External Review Draft No. 2
December 1980

Draft
Do Not Quote or Cite

Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume IV

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

NOTE TO READER

The Environmental Protection Agency is revising the existing criteria documents for particulate matter and sulfur oxides (PM/SO_x) under Sections 108 and 109 of the Clean Air Act, 42 U.S.C. §§ 7408, 7409. The first external review draft of a revised combined PM/SO_x criteria document was made available for public comment earlier this year.

The Environmental Criteria and Assessment Office (ECAO) filled more than 4,000 public requests for copies of the first external review draft. Because all those who received copies of the first draft from ECAO will be sent copies of the second external review draft, there is no need to resubmit a request.

To facilitate public review, the second external review draft will be released in five volumes on a staggered schedule as the volumes are completed. Volume I (containing Chapter 1) Volume II (containing Chapters 2, 3, 4, and 5) Volume III (containing Chapters 6, 7, and 8) Volume IV (containing Chapters 9 and 10) and Volume V (containing Chapters 11, 12, 13, and 14) will be released during January-February, 1981. As noted earlier, they will be released as volumes are completed, not in numerical order by volume.

The first external review draft was announced in the Federal Register of April 11, 1980 (45 FR 24913). ECAO received and reviewed 89 comments from the public, many of which were quite extensive. The Clean Air Scientific Advisory Committee (CASAC) of the Science Advisory Board also provided advice and comments on the first external review draft at a public meeting of August 20-22, 1980 (45 FR 51644, August 4, 1980).

As with the first external review draft, the second external review draft will be submitted to CASAC for its advice and comments. ECAO is also soliciting written comments from the public on the second external review draft and requests that an original and three copies of all comments be submitted to: Project Officer for PM/SO_x, Environmental Criteria and Assessment Office, MD-52, U.S. Environmental Protection Agency, Research Triangle Park, N. C. 27711. To facilitate ECAO's consideration of comments on this lengthy and complex document, commentators with extensive comments should index the major points which they intend ECAO to address, by providing a list of the major points and a cross-reference to the pages in the document. Comments should be submitted during the forthcoming comment period, which will be announced in the Federal Register once all volumes of the second external review draft are available.

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PREFACE

This document is a revision of External Review Draft No. 1, Air Quality Criteria for Particulate Matter and Sulfur Oxides, released in April 1980. Comments received during a public comment period from April 15, 1980 through July 31, 1980, and recommendations made by the Clean Air Scientific Advisory Committee in August have been addressed here.

Volume IV contains Chapters 9 and 10 which cover effects on visibility and climate and effects on materials. A Table of Contents for Volumes I, II, III, and V follows.

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9. EFFECTS ON VISIBILITY AND CLIMATE

9.1 INTRODUCTION

Airborne particles are among the most conspicuous trace constituents of the atmosphere; their presence can be detected from afar by the unaided eye. Particles scatter and absorb visible radiation, redirecting a portion of it to form "air light," which obscures distant objects. As such, degradation of visual air quality is unique in that it is an effect that can be seen by everyone. Section 9.2 outlines attempts to quantify the value of visibility to individuals and to society. Section 9.3 discusses the subjectively perceived effects of particles on visibility. Section 9.4 covers the objective methods for measuring aerosols' influences on light transmission through the atmosphere, and the fundamental physics involved. Historical patterns are discussed briefly in Section 9.5.

Particles also indirectly affect the properties of the atmosphere. For example, essentially all atmospheric water vapor condensation occurs by nucleation, that is, water deposition onto cloud condensation nuclei or ice nuclei. Addition of such particles to the atmosphere therefore affects cloudiness, which in turn influences insolation. Section 9.6 of this chapter discusses the effects of particles on climate.

The incorporation of aerosols into cloud and fog droplets can change the quality as well as the quantity of precipitation as discussed in Section 9.7. The mechanisms and effects of acid precipitation are discussed in Chapter 8.

In 1977, the National Science Foundation Workshop on Inadvertent Weather Modification (Robinson, 1977) identified five major areas in which effects on the atmosphere can be attributed to presence of particles: visibility, solar radiation, cloudiness, precipitation quantity, and precipitation quality. On the basis of current scientific knowledge, weather phenomena were assessed to determine the likelihood and qualitative scale of their inadvertent modification by human activities. Evidence of <u>major</u> inadvertent modification is considered scientifically established for three areas: changed precipitation quality, increased haze, and increased cloudiness. Evidence of <u>moderate</u> inadvertent modification is established for decreases in solar radiation and sunshine and for urban-scale increases in quantity of precipitation and thunderstorms. There is <u>probable</u> but not yet firmly established evidence of inadvertent modifications in mesoscale increases or decreases in cloudiness and thunderstorms.

9.2 THE VALUE OF VISIBILITY

Reductions in visibility can adversely affect transportation safety, property value, and aesthetics. Impaired visibility has triggered automobile accidents when smoke stack plumes smothered a roadway. When visibility drops below 3 miles, FAA regulations restrict flight in controlled air to aircraft equipped with IFR instrumentation (14 CFR 91.105). Aside from these hazards, reduced visibility carries social and economic costs. The value of the "wilderness experience" and the importance of preserving natural heritage have long been

recognized in the United States (Environmental Protection Agency, 1979). Accordingly, the unique charm of the expansive, scenic vistas of the Southwest suggests that long-range visibility may be what economists call a public good--an asset held in common by the population (Rowe et al., 1980). The key issue concerning visibility is the amount of its value nationwide.

To establish visibility values, it is necessary to develop ways to quantify visibility impairment as perceived by the human eye. The Park Service, in a brochure entitled "My Eyes Need a Good Stretching" (NPS, 1978), attempted to summarize this relationship between visibility and experience by relating the views of artists, humanists, and scientists on the subject of visibility degration. According to the Environmental Protection Agency (1979), establishing visibility values must, therefore, involve relating the whole visual experience to indices such as visual range, contrast transmittance, and color alteration. Although the value of visibility may prove intangible, it is conjectured that it is to some extent quantifiable (can be identified as a discrete point on a scale) and, hence, can be generalized for display to the public. Given the lack of consistent units for the evaluation of aesthetic qualities such as visibility, values can be categorized according to: (1) economic criteria, the dollar cost/ benefit associated with visibility; (2) psychological criteria, the individual need and benefits resulting from visibility; and (3) social/political criteria, community opinions and attitudes held in common with regard to visibility (Environmental Protection Agency, 1979).

Economists have made some progress toward quantifying the values of visibility using dollars as the measure. While market values and prices reflect the marginal value of visibility, total value must be estimated from revealed consumer preference, either in a market or market-like similation. According to Rowe et al. (1980), one approach that has appeared in the literature is to estimate directly an individual's economic values for a unit reduction in visibility, usually drawn from the work of Bohm (1971), Bradford (1970), and Davis (1963). Other studies have used iterative bidding techniques such as those conducted by Randall et al. (1974) and Brookshire et al. (1976). Brookshire (1979) explains the iterative bidding technique as "a direct determination of economic values from data which represent responses of individuals to contingencies posited to them via a survey instrument." The iterative bidding technique in its current form was first developed and applied by Randall et al. (1974) in the Four Corners region of the Southwest. Three contingencies were considered: (a) limited visibility reductions and a view of a power plant with limited visibile emissions; (b) moderate emissions from the plant, moderate visibility reductions and moderate existence of unreclaimed soil banks and transmission lines; and (c) extensive emissions, visibility reductions and unreclaimed soil banks and transmission lines. Unfortunately this selection of scenarios prohibits disaggregation of results into component values for visibility, power plant location, and unreclaimed soil banks and transmission lines. A mean reduction in sales tax of $85 per household was required to make bidders accept scenario C instead of scenario A;

and a reduction of $50 to accept C in place of B (Environmental Protection Agency, 1979). Biases are associated with these techniques; however, no bias tests were conducted in this experiment. Because bids are requested without actual payment, there may be incentives to misrepresent one's bids or the questions may distort an accurate response.

According to Rowe et al. (1980), the current state of methodological and empirical knowledge about obtaining the economic value of atmospheric visibility suggests that much work is left to be done. While Randall, et al. (1974) and Brookshire et al. (1976) used a series of pictures in depicting the varying levels of the environmental good under question, no linkage was defined between the pictures and actual physical parameters of visibility. Clearly, differing levels of visibility and other aesthetic effects were depicted, but the question remains as to the relationship of economic value to the level of visibility and to the level of emissions from power plants. For benefit-cost type of evaluations for policy purposes in satisfying the U.S. Environmental Protection Agency guidelines, a decision regarding a reduction in the aesthetics (visibility) of a region would necessitate all such linkages. According to Environmental Protection Agency (1979), certain psychological benefits, actual or perceived, are associated with good visibility. These benefits include those associated with a person's wish to preserve the option for a clear view of a scenic area and those from just knowing pristine areas exist, regardless of any intent of visiting them.

9.3 PERCEIVED EFFECTS ON VISIBILITY

The term "visibility" is used colloquially to refer to various characteristics of the optical environment, such as the clarity with which distant details can be resolved and the trueness of their apparent coloration.

Traditionally, visibility has been defined in terms of visual range the distance from an object that corresponds to a minimum or threshold contrast between that object and some appropriate background. Threshold contrast refers to the smallest difference between two stimuli that the human eye can distinguish. The measurement of these quantities depends on the nature of the observer, his or her physical health, and mental attitudes of attention or distraction such as effects of boredom and fatigue.

Although visibility defined in terms of visual range is a resonably precise definition, visibility is really more than being able to see a black target, or any target, at a distance for which the contrast is reduced to the threshold value. Visibility also includes seeing vistas at shorter distances and being able to appreciate the details of line, texture, color, and form. The definition of visibility and the selection of methods for monitoring visibility impairment should relate to these different aspects of perceiving distant objects. Visual impairment resulting from air pollution can manifest itself in two distinct ways; as layered or as uniform haze (Malm et al. 1980a and b). Layered haze can be thought of as any confined layer of pollutants that results in a visible spectral discontinuity between that layer and its background (sky or landscape) while uniform haze exhibits itself as an overall reduction

in air clarity. The classic example of a layered haze is a tight vertically constrained coherent plume (plume blight). However, as an atmosphere moves from a stable to unstable condition and a plume mixes with the surrounding atmosphere, the plume impact on visual air quality may manifest itself in an overall reduction in air clarity rather than as a layer of haze.

Quantifications of the perceptible effect of these two types of impairment is really quite different. The eye is much more sensitive to a sharp demarcation in color or brightness than it is to a gradual change in brightness or color over a period of time (Green 1965 and Patel 1966).

Since a change in uniform haze takes place over time periods of hours or days, an evaluation of visual air quality change resulting from a uniform haze requires a person to "remember" what the scene looked like before a given change in air pollution took place. A layered haze is evaluated at only one point in time in that the layer of haze is directly compared to its background. Judgments of visual air quality as a function of air pollution, whether the pollution manifests itself as layered or uniform haze, might be made different by variations in sun angle, cloud cover, and landscape features. These and other aspects of visibility are addressed in an EPA report to Congress (U.S. Environmental Protection Agency 1979).

The selection of a good parameter (or parameters) to characterize visibility is dependent on whether one's interest is in human perception of visual air quality or the cause of visibility degradation, that is, the air pollution itself. The variable, apparent target contrast, relates well to how a person perceives visual air quality and serves as the fundamental measure of visibility impairment (Mulu et al., 1980a). Color change also meets the first criteria. Fine particulate concentration and scattering coefficient are good measures when relating visual impact to pollutant sources. Visual range cannot be directly measured by an instrument. However, when site intercomparisons are required (such as for establishing regional trends) it will be necessary to use visual range as a normalizing parameter. Also, because of its historical popularity, it remains a useful concept to indicate atmospheric "clarity" to the lay person.

As assessment of visibility impairment produced by air pollution must consider the process of human visual perception as well as changes in the optical characteristics of the atmosphere. The perception of brightness, contrast, and color is not determined simply by the pattern and intensity of incoming radiation; rather, it is a dynamic searching for the best interpretation of the visible scene. For example, notice the difference between a candle in a brightly lit room compared with one in a dimly lit room, or how sunlit treetops may appear dark against the horizon sky but bright when viewed against the shadowed forest floor (EPA, 1979). The detection of contrast between an object and its surroundings is fundamental to visibility. Without contrast, as for example in a thick fog, objects cannot be perceived. As the contrast between object and background is reduced (for example, by increased pollution), the object becomes less distinct. When the contrast becomes very low, the object will no

longer be visible. This liminal or threshold contrast has been the object of considerable study. The threshold contrast is of particular interest for atmospheric visibility, since it influences the maximum distances at which various components of a scene can be discerned. Of equivalent importance to threshold contrast is the smallest perceptible change in contrast of a viewed scene caused by a small increment in pollution haze (EPA, 1979).

For small objects, the size of the visual image on the retina of the eye also plays an important role in the perception of contrast. We all know from experience that, as an ojbect recedes from us and apparently becomes smaller, details with low contrast become difficult to perceive. The reason for this loss of contrast perception is not only that the relative brightness of adjacent areas changes but also that the visual system is less sensitive to contrast when the spacing of contrasting areas decreases. If the contrast spacing is a regular pattern of light and dark bands, e. g., a picket fence, a "spatial frequency" can be readily described in terms of the number of pattern repetitions or "cycles" per degree of viewing angle. The human visual system is much more sensitive to contrast at certain spatial frequencies than to contrast of other spatial frequencies (EPA, 1979).

Data reported by Van Nes and Bouman (1967) can be used to estimate the reduction of viewing distance which is needed to compensate for loss of contrast. For example, a regular pattern of 40 cycles per degree can normally be resolved with about 5.2 percent contrast. If the contrast is reduced to 0.26 percent the pattern would remain visible only if the viewing distance is reduced to 1/5 its original value.

The relationship between perceived contrast threshold and target characteristics (size and pattern) is important for visibility, because a scenic vista usually contains a number of targets of varying sizes and arrangement. The calculation of the perceptibility of all targets would require specification of their angular size distribution. The perception of "texture," consisting of contours of small angular size and high spatial frequency, is particularly affected by this loss of threshold sensitivity.

At the practical level, measurements of pattern preception thresholds by several researchers (Van Nes and Bouman, 1956; Schober and Hilz, 1965; Cornsweet, 1970; Henry, 1977) make it particularly clear that the scattering and absorption of light by particles and gases added to the atmosphere can lead to a dramatic loss of visibility through contrast reduction. The operator of a motor vehicle or the pilot of an airplane who must react quickly to minimal visual cues may be greatly disadvantaged by an increase in atmospheric pollutants. In the above illustration of visibility loss by contrast reduction a target that is normally visible at 100 m would only become visible at 20 m. For the operator of a high-speed vehicle, this loss of visibility may be fatal given the limits of human reaction time.

An insight into general visibility conditions in the United States can be obtained by examining available regional airport visibility data. Figures 9-1 and 9-2 (Trijonis and Shapland, 1979) show isopleths of median yearly and summer visibility, a statistic that is insensitive to the site-specific availability of markers as long as the farthest markers

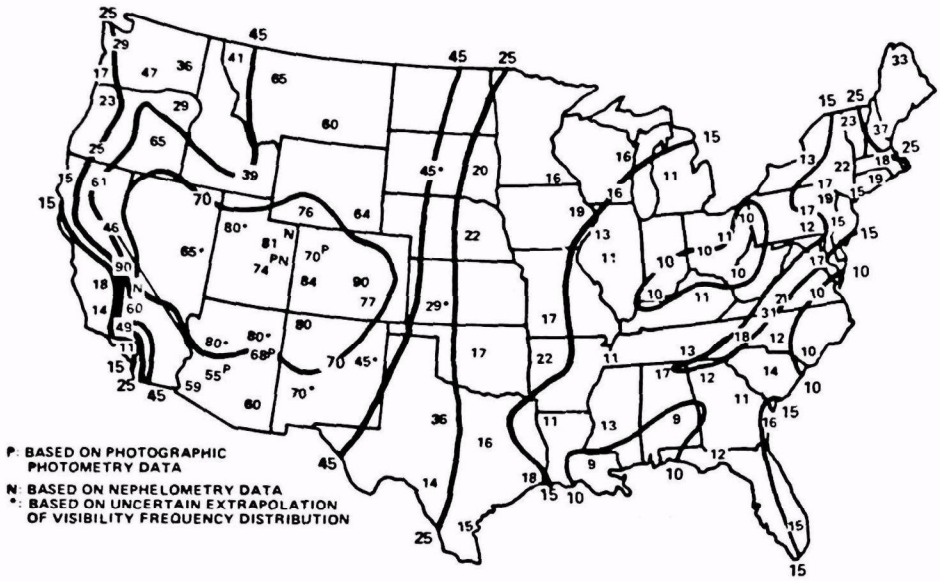

Figure 9-1. Map shows median yearly visual range (miles) and isopleths for suburban/nonurban areas, 1974-76.

Source: Trijonis and Shapland (1978).

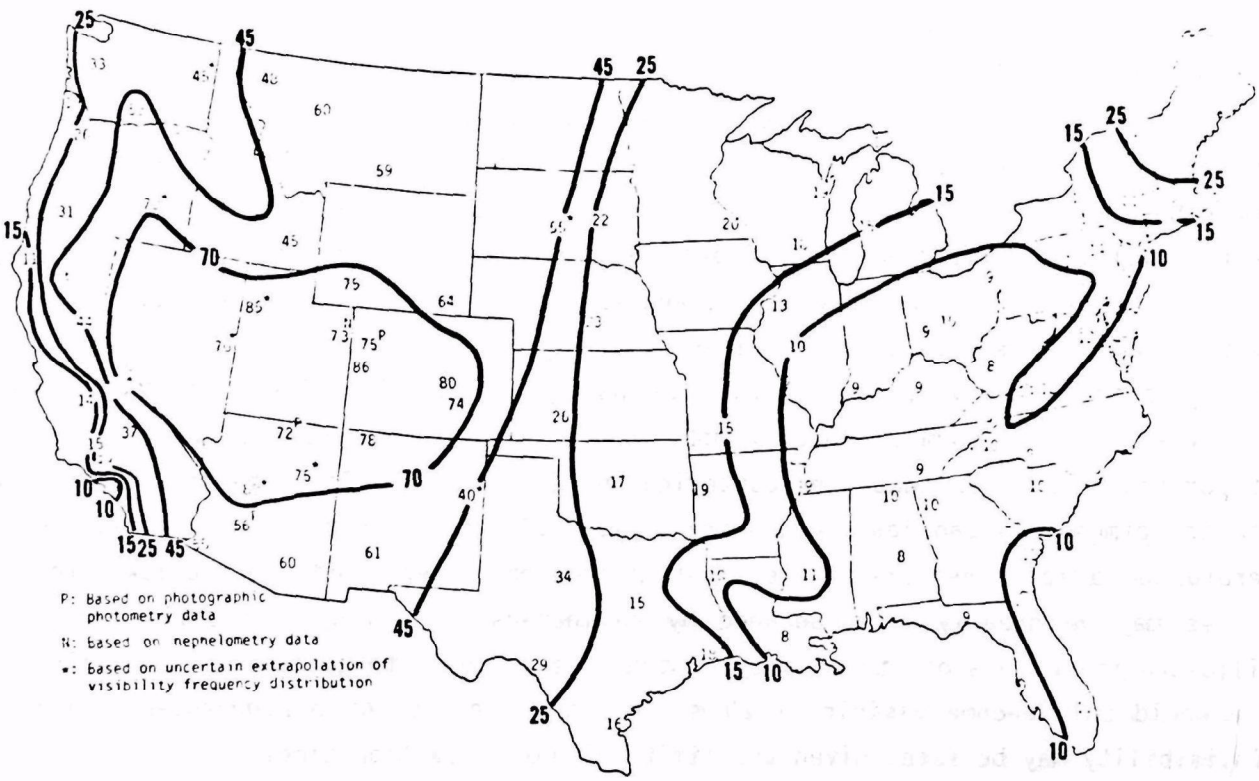

Figure 9-2. Median summer visual range (miles) and isopleths for suburan/ nonurban areas, 1974-76.

Source: Trijonis and Shapland (1978).

consistently reported lie beyond the median visibility. The data represent midday visual ranges for 1974-76 from 100 suburban/nonurban locations. Visibilities at 93 of the locations were determined from airport observations, usually by the National Weather Service. Instrumental visibility measurements from seven sites in the Southwest are also included. Although some uncertainties arise from the use of airport visibility observations, there is reasonably good consistency among airport observations within regions and between airport and instrumental results in the Southwest.

The best visibility (70+ miles, 110+ km) occurs in the mountainous Southwest. Visibility is also quite good (45-70 miles, 70-110 km) north and south of that region, but sharp gradients occur to the east and west. Most of the area east of the Mississippi and south of the Great Lakes has a median visibility of less than 15 miles (24 km). Within the East, the lowest visibilities occur along the heavily industrialized Ohio River Valley.

Although natural sources of visibility impairment are undoubtedly an important factor in producing these geographical and seasonal patterns, analysis of visibility trends and other information discussed in later sections suggests that manmade air pollution has a significant impact. It is also important to note that the regions with the best existing visibility levels are the most sensitive to additional impairment and most responsive to incremental pollution reductions. The reasons for this are discussed in the next section.

9.4. FUNDAMENTALS OF ATMOSPHERIC VISIBILITY

The effect of the intervening atmosphere on the visual perception of distant objects (e.g., structures, mountains, and vistas) is determined by the concentration and characteristics of air molecules, particles, and nitrogen dioxide along the line of site along with the illumination conditions. The rigorous treatment of visibility requires a mathematical description of the interaction of light with the atmosphere known as the radiative transfer equation. The description presented here is intended to provide a qualitative understanding of the underlying theory. Detailed treatments are available in a number of publications (Middleton, 1952; Chandrasekhar, 1960).

Figure 9-3(A) shows the simple case of a beam of light (e.g., from the sun or a searchlight) transmitted horizontally through the atmosphere. The intensity of the beam in the direction of the observer, I(x), decreases with distance from the source as light is absorbed or scattered out of the beam. Over a short interval, this decrease is proportional to the length of the interval and to the intensity of the beam at that point:

$$-dI = b_{ext}\, I\, dx$$

where dI is the decrease in intensity, b_{ext} is the extinction coefficient (the proportionality constant), I is the original intensity of the beam, and dx is the path length. The extinction coefficient b_{ext} has units of inverse distance. The extinction coefficient is determined by the scattering and absorption of particles and gases and varies with particle and gas concentration and wavelength of light.

Consider an observer looking at a distant target in the daytime as depicted in Figure 9-3. Just as a light beam is attenuated by the atmosphere, the light from the target reaching the observer is diminished by absorption and scattering. In addition, the observer receives extraneous light (often called "air light") scattered into the line of sight by the intervening atmosphere. The net effect is that, as shown in Figure 9-4, a target darker than the horizon appears brighter than it actually is and a target brighter than the horizon appears darker than it actually is. At increasing distances, the apparent brightness of dark and bright targets approaches the horizon brightness. At sufficient distance, the target and horizon are so close in brightness that the target is indistinguishable; this distance is the "visual range," or "visibility."

The example just discussed can be restated in terms of a target's "contrast," defined as target brightness minus horizon brightness, divided by horizon brightness. A target's apparent contrast begins with some inherent value at the target and approaches zero as one backs away from the target. When the observer's "contrast threshold" is reached, the target cannot be distinguished and the visual range is known.

In a uniform atmosphere, the apparent contrast between a target and the horizon sky decays exponentially with observer-target distance x (Middleton, 1952):

$$C = C_0 \exp(-b_{ext}\, x) \qquad (9\text{-}1)$$

where C_0 is the initial contrast at $x = 0$. The maximum distance at which a given large target can be distinguished from the horizon is therefore inversely proportional to the extinction coefficient:

$$x_{max} = \frac{\log_e |C_0| - \log_e \varepsilon}{b_{ext}} \qquad (9\text{-}2)$$

where ε is the observer's contrast threshold.

The proportionality factor, $\log_e |C_0| - \log_e \varepsilon$ in equation 9-2, depends on the target's intrinsic contrast with the horizon and on the observer's contrast threshold. For a black target, $C_0 = -1$, so that $\log_e C_0 = 0$ and the proportionality factor reduces to $-\log_e \varepsilon$. The visual range (V) in a uniform atmosphere is thus given by the Koschmieder formula:

$$V = \frac{-\log_e \varepsilon}{b_{ext}} \qquad (9\text{-}3)$$

The observer's contrast threshold, ε, is of course no universal constant. It varies with apparent target size and overall illumination, and it varies with observer (Figure 9-5; Middleton, 1952). However, it enters equation 9-3 only logarithmically, so that the relationship of visual range to extinction is not unduly sensitive to the psychological and physiological nature of the observer. A sevenfold increase in ε, for example, does not quite

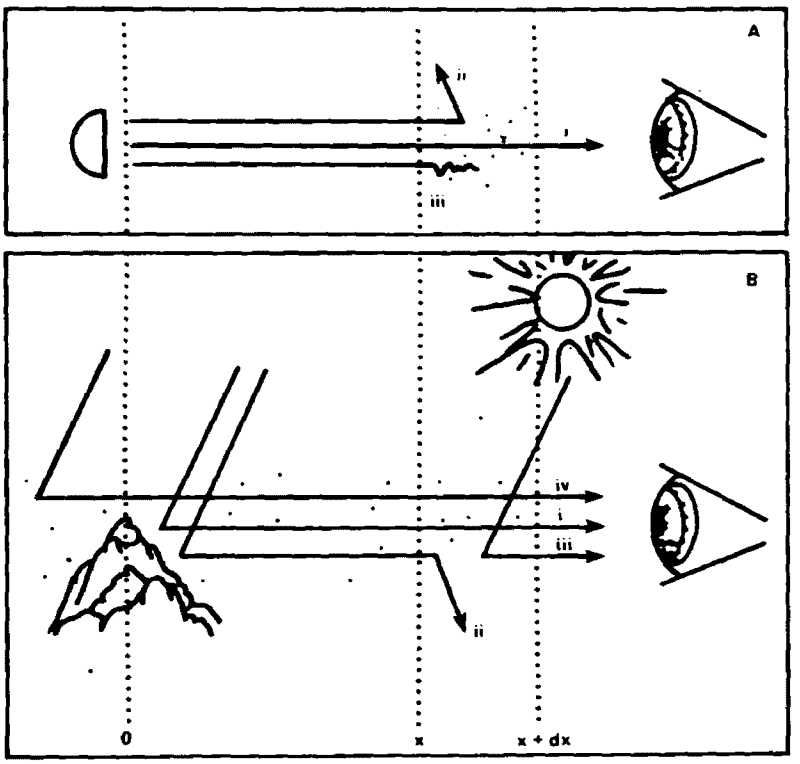

Figure 9-3. (A) A schematic representation of atmospheric extinction, illustrates (i) transmitted, (ii) scattered, and (iii) absorbed light. (B) A schematic representation of daytime visibility illustrates: (i) residual light from target reaching observer, (ii) light from target scattered out of observer's line of sight, (iii) air light from intervening atmosphere, and (iv) air light constituting horizon sky. (For simplicity, "diffuse" illumination from sky and surface is not shown.) The extinction of transmitted light attenuates the "signal" from the target at the same time as the scattering of air light is increasing the background "noise."

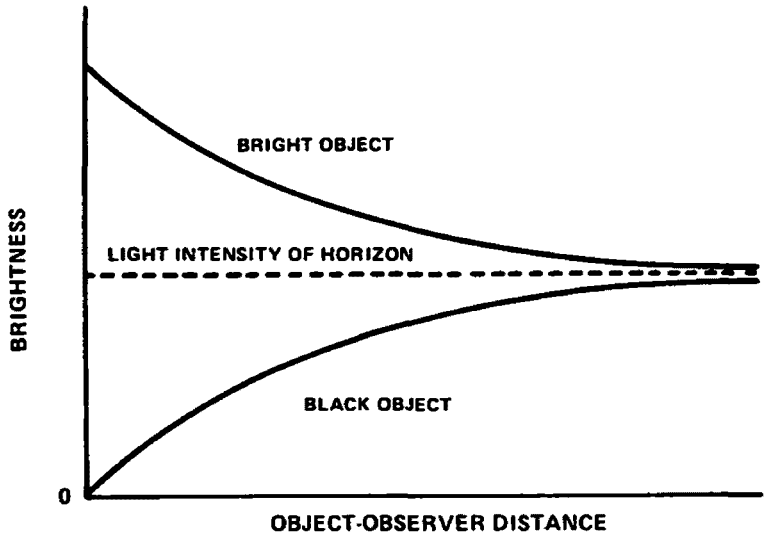

Figure 9-4. The apparent contrast between object and horizon sky decreases with increasing distance from the target. This is true for both bright and dark objects.

