIALS

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INTRODUCTION

The deleterious effects of sulfur pollution on both health and the functions of the various life-support systems for living things are now widely recognized. In this volume the effects of sulfur pollution on the biota, flora, and climatic conditions are discussed in several other chapters. The present chapter focuses on the deteriorative effects of pollutant sulfur on cultural artifacts. The environmental impact of pollutant sulfur oxides shown in Figure 1 may be viewed against the available data (Table 1) on the exposure of materials and the general

Table 1. Percentage of Total U.S. Population (and Materials) Exposed to Different Minimum Average SO₂ Levels between 1967 and 1972^a

Minimum Annual Average SO ₂ (μg/m ³)	Exposure by Year (% of total material) population × 10 ⁶					
	1967	1968	1969	1970	1971	1972
>100	26.1 (13.2)	20.5 (10.3)	19.3 (8.6)	18.5 (9.1)		
>80	33.2 (16.8)	31.5 (15.8)	21.3 (10.1)	25.3 (12.4)		
>60	44.8 (22.7)	48.8 (24.5)	37.9 (18.8)	31.8 (15.6)	9.3 (4.5)	2.5 (1.2)
>40	66.2 (33.5)	62.4 (31.3)	55.6 (27.6)	46.1 (26.6)	35.7 (17.3)	37.9 (18.2)
>20	85.1 (43.1)	83.9 (42.1)	78.8 (39.1)	75.8 (37.1)	68.2 (33.1)	67.0 (32.2)
>0	197.5 (100)	199.4 (100)	201.4 (100)	203.8 (100)	206.2 (100)	208.0 (100)

^a Data from Gillette (1975).

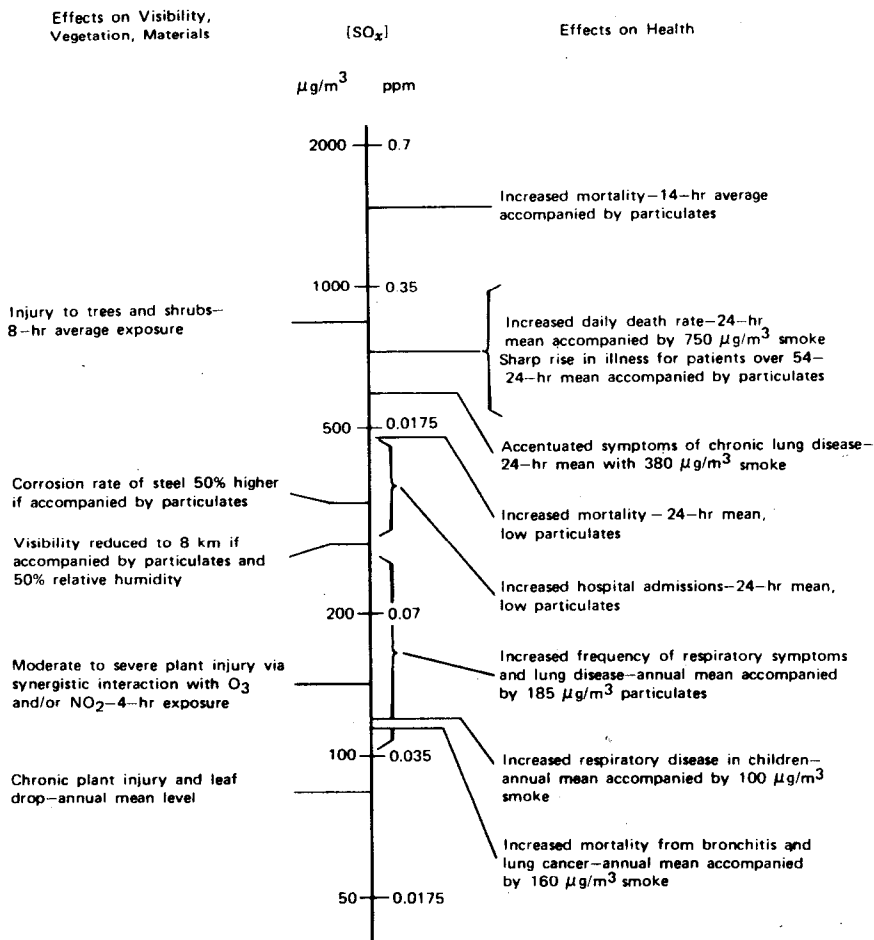


Figure 1. Air quality criteria for sulfur oxides. (Data from *Air Quality Criteria for Sulfur Oxides*, 1969, pp. 161–162.)

population in the United States to the various levels of sulfur dioxide between 1967 and 1972.

Material damage by sulfur pollution represents a major burden on the economy of industrialized societies. The annual cost of corrosion to the world has been estimated at over $\$18 \times 10^9$ (Hendrik, 1964). Babcock (Part I) estimated the *total* (including social and indirect) damage due to pollutant SO_2 in the United States to be $\$6.75 \times 10^9$ in 1970; the total damage in the Chicago area alone was estimated to be $\$525 \times 10^6$ in 1966 and $\$228 \times 10^6$ in 1971. Gillette (1975) estimated that the damage to

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building materials caused by ambient sulfur dioxide was $\$900 \times 10^6$ in 1968 and $\$100 \times 10^6$ in 1972. Kucera (1976) estimated the loss in Sweden due to material damage by sulfur pollution to be about $\$35 \times 10^6$ in 1970. No doubt ambient sulfur compounds contribute greatly to the $\$280 \times 10^6$ annual damage suffered by building materials in Canada (Sereda, 1977). The economics of sulfur pollution damage has been treated in detail by Babcock (Part I).