Source: Charlson et al. (1978).

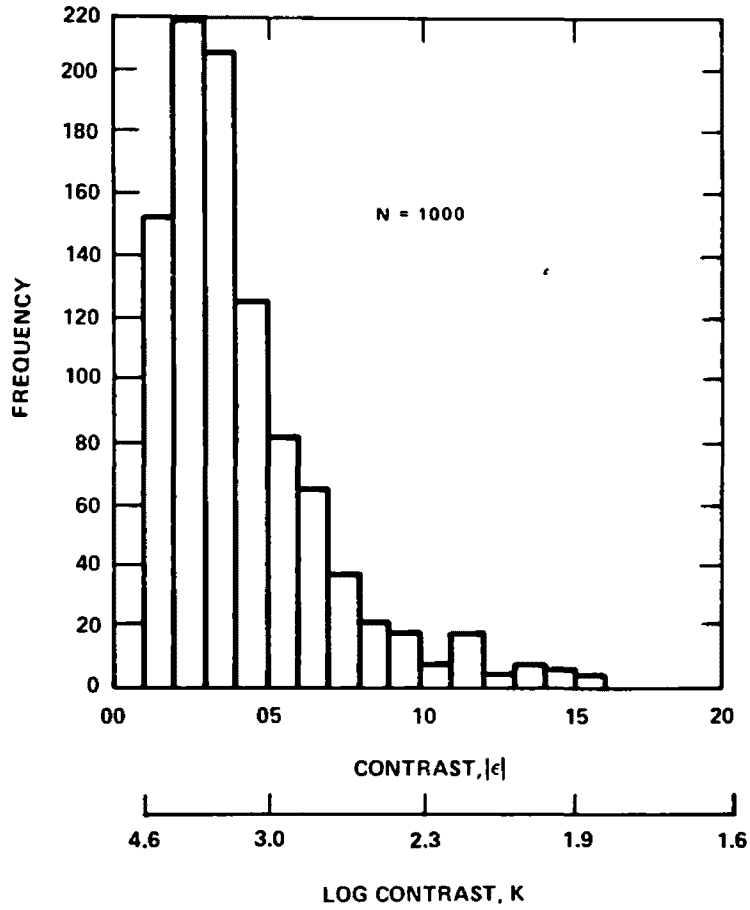

Figure 9-5. Measured apparent contrast of farthest visibility marker was identified in 1000 determinations of visual range by 10 observers. Scatter is due to both the variability of observer thresholds and the discrete nature of the marker set. The corresponding value for the Koschmieder constant, $K = -\log \epsilon$, is 3.2 ± 0.6.

Source: From Middleton (1952).

double $-\log_e \varepsilon$. The conventional choice of ε for a "standard" observer is 0.02, which yields $V = 3.9/b_{ext}$.

Little error is introduced into the determination of visual range by using as targets such nonblack features as dark forests and deep shadows. For a target whose intrinsic brightness is as much as 30 percent that of the horizon sky, for example, the limiting distance given by equation 9-2 is within 10 percent of the visual range. On the other hand, the intrinsic brightness of artificial lights or sunlit objects can approach that of the horizon sky, in which case their use as targets can lead to large underestimates of visual range. It must also be noted that nonblack targets can lead to serious underestimates of visual range if one uses a target at a distance significantly less that the visual range and then calculates or estimates visual range from the apparent contrast of the target. For example, for an intrinsic target brightness of 30 percent of the horizon brightness, an error of 18 percent results from using a target at half the true visual range and an error of 91 percent results if the target is at one-tenth the true visual range.

The Koschmieder formula's neglect of pollution gradients and the earth's curvature and topography limit its applicability near sources of primary particulate matter and in very clean air. Where visibility is restricted by diffuse haze, however, equation 9-3 performs well. Comparisons of daytime visual range, as measured by a human observer, and extinction from scattering, as measured instrumentally at a single point, show visual range to correlate with the reciprocal of extinction, as illustrated in Figure 9-6 (Horvath and Noll, 1969; Samuels et al., 1973). The correlation coefficients are commonly in the neighborhood of 0.9, which is quite good considering that the point measurement of extinction is being extrapolated along a sight path several tens of kilometers long.

In summary, visibility (or visual range) is inversely proportional to the atmospheric extinction coefficient.

9.4.1 Measurement Methods

The term "visibility" is often used to mean visual air quality which takes into account not only how far one can see, but also how well one can see nearby objects (i.e., their apparent contrast or discoloration). These multiple meanings have confounded the choice of a particular method for measuring and ultimately regulating visual air quality.

The extinction coefficient introduced in Section 9.4 represents a summation of contributions from scattering and absorption by gases and by particles: $b_{ext} = b_{Rg} + b_{ag} + b_{scat} + b_{abs}$, where b_{Rg} is scattering by air molecules (Rayleigh scatter); b_{ag} is absorption by nitrogen dioxide gas; b_{scat} is scattering by particles; and b_{abs} is absorption by particles. A number of methods are in use which measure or allow estimation of the various terms of this equation. A full discussion of the more common methods follows. For more detailed accounts, see Middleton (1952), Charlson et al. (1978), Tombach and Allard (1980), Ellestad and Speer (1980), and Waggoner et al. (1980).

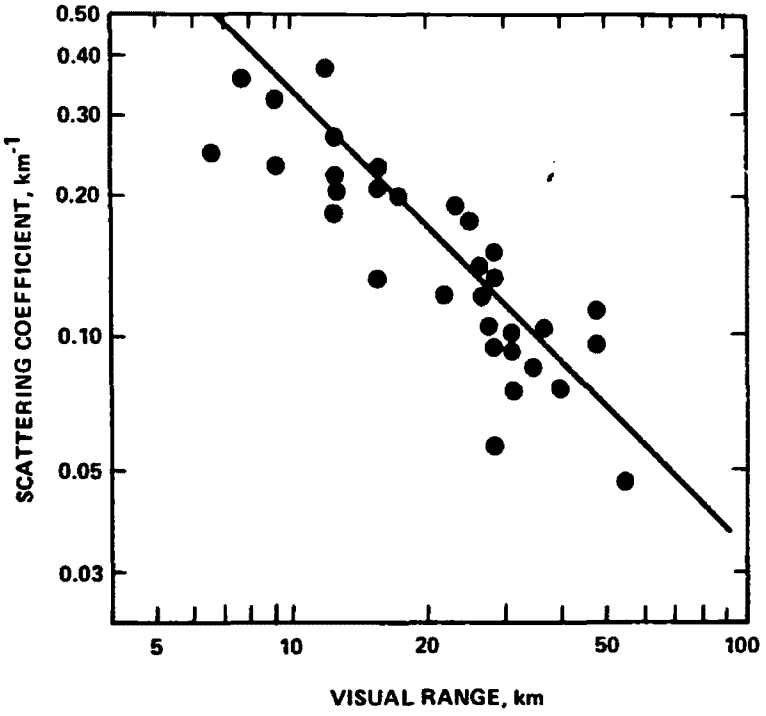

Figure 9-6. Inverse proportionality between visual range and the scattering coefficient, b_{scat}, was measured at the point of observation. The straight line shows the Koschmieder formula for nonabsorbing ($b_{ext} = b_{scat}$) media. $V = 3.9b_{scat}$. The linear correlation coefficient for V and $1/b_{scat}$ is 0.89.

Source: Horvath and Noll (1969).

9.4.1.1 Human Observer (Total Extinction)--The human observer can make qualitative statements about overall visual quality, unusual coloration, and the presence of plumes. However, the observer has been most often used to determine the visual range. In standard practice, a set of dark targets at known distance is selected and an observer then records whether or not he can see each target. Different days or studies are difficult to compare because even minute changes of scenes from day to day may affect human perception. This shortcoming can be resolved by photography. The observer method has been widely used for many years and its qualitative judgments of visual air quality are the ultimate reference for any regulatory effort. However, the method is labor intensive, subjective, and often must use ill-placed or non-ideal targets. The intercomparison of qualitative judgments from the visual range data may be converted to b_{ext}, if one accepts certain assumptions (Middleton, 1952), by Koschmieder's formula:

$$b_{ext} = \frac{3.9}{\text{visual range}}$$

9.4.1.2 Photography (Total Extinction)--Photographs can be used to document scenes for later qualitative analysis by humans or for later analysis of a target's apparent contrast by film densitometry. Photographs provide for more accurate long-term retention of a scene than does the human mind and enable large numbers of people to evaluate a given scene for perception studies. However, photography may introduce significant errors in reproducing a scene due to varying film characteristics and exposure, aging, storage, and reproducibility of the image. The faithfulness of rendition may, therefore, not be true and densitometry and even some qualitative applications may be seriously affected.

9.4.1.3 Telephotometry (Total Extinction)--A telephotometer is a telescope which can measure the apparent brightness of a far away object. By measuring the brightness of an object and the horizon sky around it, one can compute the object's apparent contrast. This number may be used directly or, if one is willing to assume Koschmeder's restrictions (Middleton, 1952), may be converted to b_{ext} by the equation:

$$b_{ext} = \frac{-1}{x} \ln\left(\frac{C}{Co}\right)$$

Telephotometry is attractive because it is a path measurement (thus atmospheric nonuniformities are averaged), the instrument's absolute calibration is unimportant (only its linearity and short-term stability matter), it requires no sample aspiration (and thus avoids large particle losses and sample heating or cooling), and is perhaps the closest instrumental approximation to human observation. The method has limitations when the target's intrinsic contrast is unknown or assumed (a very common situation), when measuring dark objects at close range (due to internal stray light errors), and when clouds cause uneven illumination. The cloud problem makes telephotometry difficult to automate and thus the method remains labor intensive.

9.4.1.4 Long-path Extinction (Total Extinction)--The most direct way to measure b_{ext} is to measure the decrease in intensity of a light beam over a known distance x,

$$b_{ext} = \frac{-1}{X} \ln \frac{I}{I_o}$$

where I and I_o are the final and initial intensities, respectively. The method is appealing in that no assumptions are involved, it measures average extinction over the path, and it requires no sample aspiration. Unfortunately, even for values of b_{ext} about 0.2 km^{-1} (typical at the eastern U.S.) decrease over short paths (about 1 m) is extremely small (200 parts per million) and cannot be measured accurately. An alternative is to increase the path length, but source intensity fluctuation (or mirror reflectivity changes for single-ended systems), alignment, thermally-induced scintillation, and the large background light of daytime make the measurement difficult again.

Hall and Riley (1976) have measured extinction by observing an uncontaminated source at two ranges. Any decrease in intensity with range in excess of the inverse-square decrease is due to extinction. This method avoids any need for absolute calibration, since only the ratio of intensities at two ranges need be measured. This method as used by Hall and Riley is labor intensive but has been demonstrated in clean and urban environments during night operation.

9.4.1.5 Nephelometer (Scattering)--The integrating nephelometer measures only the scattering coefficient, b_{scat}, of an aerosol. By simple adjustment, Rayleigh scatter, b_{Rg}, can be subtracted or included. The instrument consists of an enclosed volume painted black, a sensitive light detector looking through the volume, and a light source at one side of the volume. The only light reaching the detector is that scattered by gas molecules and particles within the volume. The nephelometer is sensitive, is easily calibrated, is easily automated, enables one to modify the sample if desired, and provides a point measurement for correlation analysis with point measurements of mass loading and chemical composition. Errors of application of the nephelometer include sites where the atmosphere is nonuniform (e.g., near aerosol sources or in mountainous terrain) or sites which may have significant absorption occurring (e.g. urban sites), unless a measurement of absorption is being made as well. Nephelometers can also give suspect data if the operator is not careful to avoid inadvertent heating or cooling of the sample and resulting modification of the aerosol size distribution. The nephelometer has two sources of inherent errors, that of angular truncation (which results in underestimates of scattering, especially when large particles are present) and that of sample aspiration (which results in large particles being impacted on the ductwork and thus never measured). These inherent errors may result in depressed scattering/total mass correlations and elevated scat/fine mass correlations when significant large particle concentrations occur. Despite these limitations, the nephelometer remains one of the most widely used visibility measurement methods. Most of the data relating cause and effect (i.e., particulate concentration or composition and optical effect) have been acquired with the nephelometer. Agreement between

the nephelometer and the long-path transmission has been demonstrated in several cases (Waggoner and Charlson, 1976; Weiss et al., 1978).

9.4.1.6 Light Absorption Coefficient--Without doubt, the absorption component of extinction, b_{abs}, is the most difficult to measure. As yet, no single method has proven to be the most effective. Were it not for the fact that graphitic carbon as soot is a prominent species in cities and industrial regions, b_{abs} would be inconsequentially small. However, even a few percent of the submicrometer mass as soot produces a significant effect on b_{abs} or b_{ext}. The methods that have so far been used to evaluate b_{abs} include: (1) determining the difference between b_{ext} and b_{scat} by combining long-path transmissometer with nephelometer (Weiss et al., 1978); (2) determining absorption on Nuclepore filters with scattered light removed by an integrating plate of opal glass (Lin et al, 1973); (3) determining absorption on Millipore filters (Rosen et al., 1980); (4) determining the reflectivity of a white powder with aerosol mixed into it, called the Kubelka-Monk method (Lindberg and Laude, 1974); (5) determining absorption of light by a sample of particles inside a white sphere (integrating sphere) (Fischer, 1975); (6) estimating an imaginary refractive index from regular scattering or polarization and size distribution (Eiden, 1971); (7) measuring the amount of graphitic carbon and its size distribution and them calculating b_{abs}; (8) detecting the acoustical pulse produced when energy is absorbed by particles as light and transformed to heat (spectrophone) (Truex and Anderson, 1979).

9.4.2 Role of Particulate Matter in Visibility Impairment

As noted in section 9.2.2, the extinction coefficient comprises contributions from gas and particle scattering and absorption:

$$b_{ext} = b_{Rg} + b_{ag} + b_{scat} + b_{abs}$$

This section discusses the relative magnitudes of these contributions.

9.4.2.1 Rayleigh Scattering--A particle-free atmosphere at sea level has an extinction coefficient of about 0.012 km^{-1} for green light (wavelength 0.55 μm) (Penndorf, 1957), limiting visual range to about 325 km. The coefficient b_{Rg} decreases with altitude. In some areas of the western United States, the extinction of the atmosphere is at times essentially that of a particle-free atmosphere (Charlson et al., 1978). Rayleigh scattering thus amounts to a simply definable and measurable background level of extinction with which other extinction components (such as those caused by manmade pollutants) can be compared. Rayleigh scattering decreases with the fourth power of wavelength, and contributes a strongly wavelength-dependent component to extinction. When Rayleigh scattering dominates, dark objects viewed at distances over several kilometers appear behind a blue haze of scattered light, and bright objects on the horizon (such as snow, clouds, or the sun) appear reddened at distances greater than about 30 km.

9.4.2.2 Nitrogen Dioxide Absorption--Of all common gaseous air pollutants, only nitrogen dioxide has a significant absorption band in the visible part of the spectrum. Nitrogen

dioxide strongly absorbs blue light and can color plumes or urban atmospheres red, brown, or yellow if significant concentrations and path lengths are involved. The effects of nitrogen dioxide on visibility are discussed more fully in the criteria document for oxides of nitrogen, and in Hodkinson (1966), White and Patterson (1980), and Charlson et al. (1972). Its contribution to total extinction is in general minor.

9.4.2.3 Particle Scattering--As the particle concentration increases from very low levels, where Rayleigh scattering dominates, the particle scattering coefficient, b_{scat}, increases until eventually b_{scat} is greater than b_{Rg}. At 40-km visual range, a better-than-average value for the eastern U.S., Rayleigh scattering contributes only about one-eighth of the total extinction (Trijonis and Shapland, 1979).

Two principal problems in understanding the degradation of the visual quality of air have been: (1) defining the size range and other physical characteristics of particles most effective in causing scatter; and (2) defining the chemical composition of particles in this size range (Charlson et al., 1978). Size, refractive index, and shape are the most important parameters in relating particle concentration to particle-related extinction coefficients, b_{scat} and b_{abs}. If these properties are established and the shapes are geometrically simple, the light scattering and absorption can be calculated. Alternatively, the extinction coefficient associated with an aerosol can be measured directly as discussed in Section 9.4.1.

From the point of view of aerosol optics, a key question is whether an aerosol particle is spherical. For such particles, rigorous Mie theory (Mie, 1908) is applicable, and the optical properties can be readily calculated from their size and refractive index (Dave, 1969; Wiscombe, 1980). Measurements in St. Louis by Allen et al. (1979) show that in the fine mode less than 5 percent of the aerosol population is nonspherical. Pueschel and Wollman (1978) found that spherical particles also dominate fine-mode aerosols near Cedar Mountain, in east-central Utah.

Charlson et al. (1978) used Mie theory to calculate the light-scattering and absorption efficiency per unit volume of particles for a typical aerosol containing some light-absorbing soot (Figure 9-7). As illustrated in the figure, particles of 0.1 to 2 μm diameter are the most efficient light scatterers. The remarkably high scattering efficiencies of these particles are illustrated by the following examples: a given mass of aerosol of 0.5-μm diameter scatters about a billion times more light than the same mass of air; a 1-mm-thick sheet of transparent material, if dispersed as 0.5-μm particles, would be sufficient to scatter 99 percent of the incident light, that is, to completely obscure vision across such an aerosol cloud.

A more revealing explanation of the usual dominance of scattering by fine particles (i.e., those particles of diameter less than 1-3 μm) is possible: particles smaller than 0.1 μm, though sometimes present in high numbers, are very inefficient at scattering light and thus contribute very little to visibility loss; particles larger than about 1-3 μm, though

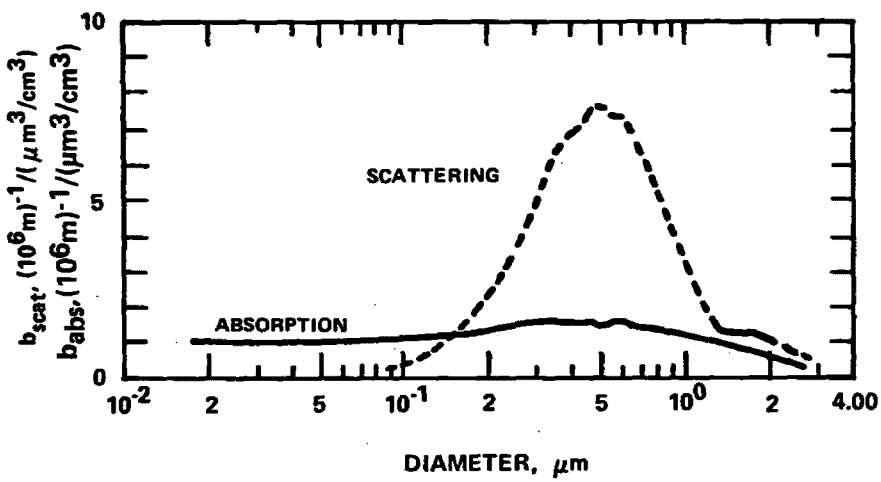

Figure 9-7. For a light-scattering and absorbing particle, the scattering per volume has a strong peak at particle diameter of 0.5 μm (m = 1.5 − 0.05i; wavelength = 0.55 μm). However, the absorption per aerosol volume is only weakly dependent on particle size. Thus the light extinction by particles with diameter less than 0.1 μm is primarily due to absorption. Scattering for such particles is very low. A black plume of soot from an oil burner is a practical example.

Source: Charlson et al. (1978).

efficient per particle at scattering light, usually exist in quite small numbers and contribute only a small fraction of visibility loss. Coarse particles (i.e., larger than 1-3 μm) are occasionally important in determining visibility, particularly near roadways and some industrial sites and during natural occurrences of fog and wind blown dust.

Coarse particles are almost exclusively nonspherical; using the Mie theory to calculate their optical properties will therefore give only a crude approximation. There is, however, an extensive body of data on the optical properties of the nonspherical particles (e.g., Pinnick et al., 1976; Fowler and Sung, 1979; Mugnai and Wiscombe, 1980).

Atmospheric particles are made up of a number of chemical compounds. All of these compounds exhibit a peak scattering efficiency in the same diameter range (0.1 to 1.0 μm) calculated to be optically important for the typical aerosol in Figure 9-7. However, because of differences in refractive index, the values of the peak efficiency and the exact particle size at which it occurs vary considerably among the compounds (Figure 9-8; Faxvog, 1975).

It is instructive to note in Figure 9-8 the high extinction efficiences of carbon and water. As will be discussed in Section 9.4.3, these compounds are often significant fine mass components and are therefore often responsible for significant amounts of extinction.

Measured particle size distributions can be used in conjunction with Mie theory calculations to determine the contribution of different size classes to extinction. The results of this kind of calculation are shown in Figure 9-9. The peak in scattering per unit volume is at 0.3 μm, so that the fine particles dominate extinction in most cases.

Because the peak and shape of the bimodal particle mass distribution curve can vary, the light-scattering characteristics of a given particle mass might also be expected to vary. However, as noted by Charlson et al. (1978), for the observed range of atmospheric particle distributions, the calculated scattering coefficient per unit mass is relatively uniform. Latimer et al. (1978) have determined the scattering per unit volume for several aerosol distributions. The calculated coefficient changes by no more than 40 percent in the size range of 0.2 to 1.0 μm (Figure 9-10; Latimer et al., 1978).

The relative consistency of calculated light scattering per unit mass over a range of particle distributions and the dominant influence of fine particles suggest that reasonably good approximations of light-scattering coefficients can be obtained by measurements of fine-particle mass. Indeed, agreement from simultaneous monitoring of the two parameters at a number of sites has been found by several investigators. Measurements by Waggoner and Weiss (1980), Weiss (1978), Patterson and Wagman (1977), Macias et al. (1975), and Samuels et al. (1973) at various sites showed scattering per unit fine mass ratios of 3-5 m^2/g. Correlations between the fine-particle mass and b_{scat} are consistently high (Table 9-1). Figure 9-11 (Macias and Husar, 1976) shows the relationship for St. Louis. The high correlations indicate that at the sites studied, fine-particle mass dominates particle scattering.

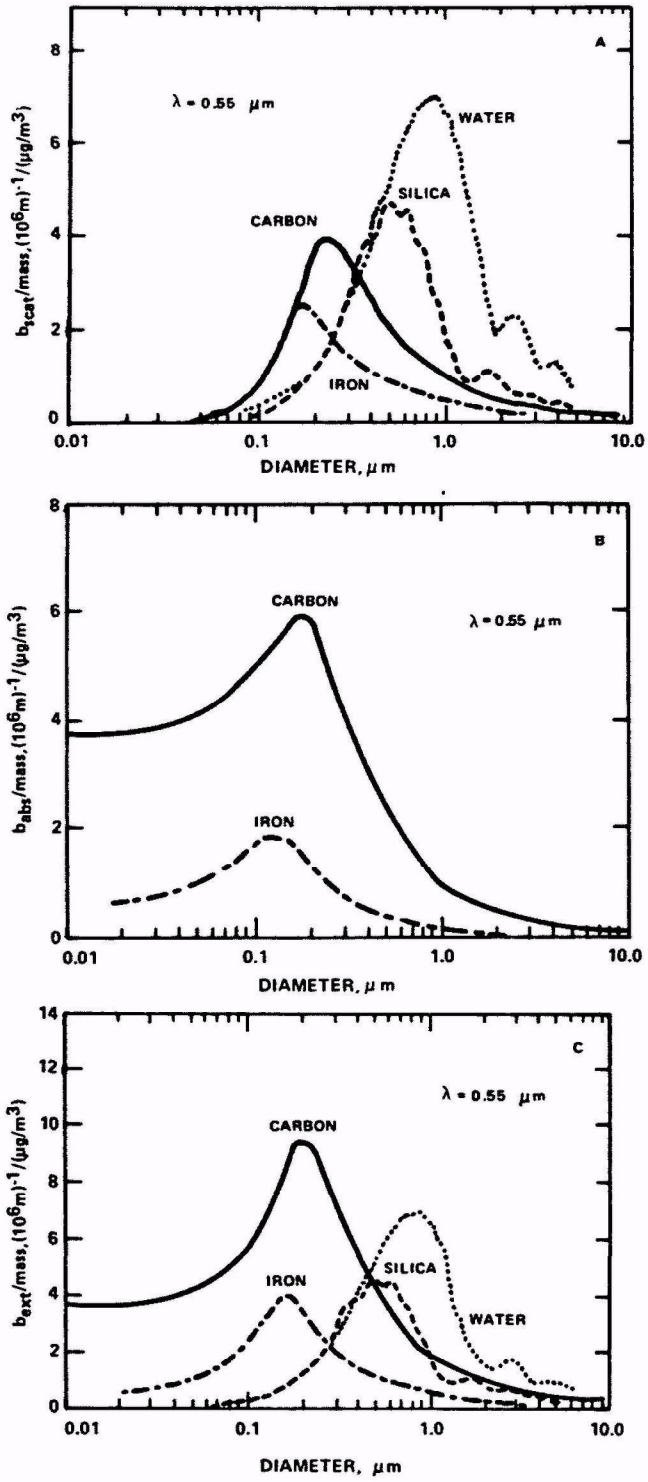

Figure 9-8. (A) Calculated scattering cross-section per unit mass at a wavelength of 55 μm for absorbing and nonabsorbing materials is shown as a function of diameter for single-sized particles. The following refractive indices and densities (g/cm^3) were used: carbon (m = 1.96-0.66i, d = 2.0), iron (m = 3.51-3.95i, d = 7.86), silica (m = 1.55, d = 2.66), and water (m = 1.33, d = 1.0). (B) Calculated absorption cross-section per unit mass at 0.55 μm for single-sized particles of carbon and iron. (C) Calculated extinction cross-section per unit mass at 0.55 μm for single-sized particles of carbon, iron, silica, and water.

(Source: (a) Faxvog (1975); (b and c) Faxvog and Roessler (1978).

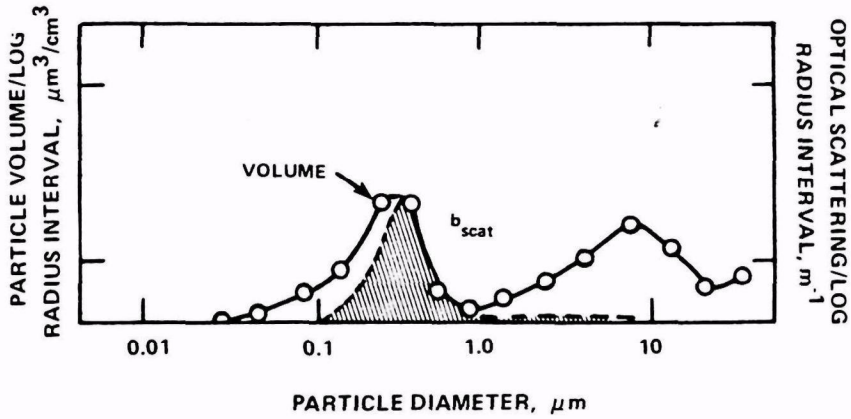

Figure 9-9. For a typical aerosol volume (mass) distribution, the calculated light-scattering coefficient is contributed almost entirely by the size range 0.1-1.0 μm. The total b_{scat} and total aerosol volume are proportional to the area under the respective curves.

Source: Charlson et al. (1978).

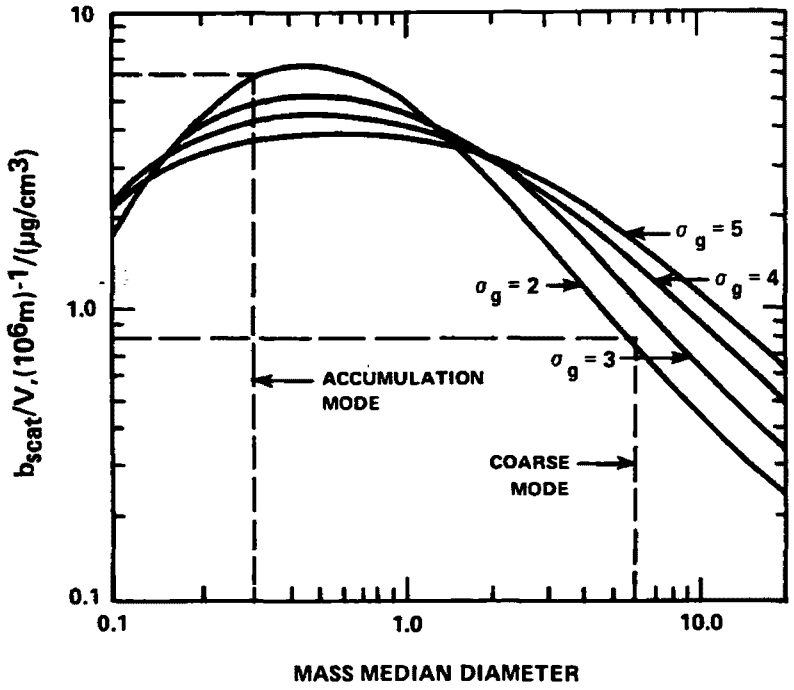

Figure 9-10. Scattering-to-volume ratios are given for various size distributions.

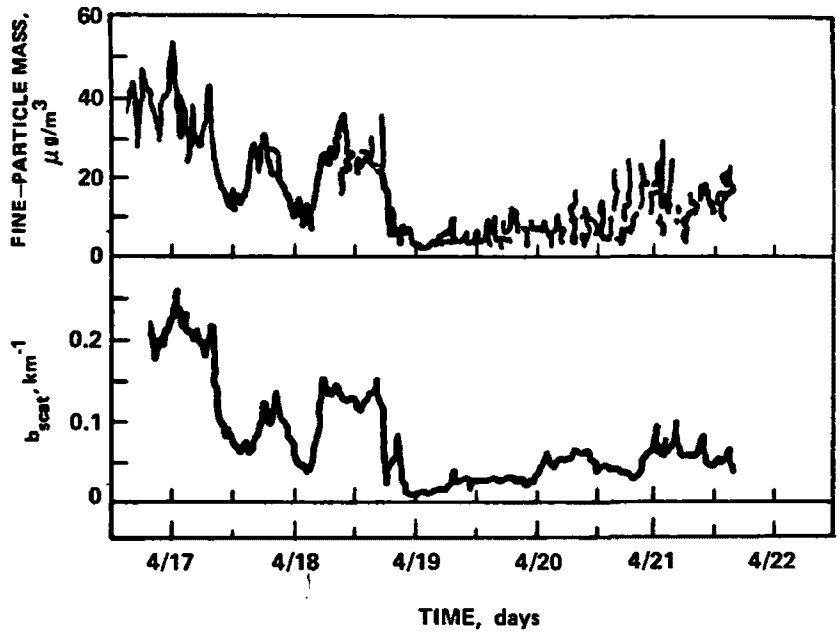

Figure 9-11. Simultaneous monitoring of b_{scat} and fine-particle mass in St. Louis in April 1973 showed a high correlation coefficient of 0.96, indicating that b_{scat} depends primarily on the fine-particle concentration.

Source: Macias and Husar (1976).

TABLE 9-1. LIGHT SCATTERING PER UNIT MASS OF FINE AEROSOL

Location	b_{scat}/mass, (m^2/g)	r	N	Reference[a]
Mesa Verde, CO	2.9	--	5	1
Seattle, WA (residential)	3.1	0.95	58	1
Seattle, WA (industrial)	3.2	0.97	64	1
Puget Island, WA	3.0	0.97	26	1
Portland, OR	3.2	0.95	108	1
New York, NY	5.0	--	--	2
St. Louis, MO	5.0	0.96	72	3
Los Angeles, CA	3.7	0.83	39	4
Oakland, CA	3.2	0.79	20	4
Sacramento, CA	4.4	0.98	6	4

[a]1, Waggoner and Weiss (1980); 2, derived by Charlson et al. (1978) from Patterson and Wagman (1977); 3, Macias et al. (1975); 4, Samuels et al. (1973).

This was documented in an experiment conducted by Patterson and Wagman (1977), who monitored the ambient aerosol size distribution by a set of four cascade impactors in the New York metropolitan area. The first impactor was operated only when the light-scattering coefficient was between 0 and 0.15 km^{-1}; impactor A was operated at 0.15-0.3; impactor B at 0.3-0.45; and impactor C when values exceeded 0.45. The measured mass distributions (Figure 9-12; Patterson and Wagman, 1977) show that at good background visibility levels, the mass concentration was largely (70 percent) contributed by coarse particles. At the low visibility level C, however, over 60 percent of the total mass was contributed by fine particles. Thus, visibility in the New York metropolitan area was found to be lowest when the concentration of fine particles reached a maximum.

It is conceivable that in the arid West the aerosol refractive index and relative amounts of coarse and fine particles are so different that the scattering mass ratios quoted above would not be applicable. However, preliminary results from project VISTTA (Macias et al., 1978) suggest that b_{scat}/fine mass ratios in the Southwest are 3 m^2/g as measured elsewhere.

In areas where fine-particle concentrations are low, coarse particles may contribute significantly to light extinction. Coarse dust particles are much less efficient scatterers per unit mass (Figure 9-7; Charlson et al., 1978), however, so that much higher mass concentrations are required to produce a given optical effect. In windblown dust, for example, Patterson and Gillette (1977) reported values of the ratio of light scattering to mass that were more than an order of magnitude lower than those noted above for fine particles.

With regard to how much of extinction is due to scattering, the measurements of Waggoner et al. (1980) made with an integrating nephelometer and the integrating plate method show that

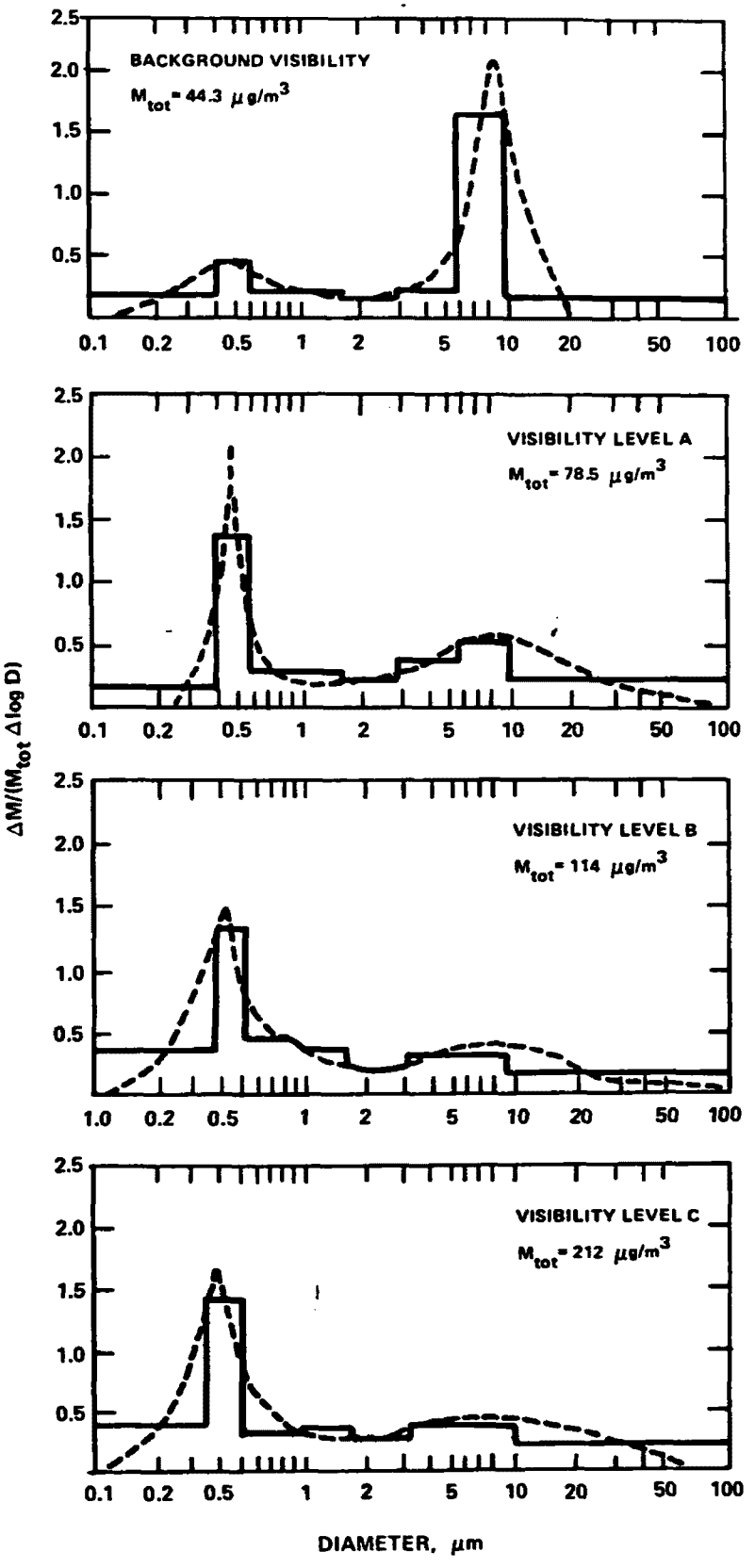

Figure 9-12. Aerosol mass distributions, normalized by the total mass, for New York aerosol at different levels of light-scattering coefficient show that at high background visibility, the fine-particle mass mode is small compared with the coarse-particle mode. At the low visibility level, ϵ, 60 percent of the mass is due to fine particles.

Source: Patterson and Wagman (1977).

in urban-industrial areas particle scattering accounts for 50 to 65 percent of extinction, in urban residential areas 70 to 85 percent, and in remote areas 90 to 95 percent. A comparison reported by Weiss (1978) which employed a nephelometer and a long path extinction device found scatter/extinction percentages of 55 to 65 percent in urban Phoenix, Arizona and about 95 percent on a plateau outside Flagstaff, Arizona. Recent studies by Wolff et al. (1980) which used a nephelometer and absorption inferred from elemental carbon loadings produced data which show scattering/extinction percentages of 60 to 85 percent at a variety of sites. In general, scattering by particles accounts for 50 to 90 percent of extinction depending on location, with urban sites in the 50 to 75 percent range and remote sites in the 80 to 95 percent range.

Particle scattering also plays a role in the perception of plumes. Suspended particles generally scatter much more in the forward direction than in other directions. This fact means a plume or haze layer can appear bright in forward scatter (sun in front of observer) and dark in back scatter (sun in back of observer) because of the angular variation in scattered air light. This effect can vary with background sky and objects. The added air light is both angle and wavelength (color) dependent and the wavelength dependence can vary with illumination angle. A visible aerosol layer will be brighter than an adjacent particle-free layer for sun angles (in front of observer) less than 30°. At larger angles, the aerosols will usually be darker. Aerosol optical effects alone are theortically capable of imparting a reddish-brown color to a haze layer when viewed in backward scatter. NO_2 would increase the degree of coloration in such a situation. Specific circumstances of brown layers must be examined on a case-by-case basis.

In many pristine areas, where viewing distances are 50 to 100 km, a reduction in calculated visual range (for example, from 350 km to 250 km) will not be the most noticeable impact of incremental pollution. The reduction in apparent contrast and discoloration of nearby objects and sky are the main effects perceived in such areas.

Calculation of contrast changes (for large targets) accompanying incremental particle levels indicate that the maximum decrease in contrast will occur for objects located at distances of about one-fourth of the visual range from the observer (Malm, 1979). Thus, in an initially clean atmosphere, a fine particle increment produces maximum contrast reduction for large objects 50 to 100 km away. A reduction in visual range of 5 percent would result in a reduction in contrast of .02 for those objects. Such a change may be just perceptible. The contrast detail (texture, small objects) and coloration of closer objects in contrast may, however, be affected to a greater degree (Henry, 1979, Malm, 1979).

The perceived color of objects and sky is also changed by the addition of aerosols. Because of the difficulties and uncertainties in specifying perceived color, only a qualitative description is possible. In general, the apparent color of any target fades toward that of the horizon sky with increasing distances from the observer. Without particles, scattered air light is blue, and dark objects appear increasingly blue with distance. The

addition of small amounts (1 to 5 μg/m^3) of fine particles throughout the viewing distance tends to whiten the horizon sky making distant dark objects and the intervening air light (haze) appear more grey. According to Charlson et al. (1978), even though the visual range may be decreased only slightly from the limit imposed by Rayleigh scattering the change from blue to grey is an easily perceived discoloration. The apparent color of white objects is less sensitive to incremental aerosol loadings. As for contrast, incremental aerosol additions produce a much greater color shift in cleaner atmospheres (Malm, 1979).

Aerosol haze can also degrade the view of the night sky. Star brightness is diminished by light scattering and absorption. Perception of stars is also reduced by an increase in the brightness of the night sky caused by scattering of available light. In or near urban areas, night sky brightness is significantly increased by particle scattering of artificial light. The combination of extinction of starlight and increased sky brightness markedly decreases the number of stars visible in the night sky at fine particle concentrations of 10 to 30 μg/m^3 (Leonard et al., 1977).

Thus, the overall impact of aerosol haze is to reduce visual range and contrast, and change color. Visually the objects are "washed out" and the aesthetic value of the vista is degraded even though the distances are small relative to the visual range. Much of the scenic value of a vista can be lost when the visual range is reduced to a distance that is several times greatest line-of-sight range in the scene.

9.4.2.4 Particle Absorption--Particle absorption (b_{abs}) appears to be on the order of 10 percent of particle scattering (b_{scat}) in low-background areas such as Bryce Canyon (Weiss et al., 1978). Its contribution may rise to 50 percent of b_{ext} in urban areas, although values of 10 to 25 percent would be more typical (Weiss et al., 1978; Waggoner et al., 1980; Wolff et al., 1980).

The apparently large role of particulate absorption on visibility in urban areas has prompted much research on absorption in recent years. Weiss (1978) fractionated aerosol at many sites into coarse and fine portions (cut at 2.5 μm) and found that the fine particles accounted for 80 to 98 percent of absorption. He also determined the wavelength (color) dependence of b_{abs} for the samples and concluded that at all U.S. sites b_{abs} is only weakly dependent on wavelength.

The extinction per unit mass raio for absorbing aerosols is a figure of some importance because current estimates show it to be significantly higher than the extinction/mass ratio of scattering-only aerosols. Figure 9-8 shows the theoretical value for carbon particles to be higher than for any other considered species (Foxvog and Roessler, 1978). Laboratory studies by Roessler and Foxvog (1980) showed values of 9.8 m^2/g for acetylene smoke and 10.8 m^2/g for diesel exhaust; they also summarized results from other investigators on various aerosols which showed values of 6.1 to 9.5 m^2/g. In developing a spectrophone, Truex and Anderson (1979) measured a value of 17 m^2/g (at 0.417 μm) for aerosol from a propane-oxygen

flame. More recently, as methods for measuring elemental carbon have improved, Wolff et al. (1980) have performed atmospheric measurements of absorption/elemental carbon mass in Denver and found values of 12.7 m^2/g. While the amount of absorption per unit mass depends on chemical composition and particle size distribution (Waggoner et al., 1973; Bergstrom 1973), the pattern emerging from these empirical and theoretical studies is that absorbing particles probably have a more significant visibility impact than their mass would indicate.

9.4.2.5 Summary--The extinction of light in rural air is generally dominated by particle scattering, while absorption can rise to levels comparable to scattering in urban settings. On a regional scale, almost all of the particle scattering is contributed by fine particles. Extinction due to scattering is closely proportional to the fine-particle mass concentration, with extinction/ mass ratios in the range of 3-5 x 10^{-6} $m^{-1}/(\mu g/m^3)$.

9.4.3 Chemical Composition of Atmospheric Particles

Given the dominance of particles in degrading visibility, it is natural that their composition should be studied. Such knowledge permits estimation of the roles various sources play in visibility impairment, so that any anthropogenic sources of impairment can be controlled in a cost-effective manner to a level the public deems desirable. Before discussing the aerosol components currently believed to be of significance, it is important to consider a number of uncertainties in our measurements and deductions.

Visibility is not the simple topic it first seems to be. Rather, it is one of the most difficult, being determined by the sum of all atmospheric constituents, lighting conditions, and the observer. Needless to say, these factors are extremely variable. Though it is generally accepted that fine particles cause most visibility problems, the concentration and composition of these particles can vary considerably at different times and sites around the country. Furthermore, field studies which characterize the aerosol need to include diverse and sometimes elaborate instrumentation and techniques in order to measure all relevant para meters simultaneously. There is evidence of volatile aerosol (e.g., ammonium nitrate) which exists in the atmosphere and thus degrades visibility, but cannot always be retained by conventional filtration for subsequent analysis. Some fine particles (e.g., diesel exhaust) are distinctly non-spherical and defy theoretical attempts to model their optical influence, or even report a size distribution. Several fine mass componenets (e.g., ammonium nitrate and elemental carbon) have been either measured inaccurately or not at all until recently. A particularly difficult-to-handle fine mass component is water. Water degrades visibility only when in the liquid phase, but it is ubiquitous and causes particles of several common species to grow or shrink, which can affect visibility drastically. Thick hazes or fogs are often dismissed as caused solely by high humidity, whereas in some cases they may not have formed without the presence of anthropogenic nuclei.

A common mistake in assessing the compounds responsible for visibility impairment is to assume that a compound's contribution to mass is equal to its contribution to visibility

impairment. Its visibility contribution can be greater or less than its mass contribution, depending primarily on its size distribution and refractive index. While refractive index is known (at least approximately) for most fine mass constituents, it is difficult to determine the size distribution of some components (because of detection limits, artifact formation, or volatilization) with the requisite accuracy.

Fortunately, there are reasons to believe we can circumvent these uncertainties. Suitably accurate analytical methods are evolving for nitrate measurement. Carbon measurement techniques have been intercompared and applied to the atmosphere. Relatively constant scatter/fine mass ratios are being reported for a variety of sites (Waggoner, 1980). Extinction calculated from gross size distribution measurements is usually within a factor of two of measured values (Ensor, 1972; Patterson and Wagman, 1977). Regression analyses show consistent correlations between scattering or visibility and sulfate concentration (White and Roberts, 1977; Cass, 1979; Trijonis, 1978a,b).

Current knowledge indicates that fine aerosol is composed of varying amounts of sulfate, ammonium, and nitrate ions; elemental carbon and organic carbon compounds; water and smaller amounts of soil dust, lead compounds, and trace species. The following discussion separates the components, whereas in reality they may exist as internal mixtures (i.e., coexist within the same particle).

Sulfate occurs predominately in the fine mass (Stevens et al., 1978; Tanner et al., 1979; Lewis and Macias, 1979; Ellestad, 1980). Sulfate ion generally comprises 30 to 50 percent of the fine mass at a wide variety of sites (Stevens et al., 1978; Pierson et al., 1980; Stevens et al., 1980; Lewis and Macias, 1979; Ellestad, 1980). Sulfate occurs with cations of H_2, $(NH_4)H$, and $(NH_4)_2$ (Stevens, 1978; Pierson et al., 1980; Stevens et al., 1980; Tanner et al., 1979). Indirect measurements of sulfate by examining the scattering response of ambient aerosol to changes of relative humidity confirm the prevalence of H_2SO_4 and its ammonium salts (Weiss et al., 1977; Waggoner et al., 1980). Regression analyses by Cass (1979), White and Roberts (1977), Trijonis (1978a,b), Grojean et al. (1976), Leaderer et al. (1978), and Heisler et al. (1980) show significant correlations between sulfate concentrations and visibility or extinction.

Ammonium ion is typically found to account for 10 to 15 percent of the fine mass (Lewis and Macias, 1979; Patterson and Wagman, 1977). It often correlates well with sulfate levels (Tanner et al., 1979). Due to the possible reaction of ammonia with previously collected sulfuric acid particles, ammonium ion values may be higher than exist in the atmosphere.

It is currently impossible to make valid statements about ambient particulate nitrate concentrations due to recognized sampling problems (Appel et al., 1979; Spicer and Schumacher, 1977 and 1979). Simple filtration (even with non-alkaline, non-reactive, high-purity filters) may not give true values, due to the tendency of ammonium nitrate to seek equilibrium with ammonia and gaseous nitric acid during sampling and storage.

Concentrations of elemental and organic carbon have been reported by Wolff et al. (1980) for a variety of U.S. sites. Elemental carbon was found to range from 1.1 $\mu g/m^3$ at a remote site to 13.3 $\mu g/m^3$ in New York City, with about 80 percent in the fine fraction. Based on concurrent Denver measurements of b_{abs} by a modified integrating plate method, Wolff calculated an absorption/mass ratio of 12.7 m^2/g, indicating that elemental carbon may have four times as much visibility impact as its mass would indicate. Wolff further concludes that elemental carbon is the only significant light-absorbing specie. This conclusion is consistent with those of Pierson and Russell (1969), Rosen et al. (1980), and Weiss et al, (1978). Weiss aspirated various solvents and acids through collected aerosol. After finishing with aqua regia, he found that 80 percent of the mass was gone, but 90 percent of the absorption remained. He reasoned that elemental carbon was the likely specie. Determinations of organic carbon concentrations will not be further discussed because of uncertainties in their measurement from adsorption or volatilization. Improved techniques for organic particulate measurement are being developed.

As mentioned earlier, water affects visibility only when in the liquid phase. Unfortunately, no direct measure of liquid water's contribution is possible, due to its rapid phase change and the fact that typically only 1 to 100 ppm of all water in a given volume exists in the liquid phase. However, Waggoner et al. (1980) have developed a nephelometer with humidity control and have shown a substantial dependence of scattering on relative humidity at a number of sites (see Figure 9-13). Waggoner's method cycles the aerosol's humidity in a very short period, so the input aerosol can be assumed to have not changed in composition or concentration.

Inasmuch as sulfate is a prominent, ubiquitous, and hygroscopic specie of fine particles (Garland, 1969; Charlson et al., 1978; Waggoner et al., 1980), water undoubtedly has a significant role in visibility impairment at higher humidities. Tang et al. (1978) have performed theoretical and experimental studies of the growth of sulfate aerosols with humidity and found the molecular composition to be of considerable importance. For example, for ammonium sulfate/sulfuric acid ratios above 0.95, deliquescence occurs at 80 percent relative humidity, for ratios 0.75 to 0.95 at 69 percent, for ratios 0.5 to 0.75 at 39 percent, and for a ratio below 0.5 growth is not abrupt (deliquescent) but smooth (hygroscopic). Thus, to predict the light scattering behavior of a sulfate aerosol, one needs detailed knowledge of its molecular composition in-situ. Compounding the problem of predicting scattering-humidity behavior, the electromagnetic scattering efficiency function varies greatly in the size region where sulfates and other secondary particles exist. Thus a small error in pre-growth size distribution measurement may produce a significant error in the predicted scattering. A further compounding problem is that as humidity decreases salt aerosols exhibit hysteresis (Orr et al., 1958; Charlson, et al., 1978) and do not lose their water at the same humidity at which they gained it. It must be concluded that the role of water in visibility impairment can be significant and is difficult to predict.

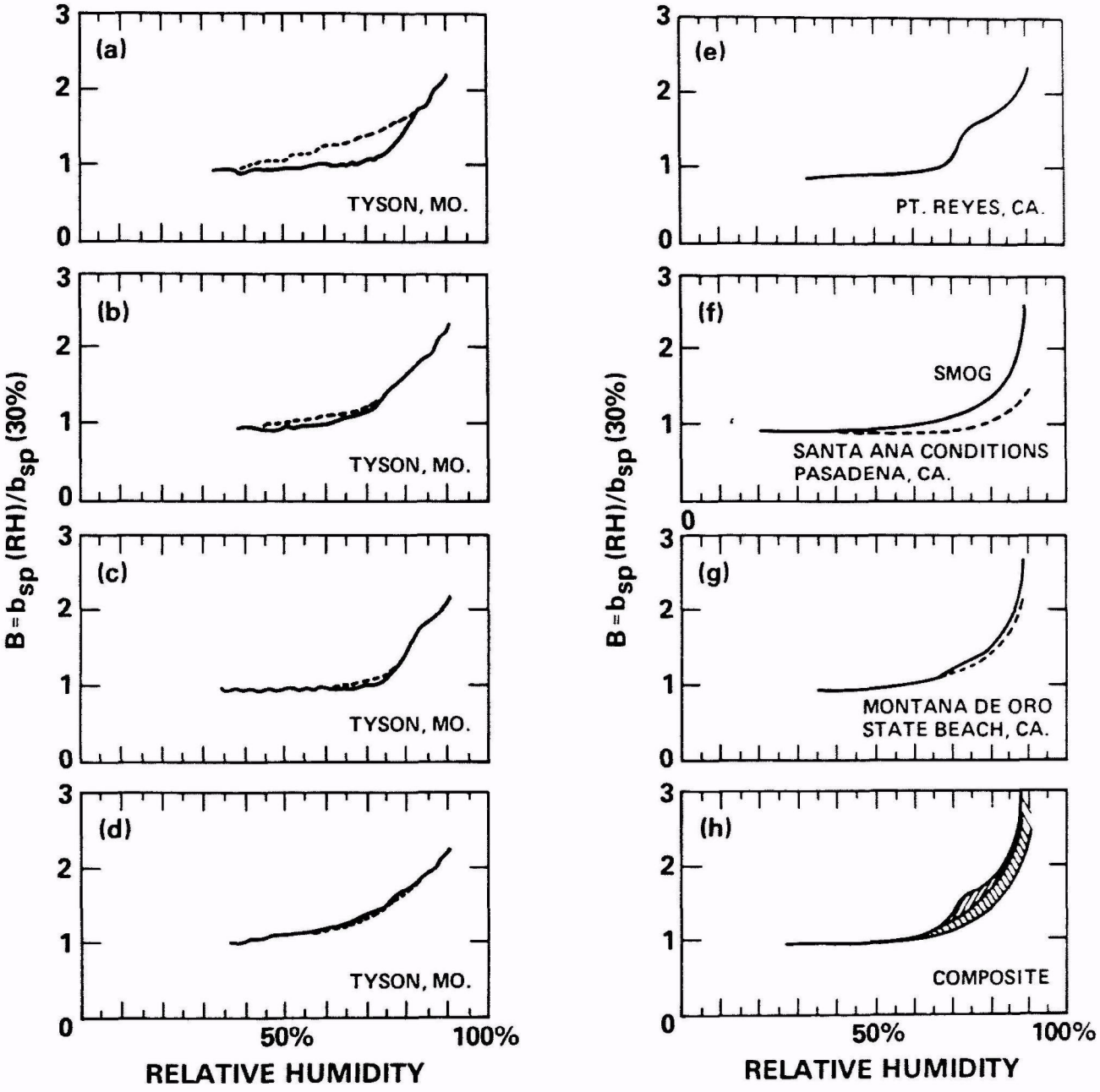

Figure 9-13. Humidograms for a number of sites show the increase in b_{sp} which can be expected at elevated humidities for specific sites or aerosol types (marine, Point Reyes, CA; sulfate, Tyson, MO) and the range observed for a variety of urban and rural sites (composite).

Source: Covert et al. (1980).

Minor contributions to fine mass are made by soil-related elements, lead compounds (especially in urban areas), and trace species (Stevens et al., 1978).

9.4.3.1 Summary--Current knowledge indicates that fine aerosol is composed of varying amounts of sulfate, ammonium, and nitrate ions, elemental carbon, organic carbon compounds, water, and smaller amounts of soil dust, lead compounds, and trace species. Sulfate often predominates the fine mass and visibility impairment, while elemental carbon is often the primary visibility impairing specie in urban areas. Significant variations can occur at different times and sites. Our knowledge of the roles of several possibly important species is hindered by the lack of sufficient good data.

9.5 HISTORICAL PATTERNS OF VISIBILITY

Records of visual range (prevailing visibility) can be used to gain insight into the effects of changing emission patterns on visibility. As one example Marians and Trijonis (1979) have derived statistical relationships between light extinction (computed from visibility data) and historical emission trends. Yearly values of extinction from four Arizona airports were regressed against statewide emissions of smelter SO_x, nonsmelter SO_x, NO_x, and RHC (reactive hydrocarbons). Smelter SO_x was found to be the most significant variable. Particularly close relationships between Arizona smelter SO_x and visibility at Tucson and Phoenix are shown in Figure 9-14.