1. MATERIAL DAMAGE BY ATMOSPHERIC SULFUR COMPOUNDS

The severity of damage done to materials by airborne sulfur compounds is determined by four principal factors: (a) the weather and other environmental conditions; (b) the physical and chemical characteristics of the material under attack; (c) the mechanisms and products of deterioration; and (d) the level and nature of the aggressive sulfur (and other) pollutants.

1.1. Weather Factors Affecting Material Damage by Airborne Sulfur Compounds

The most important factors in atmospheric corrosion of materials include moisture (in the form of rain, fog, dew, condensation, and relative humidity), temperature, air movement, sunlight, and the general "climate." It should be emphasized at the outset that weather conditions exercise unpredictable and conflicting effects on materials; minor differences in climatic conditions have been known to result in relatively major differences in material damage (e.g., see Black and Lherbier, 1968).

Moisture

Moisture is the critical controlling factor in atmospheric corrosion. In the absence of moisture, even high levels of atmospheric sulfur compounds have little, if any, corrosive effect. Vernon (1935) was the first to demonstrate that there is a "critical humidity" above which the corrosion rate increases sharply. Subsequent work have estimated the critical humidities for many materials in the presence of SO_2 ; the data for metallic surfaces may be summarized as follows (see Rosenfeld, 1972;

Yocom and McCaldin 1968):

Metal	Critical Humidity (%)
Aluminum	75-80
Brass	60-65
Copper	65-70
Iron	55-70
Magnesium	85-90
Nickel	65-70
Nickel-copper 70/30	65-75
Nickel-copper 80/20	75-80
Nickel-chrome 80/20	65-75
Steel	60-75
Zinc	70-75

The critical humidity is a function of both the hygroscopicity of the corrosion products and of the corrosive agents present. It is probably conditioned by the minimum number of layers of water molecules required for the corrosion products to accumulate. For example, zinc surfaces accommodate 15 molecular layers of water at 55% relative humidity (RH), 17 layers at 93% RH, and 92 layers at 100% RH (Spedding, 1977). The exact value of the critical humidity apparently is determined by the electrochemical processes in these molecular layers.

Basically, atmospheric corrosion is a discontinuous process with the result that the total corrosion damage is determined primarily by the percentage of time during which the critical humidity is exceeded (Sereda, 1960; Barton, 1973). A method for estimating this duration, known as time of wetness, has been developed by Sereda (1960), and the data collected subsequently by Guttman (1968) and Guttman and Sereda (1968) show that the rate of atmospheric corrosion is related in a logarithmic manner to the time of wetness. Their corrosion data were described quite well by equations of the form

$$r = aX^b(Y + c)$$

where r is the corrosion rate, X is time of wetness, Y is SO_2 concentration, and a , b , and c are empirical constants. Sereda (1974) estimated that the fractions of the total time during which the RH exceeded 70, 80, 90, and 95% were about 0.6, 0.4, 0.17, and 0.07, respectively, for continental Canadian locations; the corresponding fractional values for

coastal areas were 0.8, 0.6, 0.34, and 0.2, respectively. In Britain the relative humidity exceeds 90%, on the average, for approximately 146 days each year (Stanners, 1974). By studying zinc corrosion over a 4-year period, Guttman (1968) found that the time of wetness as determined by Sereda's dew meter corresponded to the time during which the RH exceeded 86%. The implication is thus clear that for a substantial fraction (0.2 to 0.6) of a given year, exposed materials are subjected to conditions that promote corrosion by airborne pollutant sulfur.

Several studies (Sydberger and Vannerberg, 1972; Duncan and Spedding, 1973a, 1973b) have used $^{35}\text{SO}_2$ as a tracer to study the influence of relative humidity on the absorption of SO_2 on metal surfaces. As expected, there was an increase in $^{35}\text{SO}_2$ absorbed as the RH was increased. The data for zinc are portrayed in Figure 2; representative

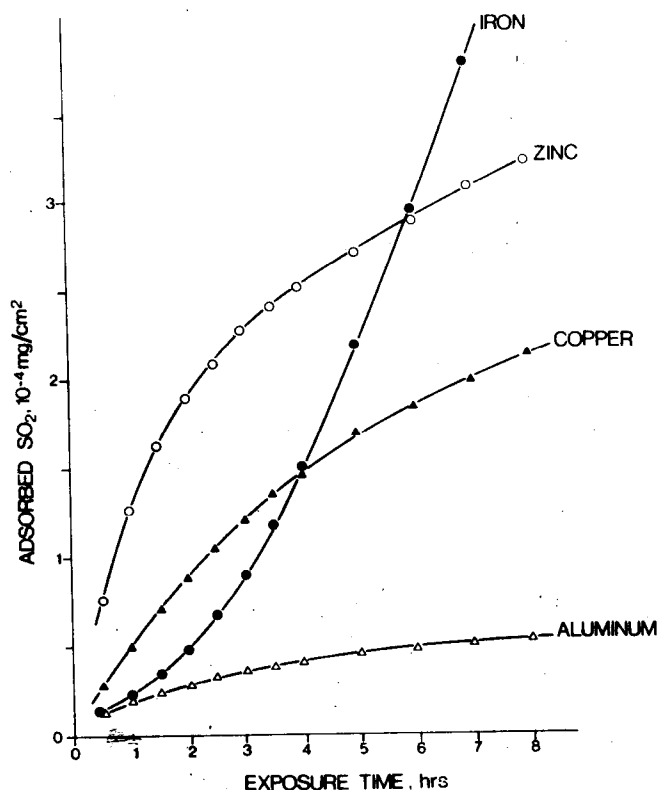


Figure 2. Adsorption of sulfur dioxide on polished metal surfaces at 90% relative humidity. (After Sydberger and Vannerberg, 1972.)