Table 9-2 summarizes the results of the correlation/regression analysis between yearly airport extinction (visibility) data and Arizona smelter SO_x emissions. The correlation coefficients and Student's t-statistics indicate significant statistical relationships at high confidence levels. The regression (extinction/emission) coefficients of 0.04 ± 0.005 $(10^4\ m)^{-1}$/(1000 tons per day of SO_x) are remarkably consistent from site to site and represent the change in yearly median extinction associated with a given change in SO_x emissions; that is, adding 1000 tons per day of SO_x tended to increase yearly median extinction by approximately $0.04\ (10^4\ m)^{-1}$.

Perhaps the best example of changed emission patterns is a strike that shut down the copper industry over a 9-month period in 1967-68. In the Southwest at this time, copper production accounted for over 90 percent of the SO_x emissions, less than 1 percent of the NO_x emissions, and less than 10 percent of the conventional particulate emissions (Marians and Trijonis, 1979), and should therefore have affected visibility primarily through its contribution to sulfate loadings Substantial decreases in sulfate occurred at five locations (Tucson, Phoenix, Maricopa County, White Pine, and Salt Lake City) within 12 to 70 miles of copper smelters as shown in Figure 9-15. More notably, sulfates dropped by about 60 percent at Grand Canyon and Mesa Verde; these remote sites are located 325 to 500 km from the main smelter area in southeast Arizona. Comparing measurement during the strike with those during the surrounding 4 or 6 years, Trijonis et al. (1978a) found a large decrease in Phoenix sulfate loadings, accompanied by a substantial improvement in visibility (Figure 9-16).

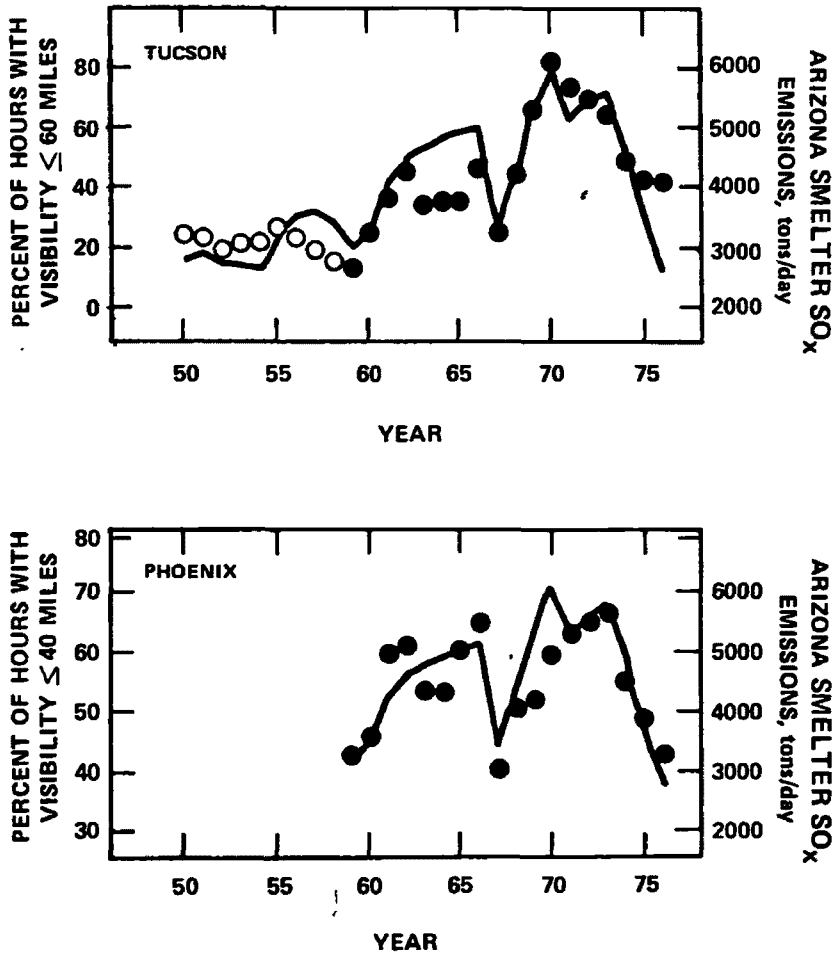

Figure 9-14. Historical trends in hours of reduced visibility at Phoenix and Tucson are compared with trends in SO_x emissions from Arizona copper smelters. Data points represent yearly percent of hours with reduced visibility. The Tucson observation site moved in 1958; although this move did not produce a statistically significant change in reported visibilities, open dots are used to distinguish data prior to 1958. Lines represent yearly SO_x emissions from Arizona copper smelters.

Source: Marians and Trijonis (1979).

TABLE 9-2. CORRELATION/REGRESSION ANALYSIS BETWEEN AIRPORT EXTINCTION AND COPPER SMELTER SO_x EMISSIONS

Data set	Correlation coefficient	Regression coefficient extinction/emissions, $(10^4\ m)^{-1}/(1000\ TPD)$	t-statistic ($t \cong 1.7$ for 95% confidence) ($t \cong 2.5$ for 99% confidence)
Tucson (1950-75)	0.91	0.035	11.1
Tucson (1959-75)	0.88	0.038	7.2
Phoenix (1959-75)	0.81	0.041	5.4
Winslow (1948-73)	0.68	0.047	4.5
Prescott (1948-75)	0.70	0.031	5.0
Prescott (1948-69)	0.70	0.039	4.4

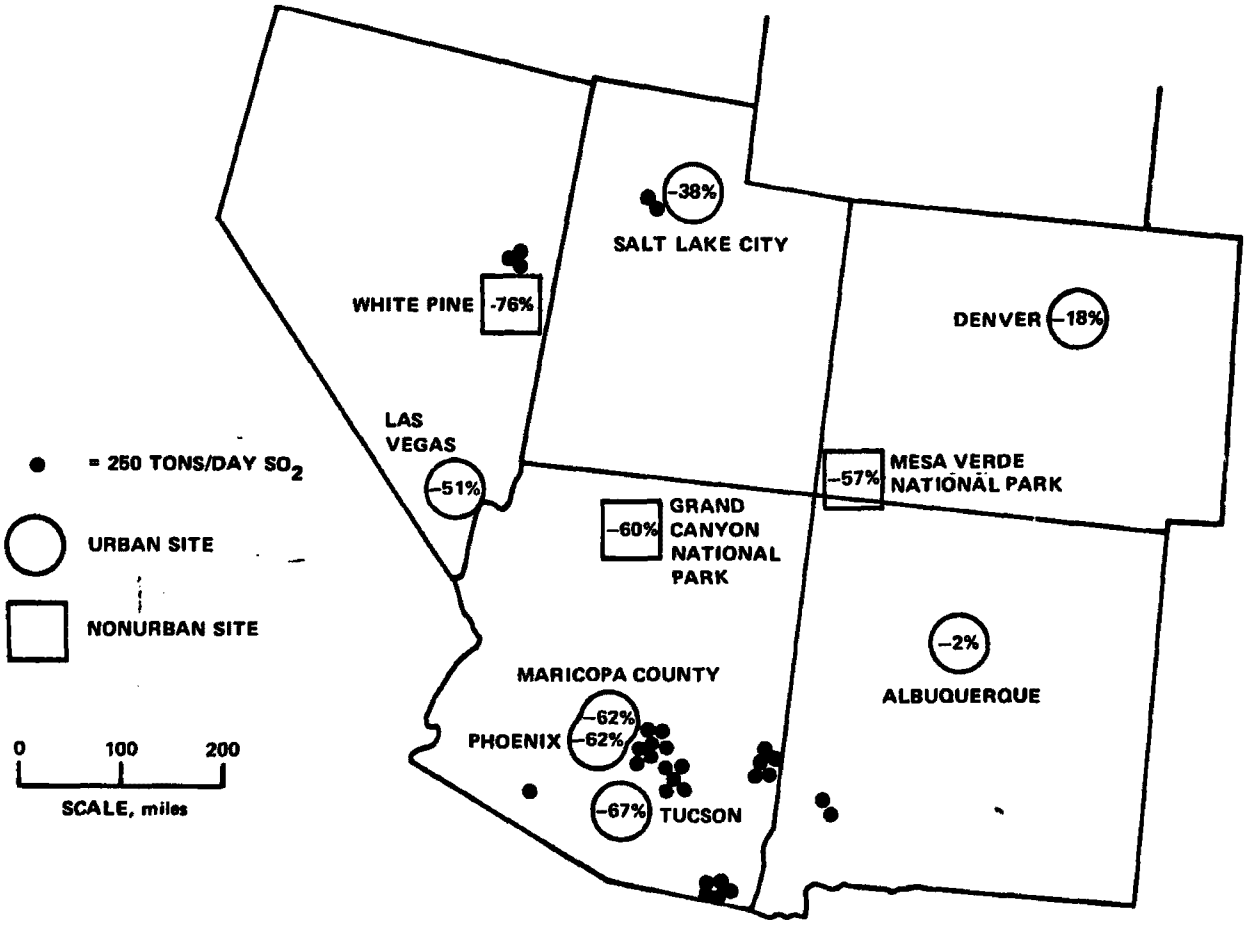

Figure 9-15. Seasonally adjusted changes in sulfate during the copper strike are compared with the geographical distribution of smelter SO_x emissions.

Source: Trijonis and Yuan (1978a).

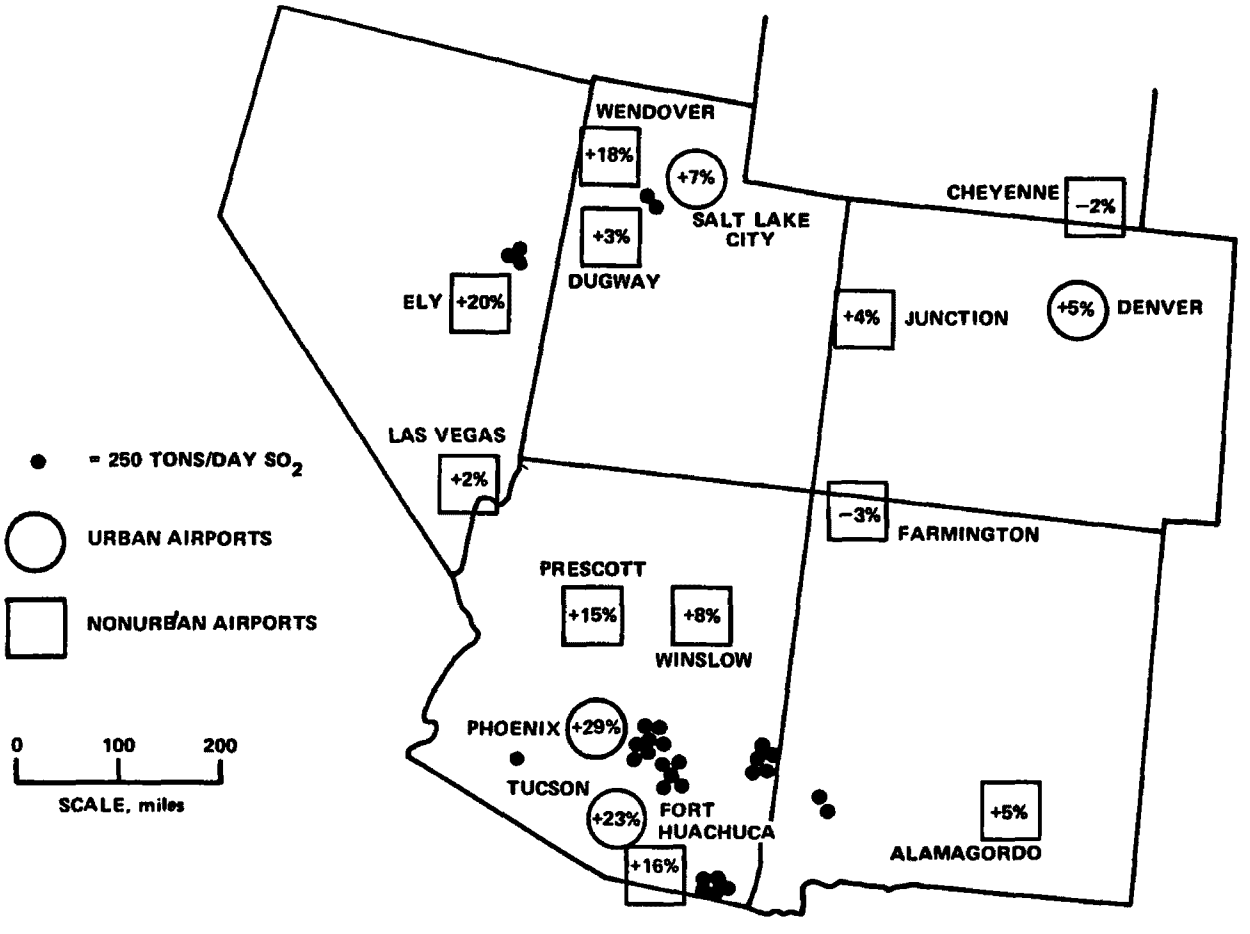

Figure 9-16. Seasonally adjusted percent changes in visibility during the copper strike are compared with the geographical distribution of smelter SO_x emissions.

Source: Trijonis and Yuan (1978a).

Visibility improved at almost all locations during the strike, with the largest improvements occurring near and downwind (north) of the copper smelters in southeast Arizona and near the copper smelters in Nevada and Utah. The nine locations showing statistically significant improvements are all within 150 miles of a copper smelter. Attributing the improvement in visibility entirely to the drop in sulfate levels yields an estimated extinction efficiency of 3.9 x 10^{-6} $m^{-1}/(\mu g/m^3)$, in agreement with data in Table 9-1.

Altshuller (1973) has noted an increase over the past decade in sulfate concentration at nonurban sites in the Eastern United States, which is not inconsistent with the decreasing trend in nonurban site median visibilities noted by Trijonis et al. (1978b). Unfortunately, the historical record of sulfate concentrations extends back only to the mid-1960's. Within the Eastern United States, over 90 percent of the SO_x emissions are associated with the combustion of coal and oil. One apparent conclusion is that visibility reduction is currently due in large part to increases in sulfate aerosols, which are formed primarily from coal combustion-related SO_2 emissions; examination of the trends and changing spatial distributions of coal use should be comparable with the change in the light extinction coefficient.

Air pollutants emitted over the Eastern United States result mainly from the combustion of fossil fuels--coal, oil products, and gas. The great spatial and seasonal variability of haziness (inverse of visibility) prompted Husar et al. (1979) to examine the patterns of coal consumption in the Eastern United States over the past few decades. For comparison with coal consumption estimates, visibility data are expressed in terms of a light extinction coefficient, b_{ext}, via the Koschmieder formula: $b_{ext} = 3.92/V$.

Figure 9-17 illustrates the striking similarity between summertime average haziness and coal use within the Eastern United States over the past three decades.

Further support for the relationship between coal consumption and haziness is given in Figure 9-18.

As shown in Figure 9-18, in 1951 the haziness was most pronounced in the wintertime, when the coal consumption was the highest. By 1974, there was a shift toward a summer peak, coincident with the increasing summer use of coal. Such coincident behavior alone cannot establish cause-effect relationships. It is nevertheless instructive to examine the more detailed spatial and temporal patterns of coal use and haziness (specifically, extinction).

Since 1940, the trend in coal consumption has been more pronounced in the summer than in the winter (Figure 9-18; U.S. Bureau of Mines, 1933-74); since 1960 summer coal use has grown by about 5.8 percent per year compared with 2.8 percent per year for winter coal demand. The monthly coal combustion peaked in the winter in the early 1950's, but the seasonal pattern had shifted to a summer peak by 1974 (Figure 9-19).

The corresponding regional trends of haziness in the Eastern United States (Figure 9-20; Husar et al., 1979) exhibit changes similar to those of coal combustion.

In the Ohio River Valley region, the winter (quarter 1) average extinction (b_{ext}, km^{-1}) decreased slightly, whereas the spring (quarter 2) average increased. The summer (quarter 3)

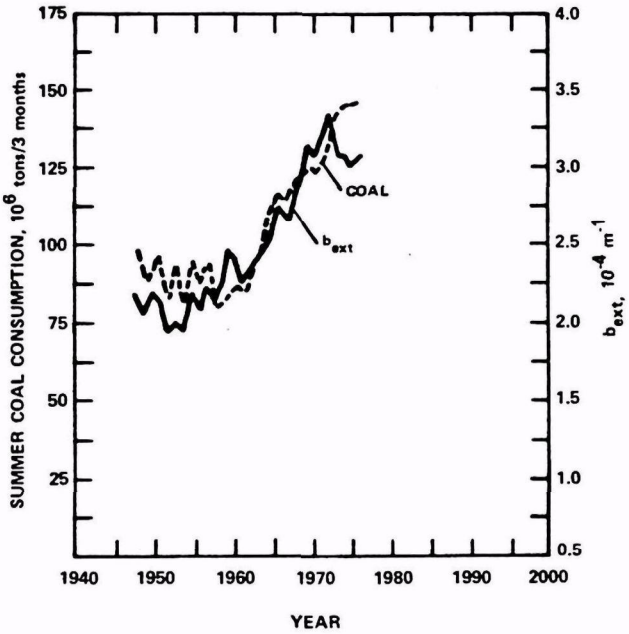

Figure 9-17. Compared here are summer trends of U.S. coal consumption and Eastern United States extinction coefficient.

Source: Adapted from Husar and Patterson (1980).

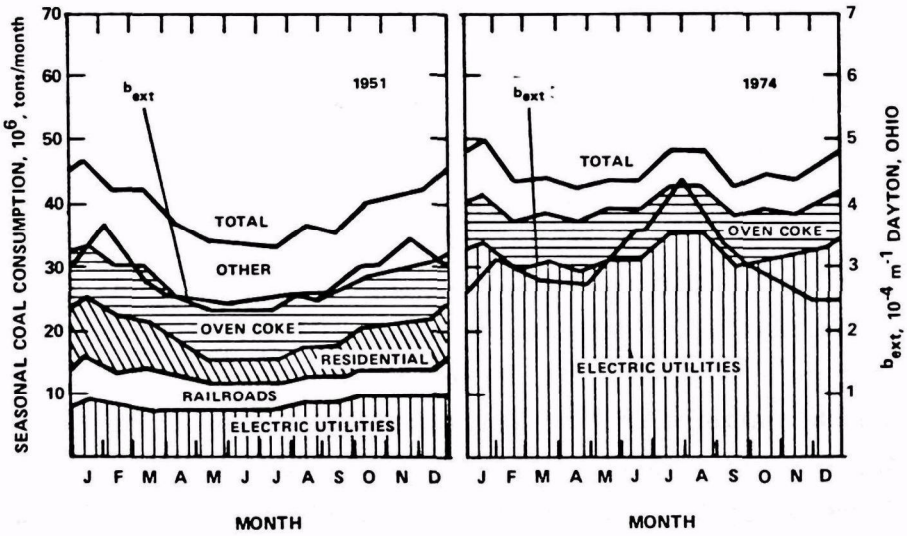

Figure 9-18. In the 1950's the seasonal coal consumption peaked in the winter primarily because of increased residential and railroad use. By 1974, the seasonal pattern of coal usage was determined by the winter and summer peak of utility coal usage. The shift away from a winter peak toward a summer peak in coal consumption is consistent with a shift in extinction coefficient from a winter peak to a summer peak in Dayton, OH, for 1948-52.

Source: U.S. Bureau of Mines Yearbooks 1933-74.

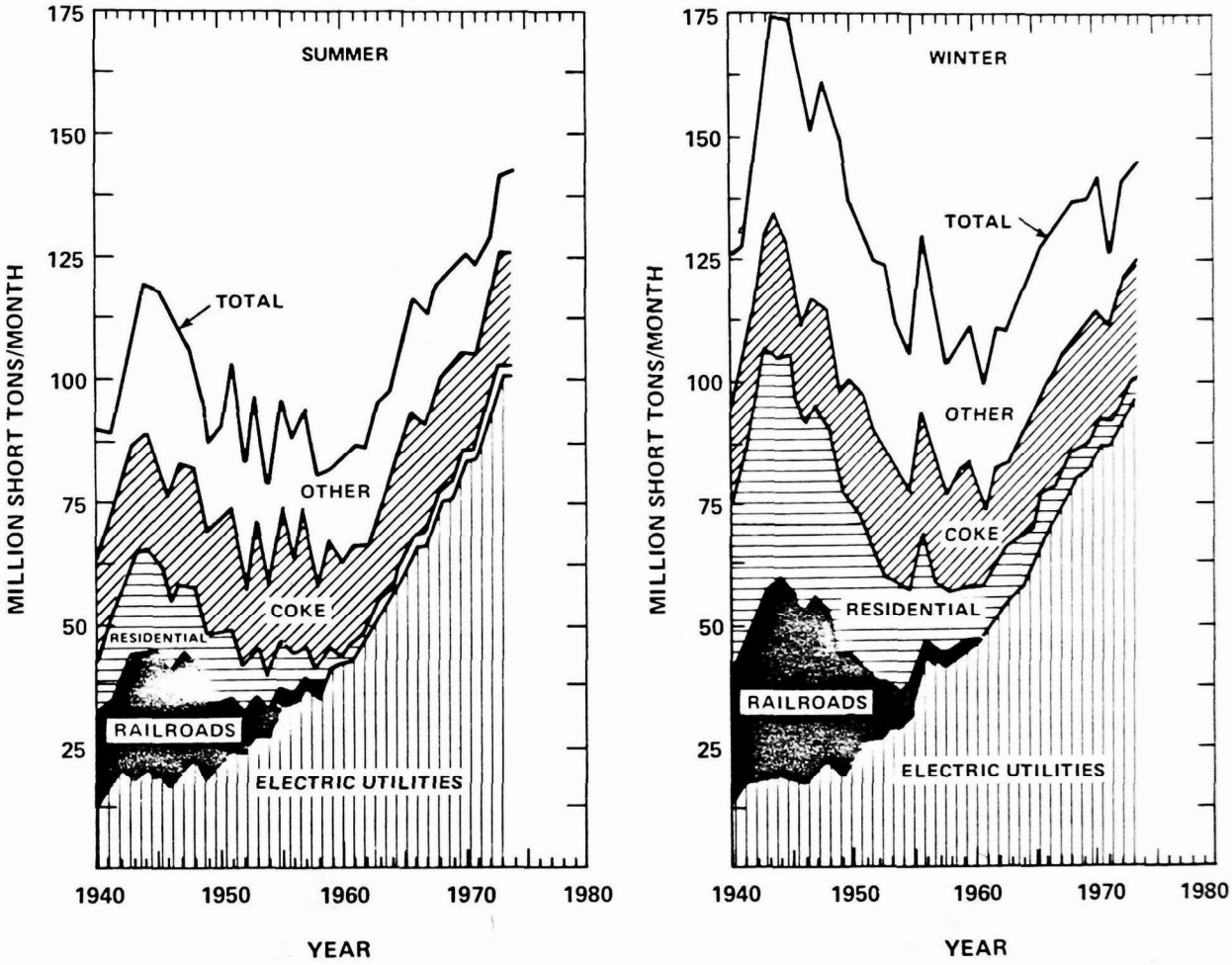

Figure 9-19. In 1974, the U.S. winter coal consumption was well below, while the summer consumption was above, the 1943 peak. Since 1960 the average growth rate of summer consumption was 5.8 percent per year, while the winter consumption increased at only 2.8 percent per year.

Source: U.S. Bureau of Mines, Minerals Yearbooks 1933-1974.

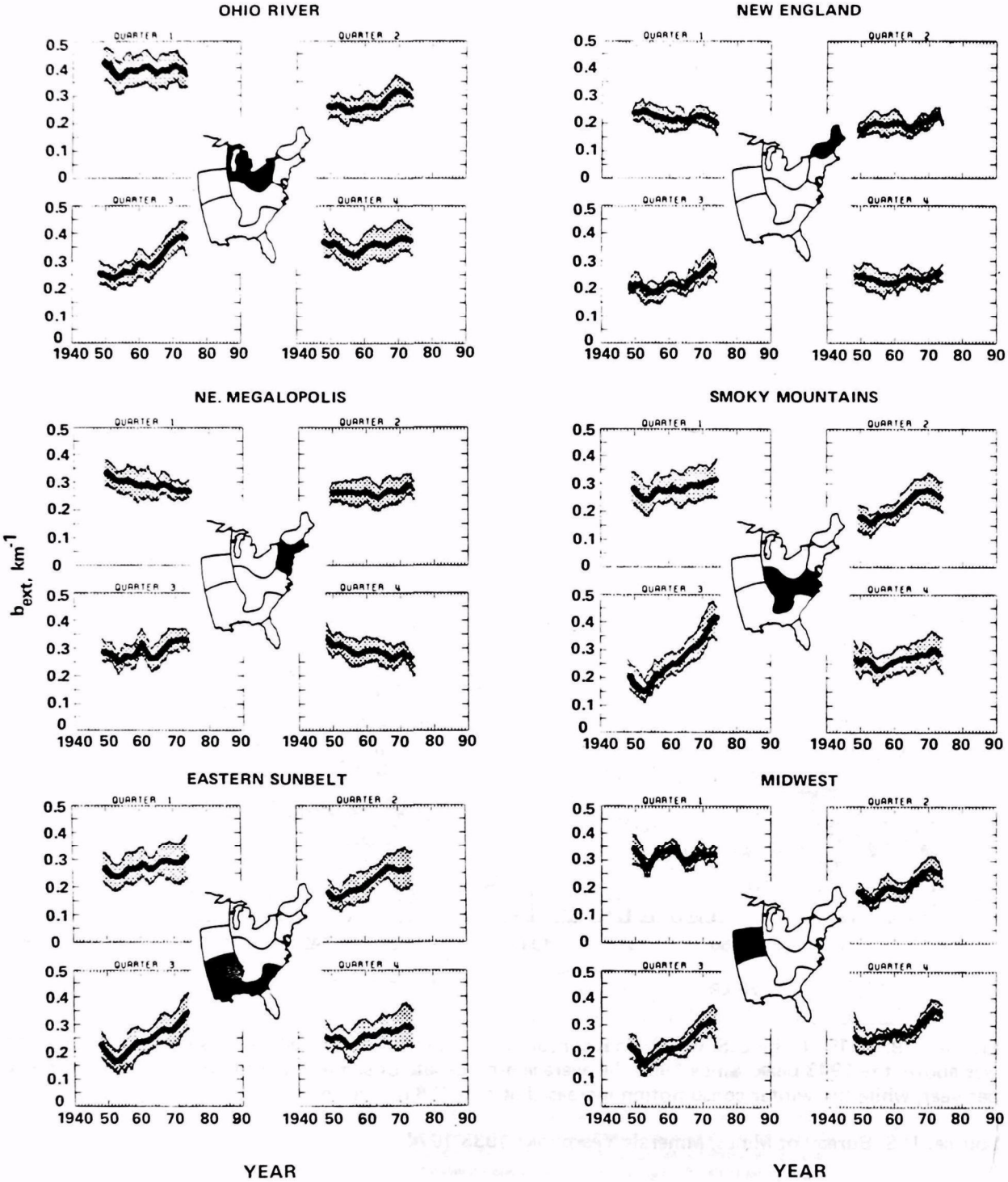

Figure 9-20. Trends in the light extinction coefficient (b_{ext}) in the Eastern United States are shown by region and by quarters; 1 (winter), 2 (spring), 3 (summer), 4 (fall).

Source: Husar et al. (1979).

extinction increased from roughly 0.25 in the 1950's (a visibility of 10 miles) to about 0.4 in the 1970's (a visibility of less than 6 miles). Fall (quarter 4) extinction remained essentially unchanged. The summer average increased from about 2 to 3, corresponding to a reduction in visibility from 12 to 8 miles (20 to 13 km). The Northeast megalopolis region shows a general decline in haziness during quarters 1 and 4, whereas quarters 2 and 3 display a slight increase from b = 2.7 (9 miles, 15 km) to 3 (8 miles, 13 km) x $10^{-4}m^{-1}$. The Smoky Mountain region displays a strong increase in the average summer quarter extinction coefficient from about 1.6 to 4, corresponding to visibility deterioration from 15 to 6 miles. Smaller but still pronounced increases are noted for quarters 2 and 4. Evidently the Smoky Mountains have become appreciably "smokier" over the past 20 summers. The Eastern Sunbelt region has an increased haziness for all quarters, most pronounced being the summer quarter, with an increased from 2 (12 miles) to 3.5 (7 miles). In the Midwest, extinction during the first quarter fluctuated slightly with no discernible trend. The spring and fall quarters have increased appreciably, but summer values have nearly doubled, from 1.5 to 3 (16 to 8 miles).

The spatial shifts of Eastern United States haziness are displayed in greater detail in Figure 9-21 (Husar et al., 1979).

9.5.1 Natural Versus Manmade Causes

Vision in the natural, unpolluted atmosphere is restricted by blue sky scattering, (air molecule light scattering is often termed Rayleigh scattering) by curvature of the earth's surface, and by suspended liquid or solid natural aerosols. Important sources of natural aerosols include water (fog, rain, snow), wind-blown dust, forest fires, volcanos, sea spray, vegetative emissions, and decomposition processes. The particle free atmosphere scatters light and limits visual range to about 200 miles at sea level.

Dark objects, such as distant mountains, when viewed in daytime through a particle-free atmosphere, appear bluish because blue light is scattered preferentially into the line of sight. Bright snow-covered mountain tops or clouds on the horizon can appear yellow to pink because the atmosphere scatters more of the blue light from bright "targets" out of the line of sight leaving the longer wavelength colors. The actual visual range in the particle-free atmosphere is also limited by the earth's curvature. Thus, Rayleigh scattering is seldom the limiting factor in the detection of the most distant objects, i.e., the visual range. Rayleigh scattering is, however, important in reduction of visual texture and in bluish coloration of distant dark visual targets. Moreover, air scattering is solely responsible for the blue color of the non-horizon sky.

Fog is a naturally occurring phenomenon which can reduce the visual range to nearly zero. It is characterized by high liquid water content, typically over 1000 $\mu g/m^3$, dispersed in droplets with a mean diameter of several micrometers or more. In "natural" fogs all colors are scattered and absorbed about equally, so the atmosphere appears white (Husar, et al., 1979).

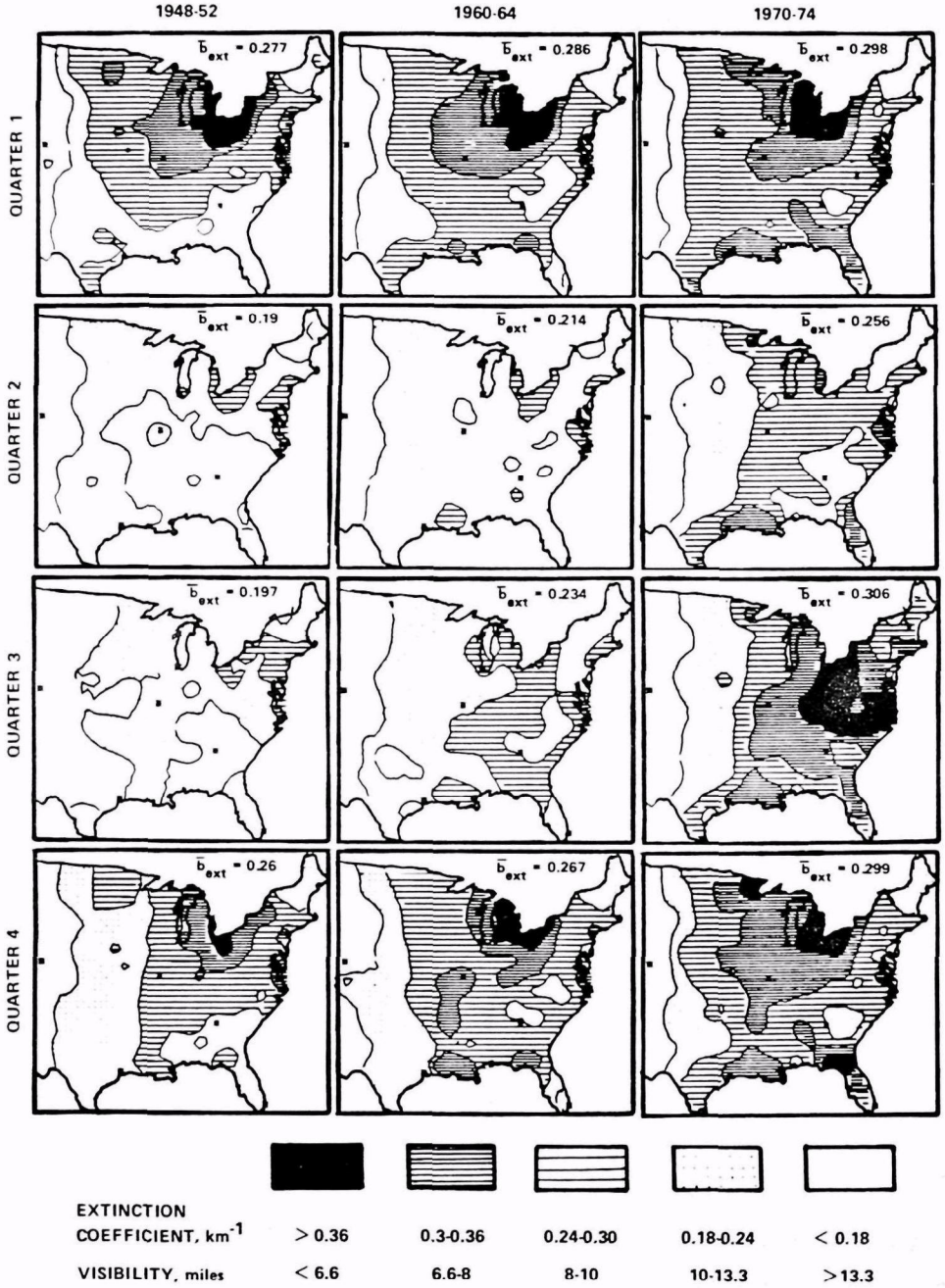

Figure 9-21. The spatial distribution of 5-year average extinction coefficients shows the substantial increases of third-quarter extinction coefficients in the Carolinas, Ohio River Valley, and Tennessee-Kentucky area. In the summers of 1948-52, a 1000-km size multistate region centered around Atlanta, GA, had visibility greater than 15 miles; visibility has declined to less than 8 miles by the 1970's. The spatial trend of winter (first quarter) visibility shows improvements in the Northeast megalopolis region and some worsening in the Sunbelt region. Both spring and fall quarters exhibit moderate but detectable increases over the entire eastern United States.

Source: Husar et al. (1979).

The historical frequency of occurrence of fogs in the continental United States reveals considerable geographic variability (Figure 9-22). Coastal areas experience the highest frequency. Most inland portions of the United States west of the Applachians can expect fewer than 20 days of fog per year, with less than five days of fog annually in the arid West.

With the exception of coastal and mountainous regions, fogs are rare during the summer months. Fogs tend to be localized events of, at most, a few hours duration, commonly during the early morning hours. On an hourly basis, fogs exist less than one percent of the time (Conway, 1963). Thus, the overall contribution of fog to the degradation of visual air quality is small, and it is an insignificant cause of reduced visibility during the daylight hours.

Thunderstorms, other rainfall, and snow can also reduce visibility. East of Nevada, most of the U.S. experiences from 30 to 50 days each year with thunderstorm activity. Such storms are most common on summer afternoons. Since thunderstorms are usually intense but brief, they also contribute to visibility reduction less than one percent of the time on an annual basis.

Snow is a major natural impediment to visibility. It is an important factor in many regions of the North and in some mountainous areas, where blowing snow occurs from 1 to 12 percent of winter hours (Conway, 1963). During the winter months snowstorms may account for most of the hours of reduced visibility, and certainly may dominate the epidoses of extremely low visibility in winter months.

The natural contribution of fog, thunderstorms, snow, and other forms of precipitation can thus cause severe degradation of visual air quality. With few exceptions, however, these intense but infrequent events do not dominate the average visual range within the continental U.S.; typically only a small percentage of the hours involve storms or fog.

In the arid West the contribution of wind-blown dust to degradation of visual air quality is an important problem. Because human activities which disturb natural soil surfaces add significantly to wind-blown dust, dust storms are only partially natural.

The suspension of particles from the surface is determined by cohesiveness of the particles to the underlying material, the force of the surface wind, and the topography of the surface layer. The ideal situation leading to suspension of surface material is a dry, crumpling or disturbed crust in flat terrain without vegetation. Agitation of such surfaces by strong winds and turbulence can transform a pristine arid atmosphere into a dust storm with severely reduced visibility. Suspended crustal material in a dust storm usually consists of coarse solid particles with volume mean diameters of tens of micrometers (μm) or more. Patterson et al. (1976) found that the optically important fugitive dust particles include those up to 40 μm in diameter. Orgill and Sehmel (1976) have analyzed the frequency of occurrence of dust storms in the continental United States in great detail, based on National Weather Service observations of wind-blown dust and sand associated with visibility of seven miles or less. The peak hours for dust are noon to eight p.m., during the period of maximum

Figure 9-22. Average annual number of days with occurrence of dense fog. Coastal and mountainous regions are most susceptible to fog.

Source: Conway (1963).

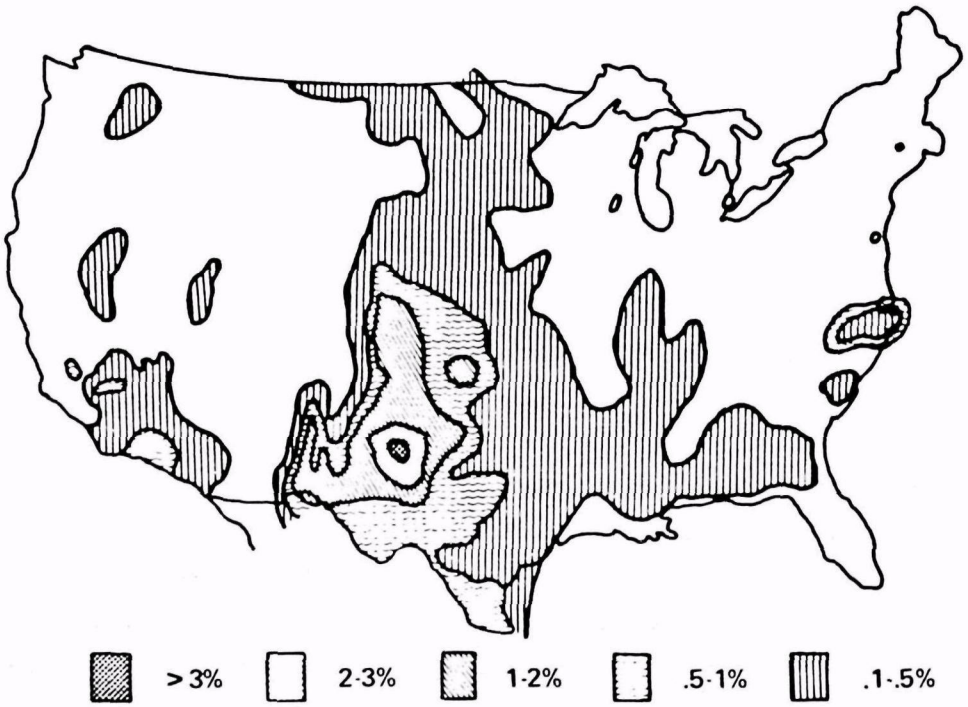

Figure 9-23. Annual percent frequency of occurrence of wind-blown dust when prevailing visibility was 7 miles or less, 1940-1970. Dust is a visibility problem in the Southern Great Plains and Western desert regions.

Source: Adapted from Orgill and Sehmel (1976).

thermal turbulence. Forested, coastal and mountainous regions have few, if any, episodes. The Pacific coast has high (>0.1 percent) incidence of dust only in the San Joaquin Valley and the Los Angeles Basin. Western desert areas in Eastern Washington, Western Nevada, Utah, New Mexico and Arizona are also prone to dust. The highest dust frequency is in the Southern Great Plains, where wind-blown dust is a serious problem up to 3 percent of the time (Figure 9-23).

9.5.2 Summary--The impact of sulfates in reducing visual air quality in individual plumes and on the regional scale of 1000 km is no longer a matter of dispute. Considerable evidence from chemical mass balance methods indicates that sulfates, which make up approximately 50 percent of the fine-aerosol mass, contribute considerably more to visibility degradation than do other chemical species. Finally, the 30-year record of the spatial and temporal trends of coal combustion and visibility suggests that the increasing emissions of SO_x since the 1950's have been associated with similar increases in haziness. This association is not as well defined as that for sulfate concentrations and visibly decreases.

9.6 SOLAR RADIATION

Incoming solar radiation is composed of the direct beam and the diffuse skylight arising from the light-scattering atmosphere (Figure 9-24; Gates, 1966). The relative contribution of the skylight is least at noon and greatest at sunrise and sunset. At sea level, and for a clean atmosphere, skylight contributes at least 10 percent of the total radiation.

Aerosol layers in the atmosphere scatter and absorb solar radiation (Figure 9-25). Some of the scattered radiation is directed upwards and lost to space; some is directed downwards to the earth's surface. Most of the solar radiation eventually reaches the surface, but its spectral and directional composition, that is, the "quality" of the solar radiation, may be changed by atmospheric haze (Weiss et al., 1978). A small fraction of the scattered radiation may also be lost back to space, in which case the amount of energy reaching the surface is reduced, contributing to the cooling at the earth's surface. A fraction of the radiation may also be absorbed by aerosols, further reducing the amount of radiation reaching the surface but at the same time heating the aerosol layer itself from the earth's surface.

It should be noted that because aerosols are not uniformly distributed in the atmosphere, their effects are spatially nonhomogeneous. First, the horizontal spatial scale encompassing aerosol source, transport, and removal in the lower troposphere is variable but often about 1000 km. The vertical spatial scale of noninfluenced aerosols is also quite variable, but often the particles are concentrated in a layer from 500 to 2000 m deep at the earth's surface. Hence, the aerosol effects should be concentrated in the lowest layers of the atmosphere, especially in industrial regions.

Global-scale effects might also occur. If the effects in industrial regions are strong enough, then the heat balance of the entire earth could be influenced. On the other hand, effects from long-lived aerosol, for example, in the stratosphere, might lead to direct physical effects on a global scale.

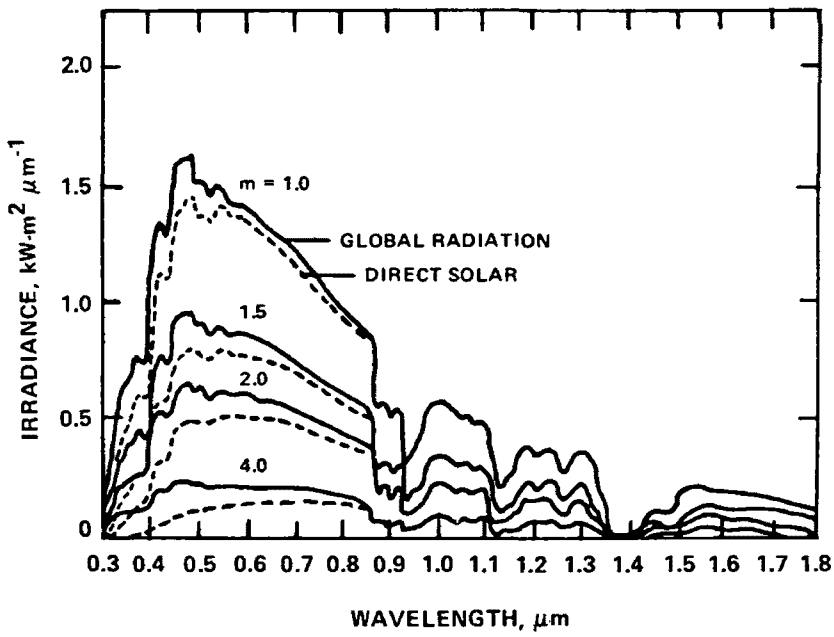

Figure 9-24. Solar radiation intensity spectrum at sea level in cloudless sky peaks in the visible window, 0.4-0.7 μm wavelength range, shows that in clean remote locations, direct solar radiation contributes 90 percent and the skylight 10 percent of the incident radiation on a horizontal surface. The airmass, m, is a measure of the amount of air the direct solar beam has to pass through.

Source: Gates (1966).

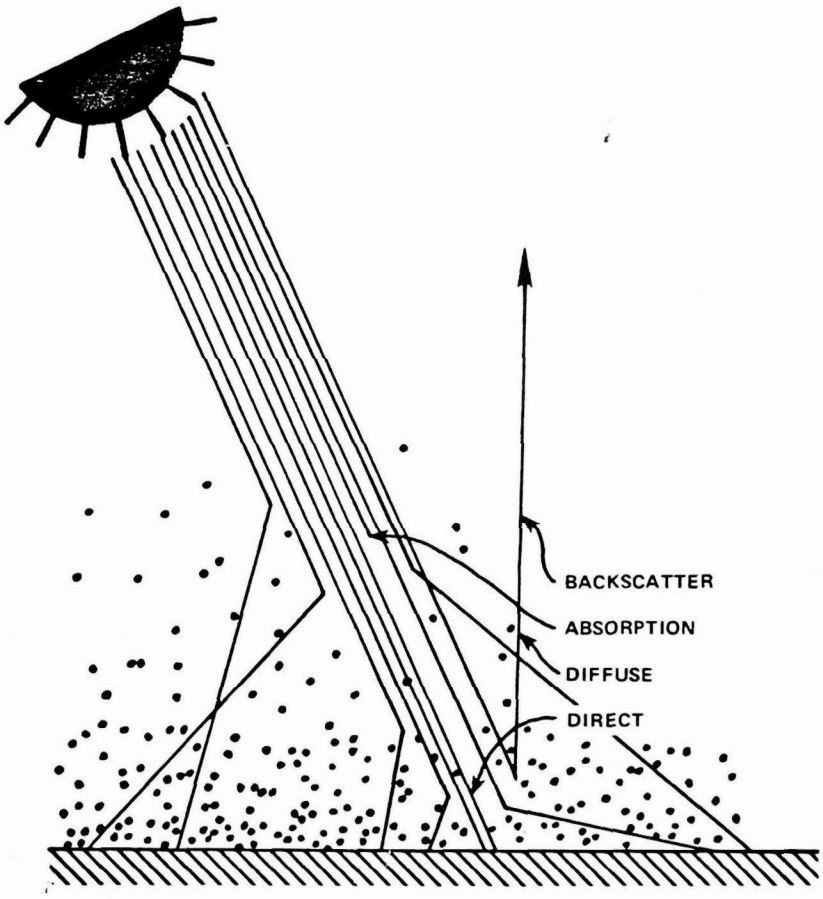

Figure 9-25. Extinction of direct solar radiation by aerosols is depicted.

9.6.1 Spectral and Directional Quality of Solar Radiation

The spectral quality of solar radiation on a clear day and on a hazy day in Texas is shown in Figure 9-26 (McCree and Keener, 1974). On the hazy day, the direct solar radiation is reduced to about one-half of that on a clear day, but most of the energy has reappeared as diffuse skylight. The net effect is that there is an overall loss of up to about 10 to 20 percent of the radiation reaching the surface.

If we take the typical backscattered fraction for haze aerosols to be 10 percent of scattering, and the absorption to be also about 10 percent, as suggested by the data of Weiss (1978), then we can estimate the amount of energy lost from the surface, the amount lost to space, and the amount absorbed by the atmosphere. On a day with half of the direct beam transmitted, we conclude that 10 percent of the other half, or 5 percent, is lost to space, and the other 5 percent results in atmospheric heating. Together, these phenomena lead to a loss of 10 percent of the radiation. Although it is not possible to calculate accurately the influence this loss might have on surface temperature, rate of thawing of frozen ground, growing season, or other climatological measures, it is highly probable that this loss cools the ground and heats the hazy lower layers of the atmosphere. In turn, if this occurs, it must increase atmospheric stability, decrease convective mixing, and therefore increase the rate at which pollutants accumulate.

No detailed and routine measurements of the quality of solar radiation are available for the United States. However, the total solar energy reaching the surface is monitored routinely at many meteorological observation sites in the United States and worldwide. Unfortunately, the large variability of such data does not allow manmade aerosol effects to be distinguished from other natural causes.

A data base that gives some information on the quality of solar radiation is the U.S. turbidity network operated at about 40 stations in the country since 1961 (Flowers et al., 1969). If there are no clouds between the observer and the sun, the intensity of direct solar radiation for a given solar elevation depends on the variable amount of dust, haze, and water vapor in the atmosphere. The extinction produced by these constituents is called "atmospheric turbidity." The seasonal pattern of atmospheric turbidity in the United States at 29 sites for 1961-66 is shown in Figure 9-27 (Flowers et al., 1969). At all sites, the highest turbidity occurs in the summertime and the lowest occurs in the winter, which is consistent with the haziness pattern obtained from visibility observations (Section 9.4.2). However, the turbidity of the atmosphere in the United States has a strong spatial dependence. In the Southwestern States with an annual turbidity coefficient of about 0.06, the incoming direct solar radiation is attenuated by only 13 percent (mostly scattered) compared with Midwestern State values of about 20 percent. The highest turbidity coefficients were observed in the Eastern United States, where summer values of 0.2 and winter values of 0.1 were typical. This means that in the summertime about 35 percent of the direct solar beam is diverted to

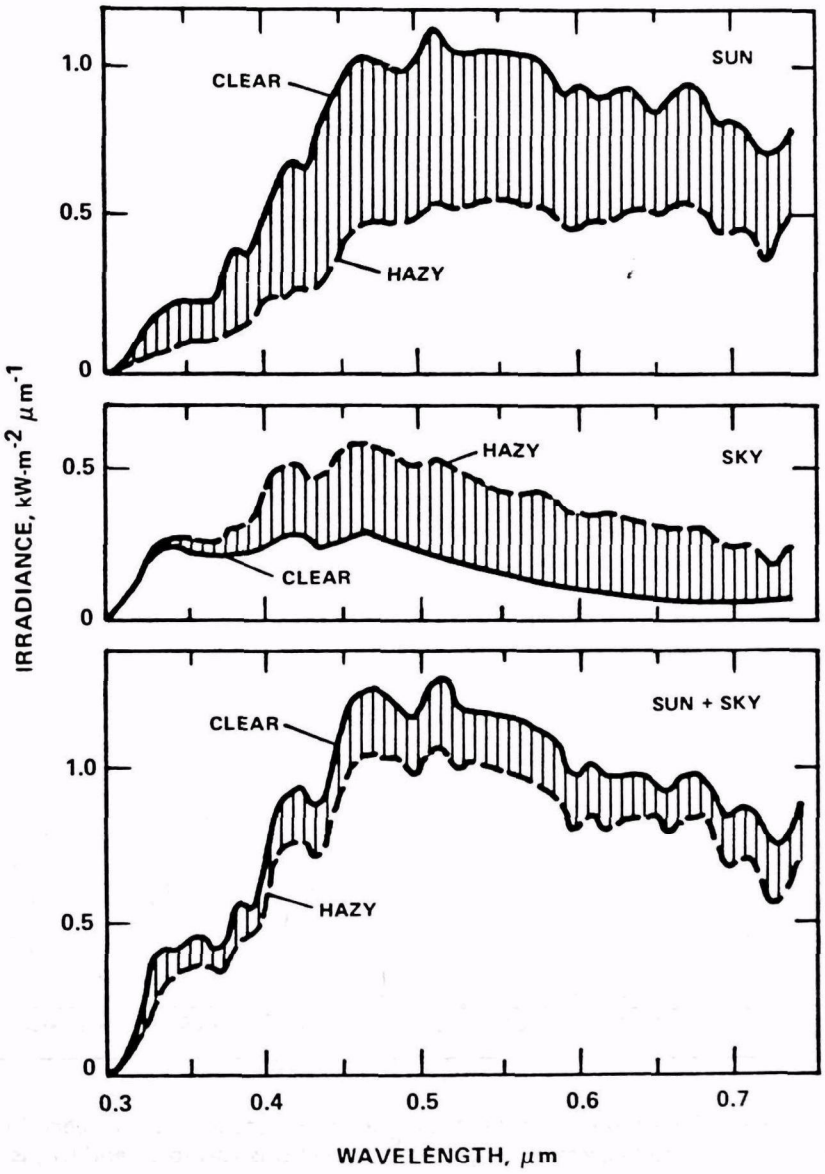

Figure 9-26. On a cloudless but hazy day in Texas, the direct solar radiation intensity was measured to be half that on a clean day, but most of the lost direct radiation has reappeared as skylight. However, there is about 20 percent of the solar radiation missing on the hazy day, some absorbed, and some backscattered to space.

Source: McCree and Keener (1974).

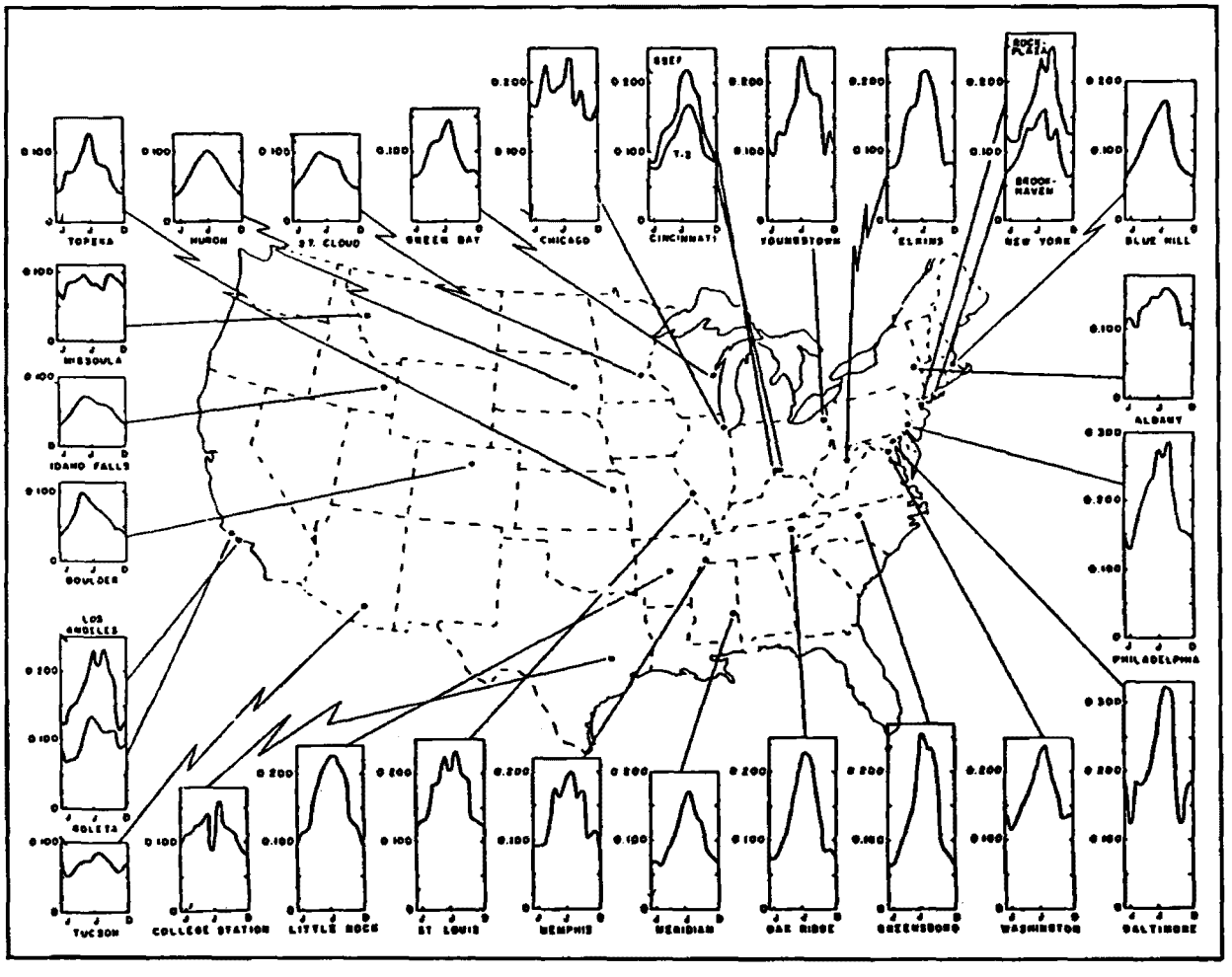

Figure 9-27. To interpret these 1961-1966 monthly average turbidity data in terms of aersol effects on transmission of direct sunlight, use the expression $I/I_o = 10^{-B}$, where B is turbidity and I/I_o is the fraction transmitted.

Source: Flowers et al. (1969).

skylight, backscattered to space, or absorbed. This means that about 3.5 to 7 percent is backscattered to space and another 3.5 to 7 percent is absorbed into the atmosphere.

Since the first report of Flowers et al. (1969), the turbidity data have been reported yearly by the World Meteorological Organization (WMO, 1977). Comparison of the seasonal turbidity pattern for 1961-66 and 1972-75 is shown in Figure 9-28. Since the mid-1960's there has been a further increase in Eastern U.S. turbidity, particularly in the summer season. Currently the summer average turbidity in the region including Memphis, TN, Oak Ridge, TN, Greensboro, NC, and Baltimore, MD, is about 0.3. This corresponds to a 50 percent attenuation of the direct solar beam on an average summer day. During hazy episodes, turbidity coefficients of 0.6 to 1.0 are often reported, resulting in a condition in which 75 to 90 percent of the solar radiation is removed from the direct beam, 7.5 to 18 percent is lost to space, and 7.5 to 18 percent is lost as atmospheric heating. One of the consequences of such hazy atmosphere is the disappearance of shadow contrasts. It is strongly suspected but has not yet been proved that there are effects on agricultural productivity.

The spatial distribution and trends of regional-scale turbidity in the Eastern United States are consistent with the observed pattern of haziness obtained through visibility observations. Both the turbidity and visibility reduction by haze in the Eastern United States can be attributed primarily to manmade fine particles (Section 9.4.3). Bolin and Charlson (1976) suggest that many of these radiative effects are due to sulfates and conclude that the magnitude of effects is comparable to that summarized here.

9.6.2 Total Solar Radiation: Local to Regional Scale

Changes in the total radiant energy have been observed within urban areas. Early measurements in central city locations, primarily in Europe, showed levels typically 10 to 20 percent below surrounding rural areas. Robinson (1962) discussed some observations made in London and in Vienna. In London the deficit was considerably reduced after the implementation of a clean air act. Measurements on 47 days in autumn 1973 in the Los Angeles area are summarized in Table 9-3 (Peterson and Flowers, 1977). In the St. Louis area, however, smaller urban-rural differences were observed. On 12 cloudless days in summer 1972, the average solar and UV fluxes at an urban site were only 3 and 8 percent, respectively, below those at a rural site about 50 km from the city. The difference between the St. Louis and Los Angeles and European urban areas appears to involve both decreased urban and increased rural attenuation, and it may be that neither the city of St. Louis nor its surroundings over a wide area modify solar radiation in a manner typical of other locations.

Recently, Angell and Korshover (1975) analyzed the solar radiation duration data (hours of sunshine) for the eastern half of the United States. Data for the 1950-70 time period were obtained with on/off detectors, and these data are believed to be more reliable for long-term trend analysis than data from recorders of solar radiation intensity. Angell and Korshover noted some marked trends: in the Southeast and South Central United States, the solar radia-

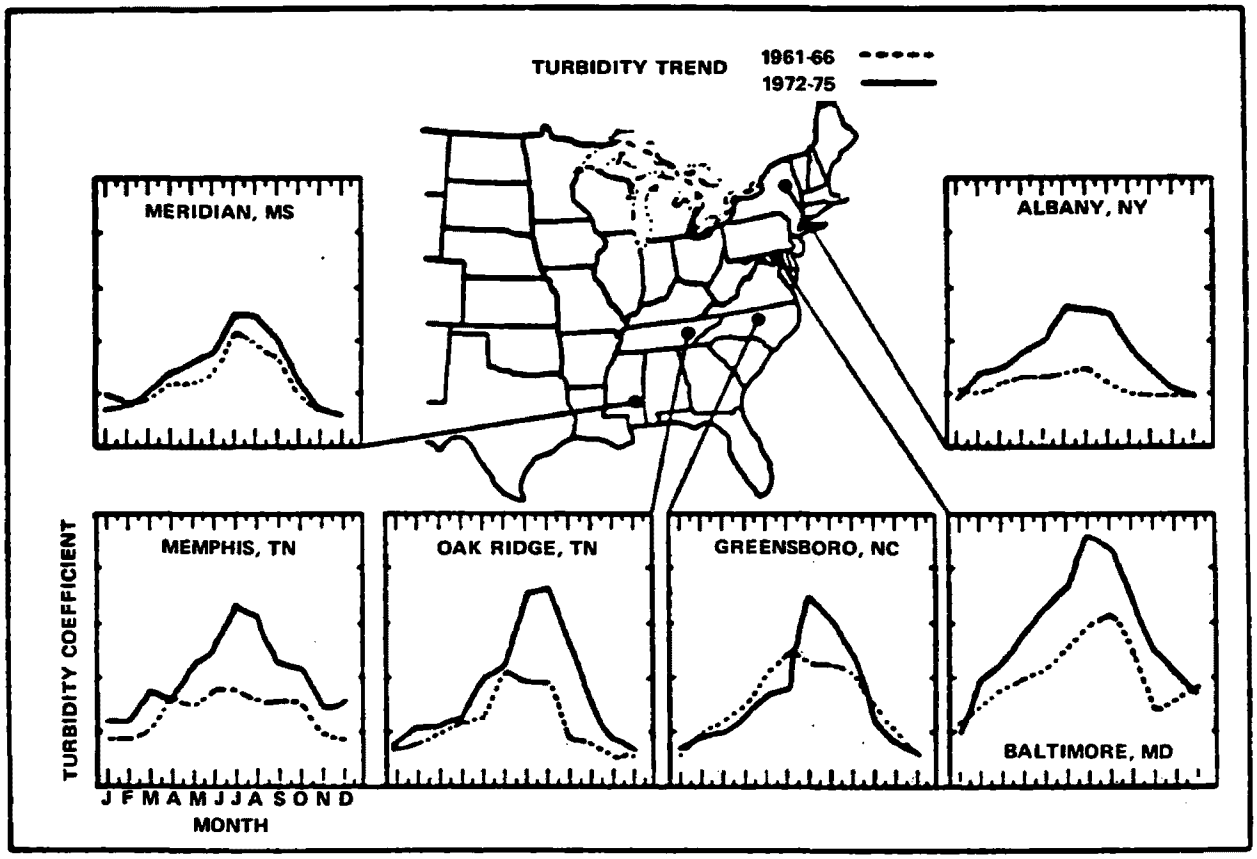

Figure 9-28. Seasonal turbidity patterns for 1961-66 and 1972-75 are shown for selected regions in the Eastern United States.

Source: Flowers et al. (1969).

TABLE 9-3. SOME SOLAR RADIATION MEASUREMENTS IN THE LOS ANGELES AREA[a]

Measurement	Total	UV
Minimum	4	15
Average	11	29
Maximum	20	44

[a]Values for the daily average percentage decrease of total and UV solar radiation between El Monte (urban) and Mt. Disappointment (rural).

Source: Peterson and Flowers (1977).

tion duration has decreased by about 4 to 6 percent; however, the North Central is increasing (Figure 9-29; Angell and Korshover, 1975). Although the authors do not attribute these trends to any specific cause, it should be noted that there has been an increase in haziness within that time period in areas with decreased solar radiation. It is conceivable, therefore, that increased haziness causes sunshine-duration detectors to delay the turn-on time in the morning and advance the turn-off time. It should also be stressed, however, that changes in the solar radiation duration may be caused by other natural or manmade phenomena.

9.6.3 Radiative Climate: Global Scale

The attenuation of solar radiation from scattering and absorption by particles in the atmosphere is probably an important factor in climatic change. The effect could arise from redirecting the photon energy, from effects on cloud structure (perturbations of the colloidal system), or from effects on optical properties, such as increased photon retention from absorption on soot particles. A report by Hobbs et al. (1974) argues that aerosols are most likely the principal agents by which pollutants may affect weather and climate, by influencing the structure and distribution of clouds. On a global scale, they noted that the effects of manmade pollutants on climate are still a matter of debate. Others, e.g., Twomey (1974), have pointed up a direct connection between pollution and the number of drops in a cloud and, hence, an influence on optical thickness and reflectance of the clouds (cloud albedo) and in doing so, affect climate.

The importance of particulate matter on climate may be overshadowed by that of carbon dioxide. A doubling of the concentration of carbon dioxide could result in a 1.5 to 3 degree centigrade of warming the lower atmosphere, according to various predictions viewed by the U.S. Department of Energy (U.S. Department of Energy, 1978). One set of calculations frequently cited in the scientific literature predicts a 2 to 3 degree centigrade rise in the

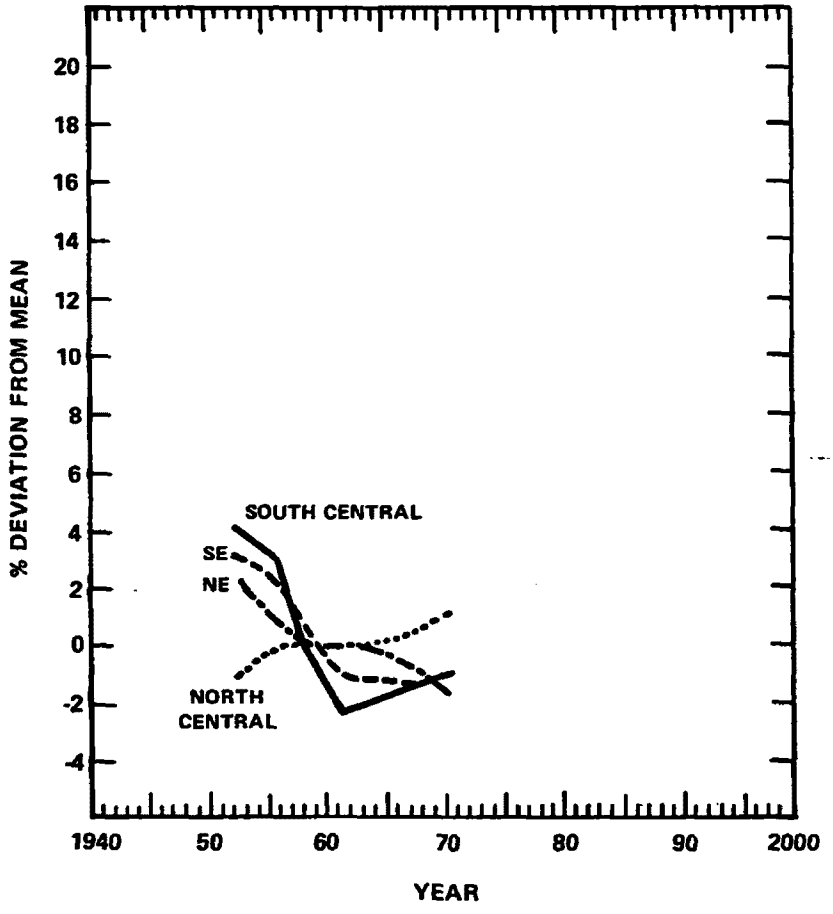

Figure 9-29. Analysis of the hours of solar radiation since the 1950's shows a decrease of summer solar radiation over the Eastern United States. There may be several causes for this trend, including an increase of cloudiness; some of the change may also be due to haze.

Source: Angell and Korshover (1975).

average temperature of the lower atmosphere in the middle latitudes with the doubling of the CO_2 content of the air and a 3 to 4 fold greater temperature increase in the polar regions (Manabe and Whetherald, 1975). Current model estimates suggest that the earth should have experienced a few tenths of a degree of warming since the late 1880s due to the increase of CO_2 concentrations from about 290 to the current 335 ppm. However, it appears that natural variations currently are large enough to mask the expected Co_2 effect on temperature (U.S. Department of Energy, 1980 and Stuivert, 1978).

Effects of volcanic emissions (see Chapter 4) on weather have also been suggested. Although "spectacular" sunsets have been associated with major eruptions, for example Krakatoa and Katmai, the effects of scattering of solar radiation from volcanic dust are not clearly understood. Whether a universal greenhouse effect is created which can result in cooler weather is still at issue. To date, surface temperature and rainfall changes are not conclusively related to volcanic events. The large variability of weather and self-preserving aspects of the atmospheric system tend to obscure all but the most dramatic changes in climate.

On local scales associated with urban and industrial areas, any significant attenuation of radiation by air pollution can, in addition to other well-recognized factors, result in changes in local weather (e.g., Landsberg, 1970). It is possible that local- and regional-scale changes in solar radiation caused by human activity may ultimately influence the heat and water vapor contents of the atmosphere on very large scales, but solar radiation and aerosol levels measured at stations remote from pollutant sources have not as yet displayed any trend that can be related to human causes (Fischer, 1967; Ellis and Pueschel, 1971; Hodge et al., 1972).

Unfortunately, there is little agreement about whether the net effect of increased airborne particulate concentrations is the warming or cooling of the earth as a whole. Most models can predict either an increase or a decrease in the effective albedo of the earth under cloudless skies, depending on which combination of surface albedo, sun angle, particle size distribution, and particle refractive index is assumed. The effects of clouds are very important, and the contributions from infrared radiation must be considered in order to obtain a complete energy budget (Wesely and Lipschutz, 1976).

9.7 CLOUDINESS AND PRECIPITATION

The global cloud cover plays a vital role in the earth's radiative budget in reflecting energy back to space, in absorbing both solar and longwave (terrestrial) radiation, and in emitting its energy downward and outward into space. Changes in cloud cover, therefore, alter the global heat balance. Cloud- and precipitation-forming processes may be divided into two broad classes: (1) macrophysical processes, which affect the rise and descent of air currents and the amount of water vapor available for condensation; and (2) microphysical processes, which affect the nature of cloud particles formed during condensation. The role of atmos-

pheric aerosols, primarily those that are strongly hygroscopic, is to influence the microphysics of cloud formation.

On a global or even regional scale, the very small amounts of moisture that man adds by land practices or combustion of fossil fuels are negligible in comparison with global evaporation. On a regional scale, only one form of increasing cloudiness suggests itself: the formation of aircraft contrails (Machta and Telegadas, 1974). Aircraft contrail formation results mainly from the injection of water vapor rather than of aerosols.

In urban areas, inadvertent changes of cloudiness as well as the quantity of precipitation have been well established. Such urban impacts also include the frequencies of thunderstorms and hail as well as total amounts of rain. In a classical study, Changnon (1968) has reported a notable increase in days of precipitation, thunderstorms, and hail occurring since 1925 at La Porte, IN. Since La Porte is 30 miles east of the Chicago urban-industrial complex, he proposed that the increased precipitation results from inadvertent manmade modifications. Figure 9-30 (Changnon, 1968) shows the 5-year running totals of days with smoke and haze restricted visibility in Chicago. This measure of atmospheric pollution has a temporal distribution after 1930 rather similar to the La Porte precipitation curve. A noticeable increase in smoke-haze days began in 1935 and became more marked after 1940, when the La Porte precipitation curve began its sharp increase.

A recent report by Clark (1979) critically reexamined this anomoly historically and technically through the use of a budgetary hydrologic model. Clark proposed several explanations of the anomoly. If the anomoly was real, it was, at most, a microscale phenomenom, and its disappearance by the mid-1960's arose from the dissipation of the precipitation-producing mechanism. He noted that although increases in local precipitation have been reported downwind of urban areas, no records exist of any alteration equalling the magnitude of the La Port precipitation variation relative to surrounding sites. Additionally, the 1929 to 1963 period coincides roughly with the tenure of the sole observer. The accuracy of the guage was also at issue. Clark concluded that errors by the observer and/or guage most likely explain the anomaly.

As part of project Metromex, studies by the Illinois State Water Survey suggest increases of about 30 percent in rain and 200 percent in thunderstorms and hail at single gauging stations downwind of St. Louis, with increases of about 10 percent over a two-county area. Here again, the physical causes of the maxima are not well understood, but they do appear to be associated with perturbations of the planetary boundary layer and enhanced cloudiness, possibly resulting from the addition of aerosols. It is regrettable that the complex interactions of cloud- and precipitation-forming processes obscure the specific role of manmade aerosols.

The incorporation of particles into rain and fog droplets can change the "quality" of precipitation by changing its chemical composition. The most important impact on precipitation water quality is probably that of "acid rain," discussed in more detail in chapter 8.

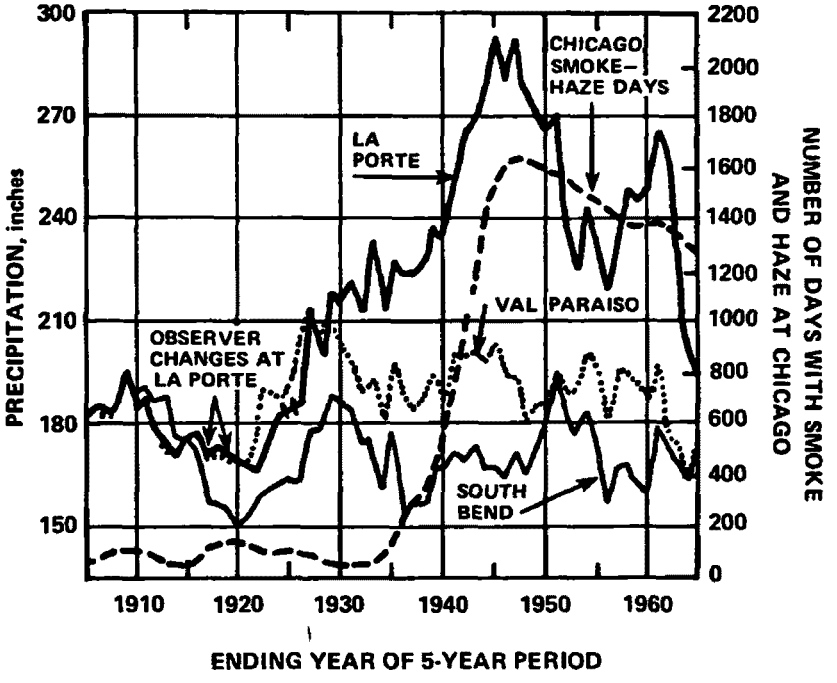

Figure 9-30. Numbers of smoke/haze days are plotted per 5 years at Chicago, with values plotted at end of 5-year period.

Source: Changnon (1968).

9.8 SUMMARY

Traditionally, visibility has been defined in terms of the distance from an object that is necessary to produce a minimum detectable contrast between that object and its background. Although visibility is often defined in terms of this "visual range," with its reasonably precise definition, visibility includes more than being able to see or not see a target. Visibility cludes seeing targets at shorter distances than the visual range and being able to appreciate the details of the target, including colors. Visibility impairment can manifest itself in two ways: (1) a layer of haze (or a plume), which is visible because it has a visual discontinuity between itself and its background or (2) a uniform haze which reduces atmospheric clarity. The type and degree of impairment are determined by the distribution, concentrations, and characteristics of atmospheric particles and gases, which scatter and absorb light traveling through the atmosphere. Scattering and absorption seem to determine extinction.

The consequences of visibility degradation range from the deterioration or loss of the aesthetic perception of scenic vistas to annoyances or outright hazards to automobile and aircraft traffic.

On a regional scale, the extinction of light is generally dominated by particle scattering. In urban areas, absorption by particles becomes important. Extinction by particles is usually dominated by particles of diameter 0.1 to 2 μm ("fine" particles). Extinction due to scattering is closely proportional to the fine-particle mass concentration, with extinction/mass ratios in the range of 3-5 x $10^{-6} m^{-1}/(\mu g/m^3)$.

Current knowledge indicates that fine aerosol is composed of varying amounts of sulfate, ammonium, and nitrate ions, elemental carbon, organic carbon compounds, water, and smaller amounts of soil dust, lead compounds, and trace species. Sulfate often predominates the fine mass and visibility impairment, while elemental carbon is often the primary visibility-impairing specie in urban areas. Significant variations can occur at different times and sites. Our knowledge of the roles of several possibly important species is hindered by the lack of sufficient good data. The 30-year record of the spatial and temporal trends of coal combustion and visibility suggest that the increasing emissions of SO_x since the 1950s have been associated with similar increases in haziness. Nevertheless, the relationship between SO_2 emissions and resulting sulfate concentrations is not as well defined as the relationships between sulfate concentrations and visibility reduction.

The currently available visibility monitoring methods measure different aspects of visibility impairment. Generally, contrast type measurements (such as photography, telephotometry, and human eye observations) relate well to the perception of visual air quality, while extinction or scattering measurements (such as transmissometry and nephelometry) relate to the cause of visibility degradation. Each of the above measurement methods can be used to approximate visual range. No single method has been proven totally effective in measuring light absorption. The methods used thus far include determining the difference between extinction and scattering, several filtering methods, and a refractive index method.

Pollutants released to the atmosphere alter the environment in ways other than visibility reduction. They may lead to slow and subtle changes in the nature of the atmosphere and, possibly, in climate. For example, a fraction of the solar radiation may be absorbed by aerosols, further reducing the amount of radiation reaching the earth's surface and, at the same time, heating the aerosol layer itself. On a hazy day, the direct solar radiation is reduced to about one-half of that on a clear day, but most of the energy reappears as diffuse skylight. However, there is an overall loss of up to about 10 to 20 percent of the radiation reaching the surface.

If there are no clouds between the observer and the sun, the intensity of direct solar radiation for a given solar elevation depends on the variable amount of dust, haze, and water vapor in the atmosphere. The extinction produced by these constituents is called "atmospheric turbidity." during hazy episodes, turbidity coefficients of 0.6 to 1.0 are often reported, resulting in a condition in which 75 to 90 percent of the solar radiation is removed from the direct beam, 7.5 to 18 percent is lost to space 7.5 to 18 percent is lost as atmospheric heating. One of the consequences of such a hazy atmosphere is the disappearance of shadow contrast.

The attenuation of solar radiation from scattering and absorption by particles in the atmosphere is probably an important factor in climatic change on all scales. On local scales associated with urban and industrial areas, any significant attenuation of radiation by air pollution can, in addition to other well-recognized factors, result in changes in local weather. It is possible that local- and regional-scale changes in solar radiation caused by human activity may ultimately influence the heat and water vapor contents of the atmosphere on very large scales, but solar radiation and aerosol levels measured at stations remote from pollutant sources have not as yet displayed any trend that can be related to human causes.

Cloud- and precipitation-forming processes may be divided into two broad classes: macrophysical and microphysical processes. Macrophysical processes involve the rise and descent of air masses and the amount of water vapor available for condensation. Atmospheric aerosols, primarily those that are strongly hygroscopic, influence the microphysics of cloud formation. The incorporation of particles into rain and fog droplets can change the "quality" of precipitation by changing its chemical composition. However, the complex interactions of cloud- and precipitation-forming processes obscure the specific role of manmade aerosols.

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10. EFFECTS ON MATERIALS

10.1 INTRODUCTION

Beginning with associative observations in the 17th century and continuing through modern analytical investigation, scientists have gathered evidence that air pollutants damage man-made and natural materials. Pollutant-related damage may lead to the need for measures such as increased maintenance, use of protective coatings, replacement of materials, or the control of emissions. The decision to pursue one course rather than another is guided, ultimately, by weighing the damage against the costs of prevention. Neither damage nor prevention cost is necessarily measured in monetary units, especially with regard to works of art or items of historical significance. However, for better or worse, society tends to assign monetary units to value gained or lost. Thus, the objective of this report is to present and evaluate studies useful for estimating the dollar cost of material damage caused by sulfur oxides and particulate matter.

The relation between pollutant emissions and economic damage is depicted in Figure 10-1. As shown in the figure, one may (1) proceed from ambient pollutant levels to economic damage estimates directly or (2) follow a route involving estimate of damage based on physical damage functions. The latter route, which we all call the damage function approach, has been the method of choice in the past. More recent studies have employed the first route. The two alternative routes have an element in common. This element is estimation of willingness to pay.

Economic damage (benefit) as a result of increased (decreased) pollutant concentrations can be estimated by willingness to pay approaches. All willingness to pay approaches attempt to estimate the aggregate monetary values that all affected individuals assign to the effects of a change in pollutant concentration. Willingness to pay approaches can be divided into three classes: damage function approaches, non-market approaches, and indirect market approaches. Damage function approaches utilize the relationship of pollutant exposure to physical damage as a first step. The second step links the physical damage to a dollar estimate of willingness to pay. With proper consideration of substitution possibilities this damage function approach can be a good estimate of willingness to pay. Non-market approaches generally utilize surveys which attempt to ascertain the monetary values assigned to the effects in question by all individuals. Indirect market approaches use information about the demand for marketed goods to estimate the willingness to pay for non-marketed environmental attributes which are closely related to the marketed good (e.g., property value studies which estimate the willingness to pay for a change in the level of pollutant concentration through the analysis of the price of residential property) (Freeman, 1979). Each of the three groups of approaches have different data requirements. The physical damage function approaches have been the most widely used in the past and will therefore receive the most extensive treatment in this chapter. Non-market and indirect market studies will be discussed later in Section 10.5.

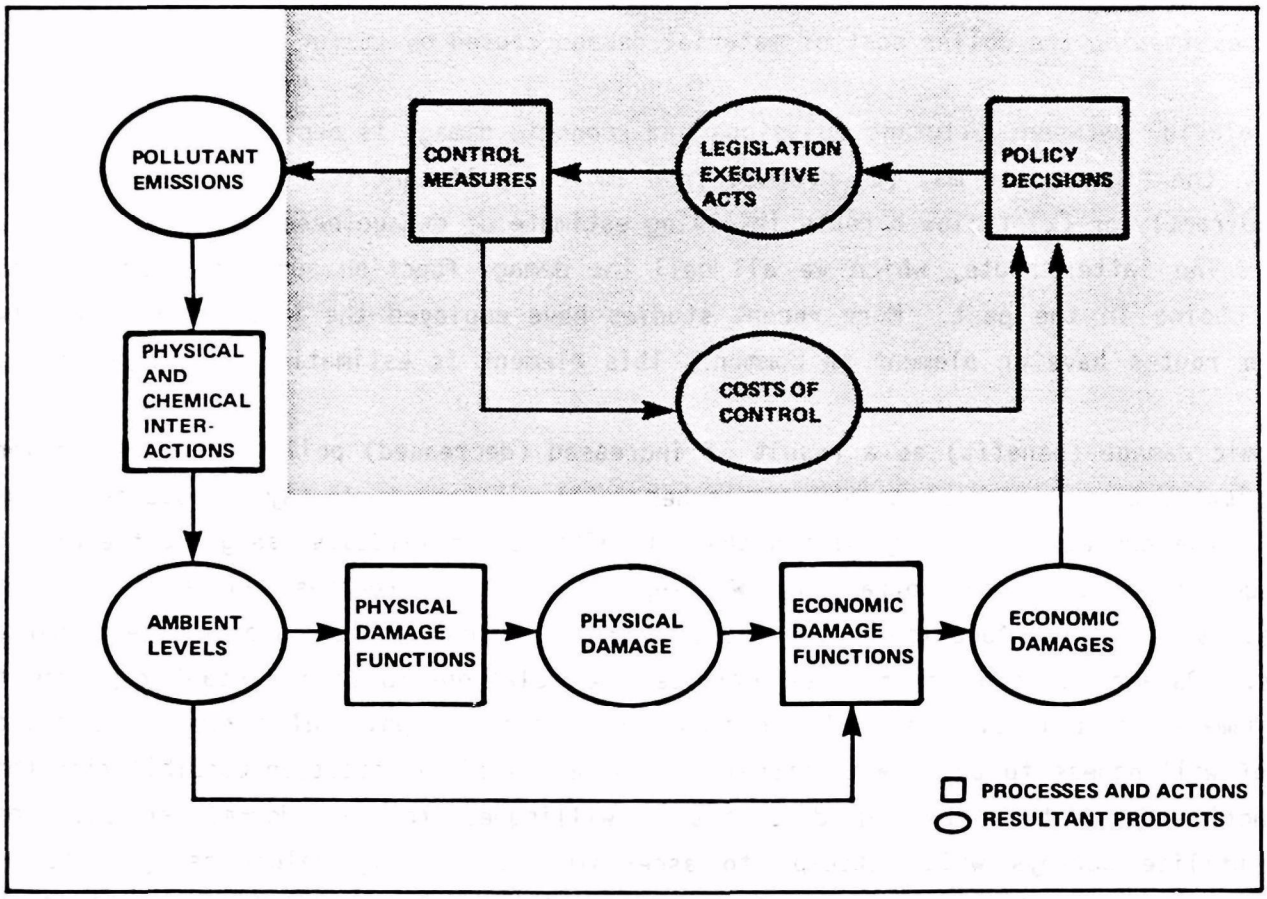

Figure 10-1. Relationship among emissions, air quality, damages and benefits, and policy decisions.

Source: Hershaft (1976)

In the damage function approach, before economic damage is estimated, physical damage must be determined. This determination begins by calculating the exposure of certain materials in specific locations. Exposure is estimated from ambient air levels over specific time intervals. Depending on the pollutants and the kinds of material studied, both average short-term and long-term exposure data may be needed. These data are used to develop a physical damage function, which is a mathematical expression linking exposure to damage. The damage function is expressed in terms appropriate to the interaction of the pollutant and material. For example, the corrosion of metal might be expressed in units of thickness lost, while the deterioration of paint could be stated in units of reflectance or thickness lost. The pollutant level may be expressed in any concentration unit. Since material damage usually develops over time, average long-term pollutant levels are often used in calculating damage. Damage studies often encompass a yearly time scale, which facilitates economic comparisons and allows averaging of conditions in changeable climates.

A major problem in establishing reliable damage function has been to separate the influence of the target pollutant from that of meteorological parameters and other air pollutants. For the corrosion of metals, relative humidity is the most important variable. Rainfall, time of wetness, sunlight, and wind speed and direction are available for many locations and, if relevant, can be factored into damage calculations. The influence of atmospheric components should be considered in the context of the material being studied. For example, in studies of SO_x-related steel corrosion, even low atmospheric chloride levels may have a significant impact on the rate of damage.

Before an economic value is placed on the incremental damage caused by pollution, a critical damage level must be determined. This level represents the point at which the service life or functional utility of the material has ended or is severely impaired. When this point is reached, replacement or repair is necessary, and cost is incurred. For example, if a typical coat of paint is 60 μm thick, the critical damage level at which repainting is necessary may be around 50 μm. By comparing the amount of surface erosion in a clean environment with that in an area with a specific pollutant, the apparent damage from the pollutant can be calculated and used in assessing physical damage. The valuation is determined through economic damage functions, (1) which may be developed from physical damage functions; (2) which may relate economic damage directly to pollutant level by comparing the life-time costs of a given material in different ambient environments; (3) which may combine both approaches. In the first case, physical damage functions are coupled to the use and value of the material. Included in the estimate are exposure, replacement, protection, and other data. None of these approaches account for irreplaceable items, such as works of art, where the only measurable cost is that of preservation. The social losses of artifacts cannot be quantified economically.

As discussed above in the context of Figure 10-1, most estimates of economic damage to materials have followed the damage function approach. This approach is discussed here to illustrate how damage functions may be used as an integral component of cost estimation. The

chapter is organized in several parts. Presented first are laboratory studies. These controlled experiments investigate variables that influence damage to a material at various pollutant concentrations. The results of these studies are used to develop damage functions, which include only those variables that affect material damage.

Field experiments are performed to test the validity of extrapolating laboratory results to ambient conditions. Parameters measured in field experiments are those found or suspected to be significant factors in laboratory experiments. For example, if relative humidity were part of the damage function derived from laboratory results, it would be carefully measured in the field experiment.

Results from field experiments are then compared with laboratory-derived damage functions. The comparisons may show similarities or differences. A field study may measure a parameter not measured in a controlled experiment but which correlates well with damage. In such a case, a laboratory experiment may be designed to determine whether or not a causal relationship between parameter and damage exists. When a damage function has been validated by field and laboratory experimental results, it may be used as a basis for determining total damage to materials exposed to an air pollutant.

In the damage function approach to cost estimation described above, the physical damage function is one of several components of an economic damage function. Other necessary components to this approach include a mathematical expression of surface area of materials exposed and cost factors associated with units of physical damage. Problems arising from this approach have been (1) valid physical damage functions do not exist for all pollutants and all materials; (2) estimates of the amount and type of material exposed have usually been based on some surrogate such as production figures modified by service life data (field surveys of exposed material in place have not been performed); (3) cost factors may or may not accurately reflect cost associated with pollution as opposed to other causes. This latter consideration is especially a problem in estimates of soiling damage, where socioeconomic factors are heavily involved.

Past estimates of costs associated with particulate matter, sulfur oxides, or other pollutants must be considered in light of the above discussion. The last section of this chapter discusses cost estimates and their limitations for decision-making purposes.

10.2 SULFUR OXIDES

10.2.1 Corrosion of Exposed Metals

Sulfur oxides in the environment accelerate the corrosion of metals. Several factors other than concentration of SO_2 are important. These are discussed first.

10.2.1.1 Physical and Chemical Considerations--The atmospheric corrosion of most metals is a diffusion-controlled electrochemical process. For electrochemical action to take place, the following are necessary: (1) an electromotive force between points on the metal surface; (2) a mechanism for charge transfer between the electronic conductors; and (3) a conduction path between the cathode and anode reaction centers. Measurements of the rate of SO_2-accelerated rusting of iron vary greatly from site to site, despite careful monitoring of pollutant

concentrations, a fact that has often puzzled researchers. Several factors might be responsible for inconsistent results. These include: (1) the deposition rate of gaseous or dissolved SO_2 and particles; (2) the variability in the electrochemical actions that cause corrosion; (3) the influence of rust on the rate of subsequent corrosion; and (4) the interaction between the pollutant effects and "wetness time" often indicated by relative humidity (RH) on surface electrolyte concentrations.

According to Nriagu (1978), once corrosion has begun, the progress of the reaction is largely controlled by the sulfate ions formed by oxidation of the adsorbed SO_2. The actual mechanism for the oxidation of SO_2 (and its hydrated products) at metal-water interfaces is little understood. Barton (1973) proposed the following reaction:

$$SO_2 + O_2 + 2e \rightarrow SO_4^{2-}$$

or

$$4HSO_3^- + 3O_2 + 4e \rightarrow 4SO_4^{2-} + 2H_2O$$

The electron is provided by the oxidation of the metal (M):

$$M \rightarrow M^{n+} + ne$$

Duncan and Spedding (1974), using an electrophoretic method, found that the rates of sulfate formation on iron and zinc surfaces were similar; the pseudo-first-order half-life was determined to be about 24 hours. Other workers (Karraker 1963; Yoshihara et al., 1964) reported higher oxidation rates (half-life, 10 to 100 minutes) in bulk solutions using Fe^{3+} catalysts as summarized in Nriagu (1978). Nriagu also noted that rust on iron and steel is first restricted to localized sites or "nests" and then spreads across the entire exposed surface. At an SO_2 concentration of about 260 $\mu g/m^3$, corrosion products were obvious on iron surfaces after 6 to 8 weeks, whereas at SO_2 concentrations of 4×10^5 $\mu g/m^3$, they could be seen after only a few hours.

Barton (1976) showed that the critical SO_2 flux for corrosion was 6 to 10 $\mu g/m^2$ per year for steel and 18 to 20 $\mu g/m^2$ per year for zinc and copper. The formation of rust drastically increases the adsorption rate for SO_2. For example, at an SO_2 concentration of >0.001 percent and relative humidity (RH) of >96 percent, virtually all of the SO_2 that comes into contact with the rusting surface is adsorbed or consumed in reaction.

10.2.1.1.1 Relative Humidity and Corrosion Rate. According to Schwarz (1972), the corrosion rate of a metal should increase by 20 percent for each increase of 1 percent in the relative humidity (RH) above the critical RH value. It is evident that RH has a considerable influence on the corrosion rate. This influence has been established in laboratory trials by Barton and Bartonova (1969) and Sydberger and Ericsson (1976). It is apparent from Figure 10-2 (Haynie and Upham, 1974) that the corrosion rate of steel increases with increasing RH as well as with increasing SO_2 concentration.

The climate of an area is usually characterized by average RH rather than RH distribution. Since average RH is calculated from the distribution, there should be an empirical relationship between average RH and the fraction of time some "critical humidity

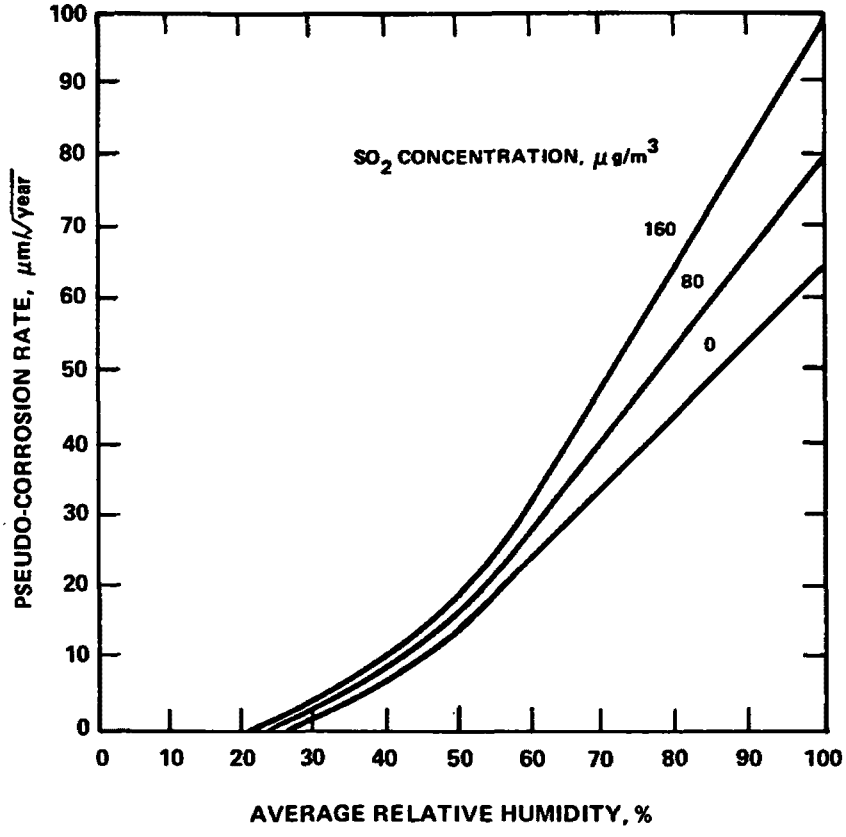

Figure 10-2. Steel corrosion behavior is shown as a function of average relative humidity at three average concentration levels of sulfur dioxide.

Source: Haynie and Upham (1974).

value" (minimum concentration of water vapor required for corrosion to proceed) is exceeded (Mansfeld and Kenkel, 1976; Sereda, 1974). The fraction of time that the surface is wet must be zero when the average RH is zero and unity when the average RH is 100 percent. The simplest single-constant first-order curve that can be fitted to observed data and that meets these conditions is described by the equation $f = [(1 - k)RH]/(100 - kRH)$, where f is the fraction of time the RH exceeds the critical value, RH is the average RH, and k is an empirical constant less than unity (Haynie, 1980).

Ten quarter-year periods of RH data from St. Louis International Airport were analyzed and fitted by the least-squares method to the above equation. The fraction of time the RH exceeded 90 percent gave a value of 0.86 for k. This fraction and the data points are plotted in Figure 10-3 (Haynie, 1980).

When the temperature of a metal is below the ambient dewpoint, condensation of water on the metal surface will take place. The metal temperature at which condensation occurs will vary with heat transfer between ground and metal and between air and metal. Condensation will occur when the RH adjacent to the surface exceeds a value in equilibrium with the vapor pressure of a saturated solution on the surface. The solution may contain corrosion products, other hygroscopic contaminants, or both. Temperature, wind, and sunshine then become factors in establishing corrosion rates, since they determine whether there will be sufficient dew condensation.

Haynie (1980) reported on the relationship between diffusion theory and thermodynamics for the observed effects of five variables: pollution level, RH, temperature, wind velocity, and surface geometry. He observed that metals must be wet to corrode electrochemically. Surfaces are wet from condensation much more often than from precipitation.

10.2.1.1.2 Influence of Rainfall on Corrosion. Steel surfaces shielded from the leaching effect of rain may corrode at a higher rate than those exposed to rain. The sulfate content of rust has been identified as a dominant factor in corrosion and is found at higher concentrations on surfaces sheltered from rain than on exposed surfaces because soluble sulfate is leached from the rust. However, sulfur deposition during rainfall must also be considered. Haagenrud and Ottar (1975) noted that the rate of corrosion of unalloyed steel and zinc correlated with the amount of sulfur (SO_2 and sulfate) in air and in precipitation.

As Kucera's (1976) review of this problem indicates, the mode of deposition complicates the analysis of acidic precipitation's effects. For example, in an area where dry deposits of hydrogen and sulfate ions exceed deposits in wet precipitation, flat steel plates corrode more rapidly on their undersides than on their upper surfaces, suggesting that rainfall has more of a washing effect than a corrosive action. However, in other areas where wet and dry deposition were about equal, the upper sides of the plates corroded more quickly, suggesting that the corrosive effect of the rainfall predominated. Other variables, including amount and frequency of precipitation, its pH level, humidity, and temperature, also determine the impact of acidic precipitation (Kucera, 1976). For a more thorough discussion of the effects of acidic precipitation on corrosion, see Chapter 7.

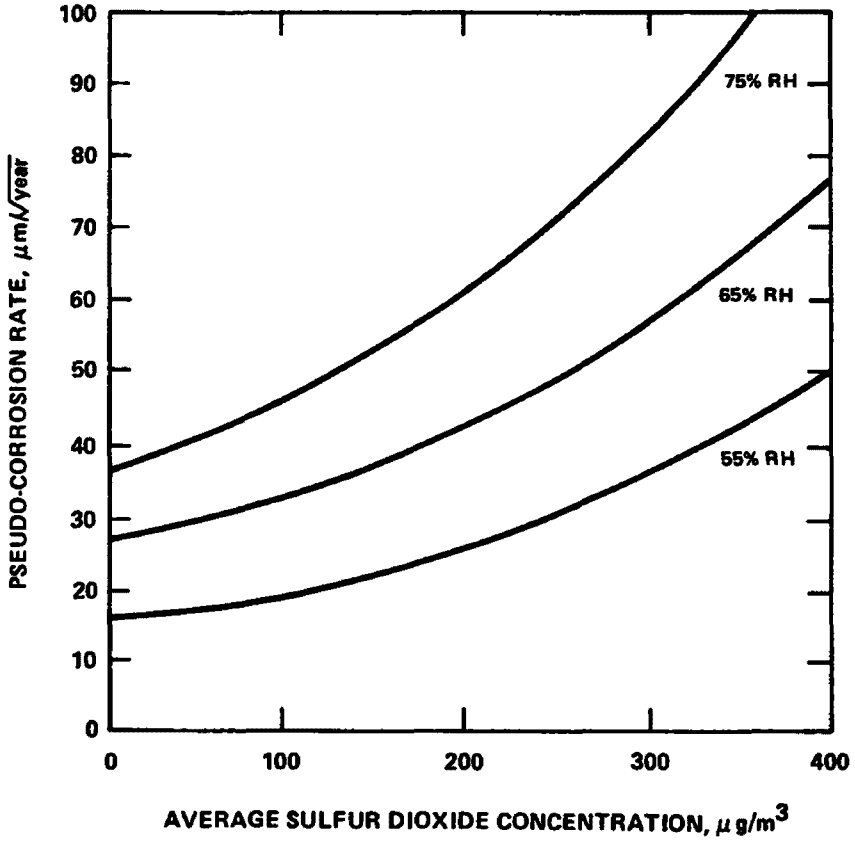

Figure 10-3. Steel corrosion behavior is shown as a function of average sulfur dioxide concentration and average relative humidity (RH).

Source: Haynie and Upham (1974).

10.2.1.1.3 Influence of Temperature on Corrosion. From chemical reaction kinetics, one might expect corrosion rates to follow the Arrhenius law according to which the logarithm of a reaction rate is inversely proportional to the absolute temperature. However, this does not appear to be a major factor controlling corrosion rates. In most cases, as discussed later, the reaction rate is controlled by diffusion, either in the corrosion product film or in the environment. In either case, the rate of diffusion is relatively insensitive to changes in ambient temperature. A decrease in temperature raises the RH while decreasing diffusivity; thus, the normal temperature range will most likely not observably affect the overall corrosion rate. Even at -20°C metal corrosion is not halted (Sereda, 1974).

Guttman (1968) and Haynie and Upham (1974), using statistical techniques of multiple linear regression and nonlinear curve fitting, did not obtain from their data a significant correlation between corrosion and temperature. However, increased temperature decreases the solubility of oxygen in the electrolyte. Moreover, temperature decreases can cause condensation, the increased quantity of condensed droplets can affect the corrosion rate, and the rate at which a surface dries depends on both temperature and air movement.

Guttman and Sereda (1968) made continuous measurements of sulfur oxides, time of wetness, and temperature in their outdoor exposure tests. The corrosion rate increased markedly with temperature, which may be attributed to a speeding up of the electrochemical process. The effects are not simply thermodynamic since other factors involved include evaporation of surface electrolyte and decrease in the solubility of oxygen and gaseous pollutants. Barton (1976) did find that the effect of increased temperature was more pronounced when the rust contained little water and sulfate. Haynie et al. (1976) found temperature to be a significant variable in chamber studies of weathering steel.

10.2.1.1.4 Hygroscopicity of Metal Sulfates. The sulfate in rust stimulates further corrosion by a mechanism that is related to the critical relative humidity at which an electrolyte film is formed. The hygroscopicity of iron sulfates in the rust lowers the critical RH for corrosion; however, sulfates are not the most deliquescent salts. For example, chloride and nitrate salts which have higher hygroscopicity than sulfates make corrosion possible at lower humidities.

Surfaces contaminated by sea salt (mostly sodium chloride) can be expected to be wet when the RH exceeds 75 percent. In contrast, calcium chloride keeps surfaces wet at an RH as low as 30 percent. A saturated solution of zinc sulfate at 20°C is in equilibrium at 90 percent RH. Thus, zinc corroded by sulfur dioxide is expected to be wet when the RH exceeds 90 percent (Haynie, 1980).

Some pollutants that react chemically with various materials and with other materials are not consumed and produce catalytic effects. The following four mechanisms act to increase corrosion rates without consuming the pollutants: (1) hygroscopic materials increase the amount of time that a corroding surface is wet; (2) conductivities of solutions and corrosion product films increase; (3) pollutants form soluble intermediate reaction products or activated complexes that destroy the protective nature of films; and (4) lowering the pH usually increases the solubility of corrosion products (Haynie, 1980).

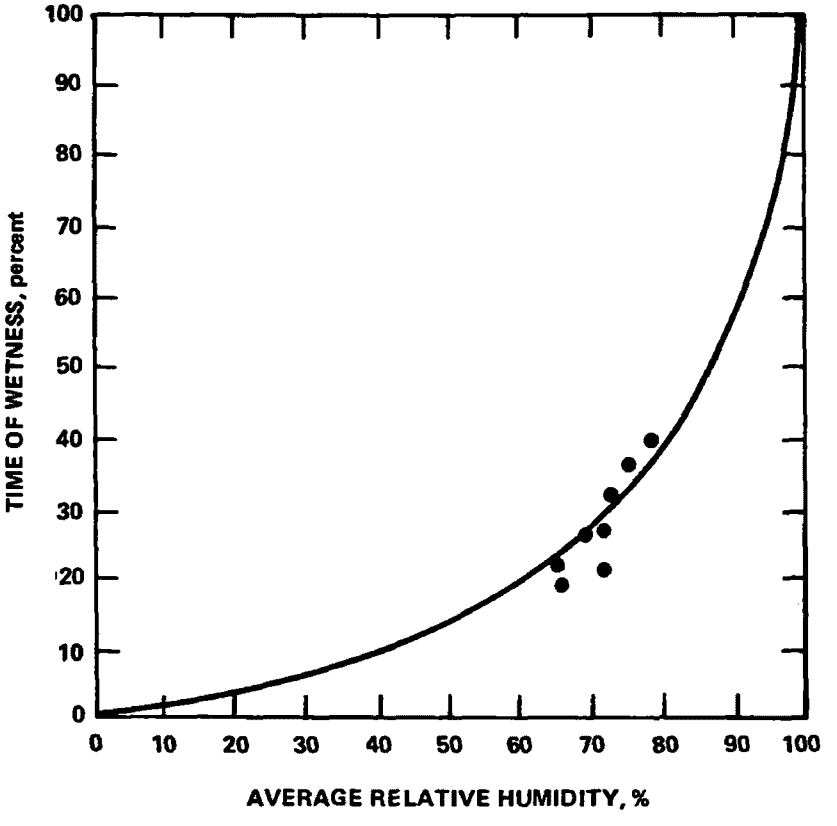

Figure 10-4. Empirical relationship between average relative humidity and fraction of time relative humidity exceeded 90 percent is shown for data from St. Louis International Airport.

Source: Haynie (1980).

10.2.1.1.5 Electronic Conductivity of Rust. Barton (1976) postulated that sulfate ions influence the anodic dissolution of iron as a function of their concentration at the steel-rust interface. The corrosion rate of the rust layer is based in part on the high electronic conductivity of rust, which allows the reduction of oxygen to occur within the rust layer. The rate is also influenced by the porosity of rust, which permits rapid diffusion of oxygen to the cathode.

In the presence of SO_2, ferrous sulfate is formed before insoluble rust develops. The amount of SO_2 required is small; each SO_2 molecule can generate 20 to 30 molecules of rust. Once ferrous sulfate is formed, rusting can continue even though SO_2 is no longer present in gaseous form.

10.2.1.1.6 Cathodic Reduction of Rust. Evans (1972) suggests that oxidative hydrolysis of ferrous sulfate occurs slowly, and would be important only in the initial stage of corrosion. He proposes that there is a rate-controlling cathodic process. Thus, the corrosion products in the ferric state would be converted to magnetite (Fe_3O_4) by a reaction involving the reduction of ferric oxyhydroxide (FeOOH):

$$Fe^{2+} + 8FeOOH + 2e^- \rightarrow 3Fe_3O_4 + 4H_2O$$

10.2.1.1.7 Corrosion-Protective Properties of Sulfate in Rust. The rust layer on steel is somewhat protective against further corrosion, though far less so than the corrosion layer on zinc and copper. A limiting factor in rust's protection of steel is the content of soluble compounds in rust.

Rust samples investigated by Chandler and Kilcullen (1968) and by Stanners (1970) contained 2 to 2.5 percent soluble sulfate and 3 to 6 percent total sulfate. The outer rust layer contained a small amount (0.04 to 0.2 percent) of soluble sulfate, compared with 2 percent in the inner rust layer. The concentration of insoluble sulfate was fairly uniform throughout the rust layers.

The emphasis on the composition of the rust layer has led to studies of the corrosion-protective properties of rust as a function of exposure history (Nriagu, 1978; Sydberger, 1976). Steel samples initially exposed to low concentrations of sulfur oxides and then moved to sites of higher sulfur oxide concentrations corroded at a slower rate than did samples continuously exposed to the higher concentrations. Exposure tests started in summer showed slower corrosion rates during the first years of exposure than did those started in winter.

The long-term corrosion rate of steel appears to depend on changes in the composition and structure of the rust layer. During the initiation period, which varies in length with the SO_2 concentration and other accelerating factors, the rate of corrosion increases with time (Barton, 1976). Because it is porous and nonadherent, the rust initially formed offers no protection; in fact, it may accelerate corrosion by retaining hygroscopic sulfates and chlorides, thus producing a microenvironment with a high moisture content (most often reported in terms of percent RH). After the initiation stage, the corrosion rate decreases as the protective properties of the rust layer improve. Satake and Moroishi (1974) relate this slowing

down to a decrease in the porosity of the rust layer. During a third and final stage, a constant rate of corrosion is attained and the amount of sulfate in rust is proportional to atmospheric sulfur oxide concentrations.

Where there is no appreciable deposition of sulfur or chloride compounds, the corrosion of steel is low, even with high atmospheric humidity and temperature (Haynie and Upham, 1974). The quantitative determination and subsequent interpretation of corrosion rates becomes difficult if it is not known how long the metal has had a surface layer of electrolyte. Variations in the "wet states" will occur with RH, temperature, rain, dew, fog, evaporation, and wind. The surface electrolyte layer may form on a metal surface as a result of rain, dew, or adsorption of water from the atmosphere. Capillary condensation in rust can be related to the minimum atmospheric moisture content that allows corrosion to occur (i.e., critical RH). Centers of capillary condensation of moisture on metals can occur in cracks, on dust particles on the metal surface, and in the pores of the rust (Tomashov 1966).

10.2.1.2 Effects of Sulfur Oxide Concentrations on the Corrosion of Exposed Metals--Most of the laboratory studies reviewed in this section have measured corrosion rates related to exposure to sulfur dioxide alone or in combination with other compounds. In field exposure studies, where sulfur oxides almost invariably occur in combination with other airborne pollutants, an attempt is made to assign separate values to sulfur oxides and to describe pollutant interactive effects on corrosion. The discussion here unavoidably overlaps somewhat with a later section on particles, since sulfur dioxide contributes to formation of secondary sulfates. Here, the emphasis is on the direct role of sulfur oxides in the corrosion process (e.g., the oxidation of SO_2 with moisture on a metal surface). In the later section, sulfates are discussed mainly in terms of their indirect role (e.g., their ability to increase wetness time of a metal surface).

10.2.1.2.1 Ferrous Metals. Ferrous metal products and structures are exposed widely to ambient pollutant levels. Rusting of these metals is the best documented form of metallic corrosion affected by sulfur oxides. This subsection reviews studies of rusting rates of ferrous metals, such as iron, steel, and steel alloys.

A number of investigators reported data during the period 1959-1968 which showed that the addition of 0.05 to 0.5 percent copper to steel results in improved corrosion resistance (Larrabee, 1959; Larrabee and Coburn, 1961; Brouns and Kalla, 1965; and Schwenk and Ternes, 1968). In an extensive series of exposure tests (Guttman and Sereda, 1968), the American Society for Testing and Materials (ASTM) corroborated previous investigations, showing that adding copper to steel improves its resistance to corrosion.

Stainless steels contain more than 12 percent chromium and are widely used in outdoor exposures; they are specified for use in many industrial processes involving corrosive liquids that rapidly attack ordinary steels. The high corrosion resistance of stainless steels that incorporate chromium, molybdenum, and nickel is attributed to the protective properties of the oxide film formed on these alloys. In heavily polluted atmospheres, however, this film is not completely protective. Particles in settled dust, including sulfates and chlorides, can

promote rupture of the oxide film and cause pitting corrosion, which may be influenced by the surface finish (see section 10.3.1). Smoothly polished or electropolished surfaces are less likely to retain solid deposits originating from airborne particles (Larrabee, 1959).

The lowest alloyed stainless steels have little corrosion resistance. In particular, #13 Cr steel suffers pitting attack in industrial atmospheres. Evgang and Rockel (1975) report that the austenitic steels of 18 percent Cr and 8 percent Ni are reasonably resistant in urban atmospheres but have shown slight rusting in industrial areas. The rusting rate is decreased when the steel surface is cleaned of atmospheric deposits.

10.2.1.2.2 Laboratory and Field Studies Emphasizing Ferrous Metals. It is useful to consider laboratory and field studies of corrosion effects separately because cause and effect is much clearer in laboratory experiments; field studies are often beset by confounding variables. Laboratory studies develop from controlled experiments, including as many variables as are thought likely to influence damage to the material being studied. Data on materials damage result from exposure to various concentrations of the air pollutant being studied. Analysis of the data resulting from such laboratory studies is used to develop a mathematical expression of the relationship between the concentration of a pollutant and damage to materials. Such a mathematical expression is called a damage function, that is, the quantitative expression of a relationship between exposure to specific pollutants and the type and extent of damage to a target population. Factors that are shown to be significant influences in producing damage are included in the damage function.

Information derived from laboratory studies is used to design field experiments, which are performed to test the possibility of extrapolating laboratory results to ambient conditions. The parameters that are measured in field studies are those found or suspected to be important factors in the laboratory experiments. The results of laboratory experiments do not easily translate to field situations, however, since ambient air pollution levels and other influencing environmental factors vary widely both in time and space. Temporal variables include fluctuations in temperature, wind moisture content, insulation, rainfall, and its chemical characteristics (e.g., acidic rain), and atmospheric pollutant concentrations. Spatial factors include differences such as aspect, altitude, electromagnetic fields, and indigenous microorganisms. Initial conditions of the material being studied must also be considered.

The results of field studies are compared with the laboratory-derived damage function. In some cases the results are comparable, and the laboratory damage function is validated. In other cases the data analysis may result in a markedly different damage function, with more or fewer variables.

10.2.1.2.2.1 Laboratory Studies. Spence and Haynie (1974) described the design of a laboratory experiment to identify the effects of environmental pollutants on various materials including ferrous metals. The environmental system consisted of five exposure chambers to control temperature and humidity and chill racks to simulate the formation of dew. Gaseous pollutants included those usually monitored in field exposures: sulfur dioxide, nitrogen

dioxide, and ozone. Experiments were statistically designed for analysis of variance, and a system was selected to study the interactive effects of pollutants and other variables. The effect of particles was not included in the design. The chambers were equipped with a xenon arc light to simulate sunlight. The system was designed to maintain air contact with the various materials at preselected temperatures, relative humidities, flow rates, and pollutant concentrations. A dew-light cycle was used; it produced faster deterioration than did conditions of constant humidity and temperature.

Haynie et al. (1976) exposed weathering steel in the chamber study described above and measured concentrations of sulfur dioxide, nitrogen dioxide, and ozone in various combinations and at two levels of pollutant concentration. Ozone was of interest since an earlier field experiment (see following Field-Studies section) had indicated that the presence of oxidants inhibited metallic corrosion. The corrosion rate was measured by loss in weight of the weathering steel. Six panels each were exposed to 16 polluted-air and 4 clean-air conditions, and measurements were taken at 250, 500, and 1000 hours of exposure. The weight losses were converted to equivalent thickness loss values. As expected, corrosion was most severe at high SO_2 concentrations and high humidity. Ozone neither inhibited nor accelerated corrosion. The authors concluded that some other oxidant or unmeasured factor that was covariant with ozone caused the inhibition effect. However, if the data from the sites with high oxidant concentrations in the field exposure experiments were excluded, the damage function from the laboratory study was an excellent predictor of the field results. The coefficient of determination for the field data using the laboratory function was 0.986. The following physical damage functions were developed by Haynie et al. (1976) to relate SO_2 concentrations to weathering steel and galvanized steel corrosion ($R^2 = 0.91$).

$$\text{corrosion} = [5.64 \sqrt{SO_2} + e^{(55.44 - 31{,}150/RT)}]\, t_w$$

$$\text{corrosion} = (0.0187\, SO_2 + e^{41.85 - 23{,}240/RT})\, t_w$$

where:

corrosion is expressed as μm

SO_2 is expressed at $\mu g/m^3$

t_w is time of wetness in years

R = gas constant (1.98 cal/gm mol/°K)

T = temperature (°K)

Sydberger and Ericsson (1976) studied the corrosion of mild steel at 1, 10, and 100 ppm (2620, 26,200, and 262,000 $\mu g/m^3$) SO_2 across the range of critical humidities (80 to 96 percent RH). The flow rate of the SO_2 atmosphere was varied, and some samples were sprayed with water to simulate rain or condensation. The chemical composition of the corrosion products was studied by X-ray diffraction, infrared spectrometry, and electron spectroscopy for chemical analyses (ESCA) techniques. The flow rates of the SO_2 atmospheres markedly

influenced the corrosion rates. It appears that corrosion rates are related not only to the SO_2 concentration in the atmosphere, but also to the supply of SO_2 per unit surface area and time. Spraying the samples with distilled water at intervals substantially increased corrosion.

Sydberger and Ericsson's (1976) analysis of the corrosion product (rust layer) was based on the concepts of Schwarz (1972) and Barton (1976) that sulfate is the primary corrosion stimulant in rust formation. Anodic activity is maintained by the concentration of ferrous sulfate in the electrolyte. An SO_2 supply of 4 $\mu g/cm^2/hr$ at the lowest humidity initiated corrosion at a low rate. A rise above 50 percent RH increased corrosion markedly. Of particular interest was the finding that a variation of the flow rate at 1 ppm (2620 $\mu g/m^3$) SO_2 with 96 percent RH gave significant differences in corrosion rates. This study of the effect of rust on corrosion showed that even at high humidity and high sulfate content, the corrosion rate decreased to a low level when the SO_2 concentration was low.

10.2.1.2.2.2 Field Studies. For outdoor exposures, the primary rate-controlling factor in the delivery of pollutants to a surface is eddy diffusion. This flux is not constant and is a function of the horizontal wind velocity gradient away from the surface. The transport of a pollutant to a surface is usually expressed as a "deposition velocity" (u), defined as the flux to the surface divided by the ambient pollution level at some specific measuring height. Reported deposition velocities for gaseous pollutants have usually been within an order of magnitude of 1 cm/sec. These values are consistent with calculated estimates based on an analogy with momentum flux and measured wind velocity profiles (Sydberger, 1976).

The amount of SO_2 reaching a steel surface depends on wind direction, wind velocity, and the orientation of the surface to the emission source. The concept that SO_2 deposition varies with flow direction and velocity suggests that data on concentration alone cannot be used to determine the supply of SO_2 to metal surfaces; therefore surface adsorption methods like the lead candle method provide valuable information in relating supply of sulfur oxides to metal surfaces (Sydberger, 1976). Upham's (1967) work indicated, however, that corrosion of mild steel at seven Chicago sites increased with time and with increasing mean SO_2 concentration (Figure 10-5).

Haynie and Upham (1971) continuously monitored urban pollutants including SO_2, nitrogen dioxide, and ozone (oxidants) to determine whether previously unconsidered variables might affect steel corrosion. Other factors considered were temperature, RH, and total suspended particulate matter (TSP). Their 5-year program, begun in 1963, involved sites in Chicago, Cincinnati, New Orleans, Philadelphia, San Francisco, Washington, Detroit, and Los Angeles. They studied three types of steel expected to show different levels of resistance to atmospheric corrosion: (1) a plain carbon steel containing some copper (0.1 percent copper); (2) a copper-bearing steel (0.22 percent copper); and (3) a low-alloy weathering steel (0.4 percent copper with 0.058 percent phosphorus). The exposure periods were 4, 8, 16, and 32 months. The same steels were exposed at rural sites as a control. The rural sites proved to have higher than expected corrosion rates; however, SO_2 concentrations were not measured at

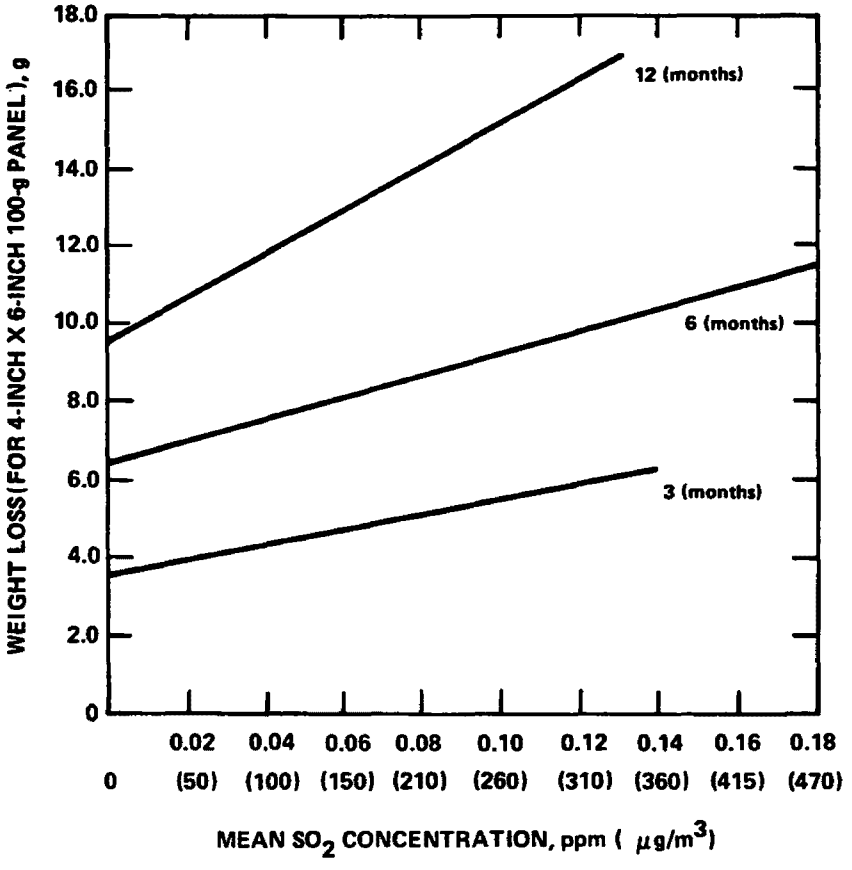

Figure 10-5. Relationship between corrosion of mild steel and corresponding mean SO_2 concentration is shown for seven Chicago sites. (Corrosion is expressed as weight loss of panel.)

Source: Upham (1967).

these sites. Multiple regression analysis established significant correlations between average SO_2 concentrations and corrosion of all three steels at the urban sites.

A first consideration was climatic conditions. For metallic corrosion to occur, a certain level of wetness on the metal surface is required to provide an electrolyte film in which electrochemical action can take place. The average humidities recorded by Haynie and Upham were high enough to produce this critical wetness threshold much of the time. Temperature was a statistically insignificant variable, although a later chamber study (see previous section) did find temperature to be a significant variable. Average RH was also insignificant because the range was only between 62 and 77 percent (Haynie and Upham, 1971).

Inspection of the monitored SO_2 and oxidant concentrations revealed wide variations from site to site. Multiple-regression analysis showed that high concentrations of oxidants correlated with lowered metallic corrosion rates.

The resulting physical damage functions for corrosion of carbon steel, copper-bearing steel, and weathering steel developed by Haynie and Upham (1971) follow:

Carbon steel:	$Y = 9.013$	$e^{0.00161\ SO_2}$	$(4.768t)^{0.7512 - 0.00582\ OX}$
Copper-bearing steel:	$Y = 8.341$	$e^{0.00171\ SO_2}$	$(4.351t)^{0.8151 - 0.00642\ OX}$
Weathering steel:	$Y = 8.876$	$e^{0.0045\ SO_2}$	$(3.389t)^{0.6695 - 0.00544\ OX}$

where:

Y = corrosion in μm

SO_2 and OX (ozone) are expressed as $\mu g/m^3$

t = time of exposure, years

The correlation coefficient for each of these equations was 0.91. A more recent laboratory investigation by Haynie et al. (1976), however, (see preceding section) has shown that ozone is not a significant corrosion controlling variable.

Mansfeld (1980) made observations at nine test sites in and around St. Louis for 30 months beginning in October 1974 as part of the Environmental Protection Agency's Regional Air Pollution Study to determine the effect of airborne pollutants on galvanized steel, weathering steel, stressed aluminum, marble, and house paint--essentially the same materials examined in the chamber study reported by Haynie et al. (1976). During 1975 and 1976, atmospheric corrosion monitors (ACM) of the type described by Mansfeld and Kenkel (1976) were installed at four sites to measure time of wetness. Each ACM consists of a copper-zinc or copper-steel couple that registers current flow when an electrolytic path forms between the two plates as a result of deposition of water from the air, dew, or rain on corrosion products. The ACM measures the time that the panel is wet enough for the electrochemical mechanism of corrosion to occur. Parameters measured in Mansfeld's study included the following: wind speed, wind

direction, temperature, ozone concentration, total hydrocarbon concentration, total sulfur and NO_x concentration, hydrogen sulfide concentration, sulfur dioxide concentration, RH, sulfate concentration, nitrate concentration, total suspended particle concentration, and time of wetness.

Mansfeld determined weight losses for galvanized steel, weathering steel, house paint, and marble; he removed aluminum tension samples after failure. Mansfeld's data show that damage to a particular material does not necessarily occur at the same corrosion rate at each site. Preliminary statistical analysis of the results failed to show significant correlation between corrosivity and pollutant concentrations. There was substantial error in the measurement of RH, an extremely important corrosion variable. Relative humidity was, therefore, not included in the regression analyses. Concentrations of SO_2 measured by Mansfeld (1980) were generally an order of magnitude lower than the 130 ppb (340 $\mu g/m^3$) concentrations reported by Upham (1967) at urban sites in St. Louis.

In another study (1974), Haynie and Upham exposed enameling steel containing 0.019 percent carbon and 0.028 percent copper at 57 sites in the National Air Surveillance Network (NASN). They measured corrosion by weight loss and quantitatively determined other pollutants, including gaseous sulfur dioxide, total suspended particles, and the amount of sulfate and nitrate in the particles. For a discussion of the measurement methodology for NASN, see Chapter 3. Sulfur dioxide levels ranged from 9 to 374 $\mu g/m^3$, total suspended particles from 11 to 182 $\mu g/m^3$, and RH from 29 to 76 percent. The average temperature remained within a fairly narrow range and was considered constant. The temperature, the quantity of total particles, and the presence of nitrate in the particles did not significantly affect the corrosion rate of steel. The concentration of sulfur dioxide was significant only when sulfate was not included in the regression analysis. At each site, sulfate content of the particles and sulfur dioxide concentration were closely related. On the basis of this study, Haynie and Upham derived the following empirical expression to obtain the best relationship between corrosion of enameling steel and atmospheric SO_2 content:

$$\text{Corrosion} = 325t^{\frac{1}{2}}e^{(0.00275\ SO_2\ -\ 163.2/RH)}$$

where: corrosion is expressed as μm

SO_2 is expressed as $\mu g/m^3$

RH = relative humidity (percent)

t = time

Average RH is a substitute variable for the fraction of time the steel is wet.

Considerable effort has gone into isolating environmental variables that predict long-term corrosion rates. Empirical expressions for corrosion of various steels exposed to the atmosphere (see Table 10-1) have been developed by Oma et al. (1965), Chandler and Kilcullen (1968), and Haynie and Upham (1974). These equations may be used to relate reduction in SO_2 and sulfates to reduction in corrosion of metals, serving as a basis for a benefit appraisal.

TABLE 10-1. SOME EMPIRICAL EXPRESSIONS FOR CORROSION OF EXPOSED FERROALLOYS

Exposure Material	Site	Study Duration	Empirical Equation	Parameter Units	Source	Note/Comments
Steel A	Sheffield England	1 year	$y = 0.51 + 0.01x$	y = corrosion rate in mils/year x = SO_2 in $\mu g/m^3$	Chandler and Kilcullen (1968)	Authors stated that SO_2 and smoke has a major influence on the corrosion rate of steel and accounted for about 50% of the variations found at the different sites. Other factors, such as time of wetness, were found equally important in determining the corrosion rate of steel. 95% confidence limit $\pm$ 0.75 mils for any point on regression.
Steel B	Sheffield England	1 year	$y = 0.82 + 0.006x$	y = corrosion rate in mils/year x = SO_2 in $\mu g/m^3$	Chandler and Kilcullen (1968)	95% confidence limit $\pm$ 0.5 mils for any point in regression.
Enameling steel	NASN sites	1-2 years	$cor = 183.5 \sqrt{t}\ [e^{(0.0642sul-163.2/RH)}]$	cor = depth of corrosion, μm sul = average level of sulfate in suspended particulate, $\mu g/m^3$ RH = average relative humidity, percent t = time in years	Haynie and Upman (1974)	std. dev. 85.0; 95% conf. limits 13.4 lower, 353 upper std. dev. 0.00451; 95% conf. limits 0.0552 lower, 0.0732 upper std. dev. 32.8; 95% conf. limits 97.6
Enameling steel	NASN sites	1-2 years	$cor = 325 \sqrt{t}\ [e^{0.00275\ SO_2-(163.2/RH)}]$	parameter units same as for previous equation except SO_2 = $\mu g/m^3$ SO_2	Haynie and Upham (1974)	Sul and SO_2 relationship defined as sul = 8.9 + 0.0429 SO_2 $\pm$ 2S = 8.2

Matsushima et al. (1974), in studies of low-alloy weathering steels, considered the impact of the washing action of rain, the ease with which water would drain off the surface, and the drying effect of sunlight to determine the effect of these variables on the retention of particles that influence the electrolytic corrosion mechanism and the time of wetness. The authors hypothesized that the geometry of unpainted weathering steels may not favor the development of a protective oxide film of rust. The model structure used in the exposure trials contained horizontal and inclined roofs, vertical wall panels, and window frames. Two sites were chosen: an industrial location and a residential site in the Kawasaki area, which has a cold, dry winter and a hot, humid summer.

The results showed that the successful use of weathering steel is related not only to the severity of pollution but also to the specific interplay between shelter and the uniform washing action of rain. Thus, for areas in which the structural factors are unfavorable, the optimal rust film is slow to form and may deteriorate. Rust films develop and are then destroyed, and the surface never develops a protective film. Generally, boldly exposed surfaces such as horizontal or inclined roofs show the least corrosion.

10.2.1.2.3 Comparison of Ferrous and Nonferrous Metals. Sydberger and Vannenberg (1972) examined the influence of RH and rust on the adsorption of sulfur dioxide on metal surfaces, using radioactive sulfur. The concentration of SO_2 was 0.1 ppm (262 $\mu g/m^3$), and RH varied between 50 and 98 percent. Polished and preexposed samples of iron, zinc, copper, and aluminum were compared for their adsorption properties. Iron, zinc, and copper were preexposed to SO_2 concentrations (100 ppm or 2.6×10^5 $\mu g/m^3$) at 98 percent RH and 22°C for 3 hr. The aluminum samples were preexposed for 30 hr. The principal corrosion product identified by X-ray diffractometry was hydrated metal sulfate. Adsorbed SO_2 was measured at 30-min intervals with a Geiger counter. The corrosion rate at 90 percent RH was initially high for zinc and copper but quite low for aluminum. Adsorption of SO_2 on preexposed iron samples was high. At 80 percent RH, almost all of the SO_2 was adsorbed. The high adsorption rate is perhaps explained by the rapid oxidation of adsorbed sulfur dioxide caused by the catalytic effect of the rust. The initial rate of adsorption on polished iron below 80 percent RH is related to the absence of corrosion; however, at increased humidity corrosion is initiated and the adsorption rate increases.

Of particular significance is the observation that SO_2 adsorption can take place at humidities below the critical humidity (Sydberger and Vannenberg, 1972). This finding suggests that SO_2 will be adsorbed on a rusty iron surface during periods of low humidity and will affect the corrosion rate when humidity rises. The critical humidities for nonferrous metallic surfaces, as summarized from Nriagu (1978) and National Academy of Sciences (NAS) (1977), appear in Table 10-2. The corrosion products of copper and aluminum have an extremely low adsorption capacity below 90 percent RH, confirming the lower sensitivity of these metals to corrosion by SO_2 (see Figure 10-6, from Sydberger and Vannenberg, 1972).

Aluminum is generally considered to be corrosion resistant. It is quite resistant to sulfur oxides when RH is less than 50 percent. At higher humidities aluminum can corrode

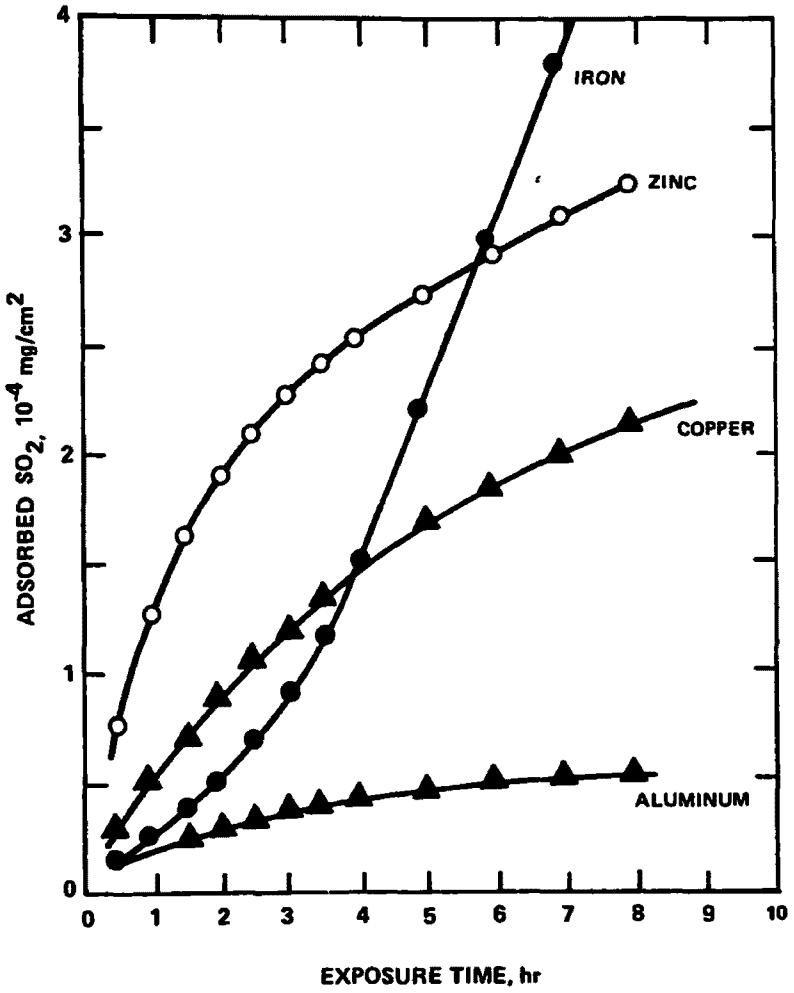

Figure 10-6. Adsorption of sulfur dioxide on polished metal surfaces is shown at 90 percent relative humidity.

Source: Adapted from Sydberger and Vannenberg (1972).

TABLE 10-2. CRITICAL HUMIDITIES FOR VARIOUS METALS

Metal	Critical humidity, percent RH
Aluminum	75-80
Brass	60-65
Copper	65-70
Nickel	65-70
Zinc	70-75

rapidly in the presence of very high SO_2 concentrations forming a hydrated aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] surface deposit. At low concentrations of acid sulfate particles it forms a protective film of aluminum oxide. However, when the film becomes contaminated with dirt and soot particles, there is a change in surface appearance characterized by mottling and pitting. Simpson and Horrobin (1970) reported that aluminum undergoing long exposure in industrial areas displayed white areas of crystalline corrosion products. Aluminum surfaces exposed for periods of more than 5 years to a sulfate concentration of 0.14 ppm (550 $\mu g/m^3$) had pits as deep as 14 mils (0.36 mm). This is, of course, much higher than typical ambient concentrations (see Chapter 5).

Fink et al. (1971) summarized measured corrosion rates and depth of pitting of aluminum surfaces in rural, mild industrial (30 $\mu g/m^3$ or 0.01 ppm SO_2), normal industrial (370 $\mu g/m^3$ or 0.14 ppm SO_2 and 80% RH), and severe industrial areas. Their overall conclusion was that, although some loss of thickness occurred in the first 2 years, structures composed of aluminum and its alloys are resistant to air pollutants.

In another study, Haynie (1976) found that stressed aluminum specimens exposed to SO_2 at concentrations of 79 (0.03 ppm) and 1310 $\mu g/m^3$ (0.5 ppm) lost approximately 8.6 and 27.6 percent of their bending strength, respectively. He also noted that 7005-T53 high-strength aluminum alloy tubing, which contains very little copper, is susceptible to stress-corrosion cracking in industrial environments.

Abe et al. (1971) exposed copper and copper alloys for 2 years in marine, rural, highly industrial, and urban areas in which there was great variation in pollutant and salt content. Analyses of the surface deposits showed the presence of basic sulfate, sulfide, and chloride of copper. The green patina on copper was analyzed and determined to be basic copper sulfate in urban areas and basic copper chloride in seacoast areas. These surfaces were protective against further corrosion.

The formation of these basic copper salts, according to Simpson and Horrobin (1970), can take as long as 5 or more years and will vary with the concentration of sulfate or chloride particles, the humidity, and the temperature. They reported the corrosion rate of copper to

be 0.9 to 2.2 μm/year in industrial atmospheres, compared with 0.1 to 0.6 μm/year in rural areas.

The high corrosion resistance of nickel and copper compared with unalloyed steel is attributed by Sydberger (1976) to the ability of these metals to form a layer of insoluble basic sulfate that protects the metal surface. Such layer formation does not occur on steel.

10.2.2 Protective Coatings

Susceptible materials are generally coated for protection against the effects of exposure. The coatings provide either sacrificial protection or barrier protection. In galvanization, zinc is applied to ferrous metal for sacrificial protection. Thus, while the galvanized surface may suffer corrosion damage, it helps to prevent rusting of steel products such as gutters, cables, wire fencing, and building accessories. Barrier protection is provided by varnishes, lacquers, and paints by sealing the underlying surface material against intrusion by moisture.

10.2.2.1 Zinc-Coated Materials--Zinc is generally exposed as a protective coating for steel products since zinc coating is fairly resistant to atmospheric corrosion. Zinc is anodic with respect to steel; when zinc and steel are in contact with an electrolyte, the electrolytic cell provides current to protect the steel from corrosion with some oxidation of the zinc.

Guttman (1968) carried out a long-term exposure of zinc panels with measurement of the atmospheric factors. He found that zinc is corroded by SO_2 and that time of wetness and concentration of SO_2 are the major factors that determine the rate of corrosion.

Fleetwood (1975) conducted 5-year exposure studies of zinc and iron in a number of locations ranging from dry tropical to industrial. He estimated the service life of galvanized steel to be 15 to 20 years in an industrial area containing pollutants and 300 years in a dry tropical unpolluted area. Kucera (1976) noted strong correlations between the corrosion rate and (1) the adsorption of SO_2 on zinc surfaces and (2) the concentrations of SO_2.

Haynie and Upham (1970) exposed zinc panels in eight cities, continuously monitoring SO_2 concentration and collecting meteorological data, including temperature and RH, from the nearest weather stations. They developed the following empirical equation, which correlates corrosion rate with average sulfur dioxide concentration (for the study range of 10 to 479 μg/m^3) and RH:

$$Y = 0.001028\ (RH - 48.8)\ SO_2,$$

where

Y = zinc corrosion rate (μm/yr),

RH = average annual RH in percent, and

SO_2 = average SO_2 concentration (μg/m^3).

The regression intercept indicated that no corrosion would occur below an average relative humidity of 48.8 percent. This expression gave a reasonably good linear fit with the experimental corrosion results obtained by Haynie and Upham for SO_2 concentration and RH.

Based on the St. Louis study results (Haynie, 1980), the corrosion of small specimens of galvanized steel follows the relationship:

$C_z = 2.32\ t_w + 0.0134\ v^{0.781} \cdot SO_2 \cdot t_w$,

C_z = corrosion in μm

t_w = time-of-wetness in years,

v = wind velocity in m/s, and

SO_2 = $\mu g/m^3$

A theoretical damage coefficient (for purposes of the chapter, damage = any measurable adverse effect) for a pollutant can be calculated from the stoichiometry of a reaction and the deposition velocity. For the reaction between SO_2 and zinc to form zinc sulfate, the coefficient is 0.045, when the zinc corrosion rate is expressed in micrometers per year, SO_2 in micrograms per cubic meter, and the deposition velocity (u) in centimeters per second. For a small zinc or galvanized steel sheet specimen, the material damage coefficient for SO_2 is calculated to be 0.0123 $v^{0.78}$ which agrees well with the above determined empirical coefficient. At a wind velocity of 4 m/sec, the value is 0.0363 (μm/yr)/ ($\mu g/m^3$). For the same conditions, a similar calculation for marble yields a coefficient of 0.136 (μm/yr)/($\mu g/m^3$).

Haynie (1980) restudied the results of six exposure investigations to relate the corrosion of zinc and galvanized steel to the concentration of sulfur dioxide. Each investigation was different and the data were evaluated differently; thus, no direct comparison of the results as they were published was possible. However, in reevaluating the data from each study, Haynie used techniques that permitted the comparison of the various data sets.

The experimental regression coefficients obtained from all of these studies are compared in Table 10-3. The SO_2 coefficient for the chamber study is low, whereas the analogous coefficients for the Community Air Monitoring Program (CAMP) (Haynie and Upham, 1970) and Interstate Surveillance Program (ISP, Cavender et al., 1971) studies are high and agree with each other. The remaining three SO_2 coefficients are generally in good agreement. The average of the time-of-wetness coefficients are within a range of $\pm$ 0.75 from a mean of 1.73 μm/yr.

The specified thickness of galvanized coating varies with intended use. Furthermore, the thickness of a particular coating varies considerably from one point to another. Bird's measurements revealed that 5 percent of coating thickness measurements varied from the mean by more than 46 percent (Bird, 1977). Haynie confirmed this variability with 475 thickness measurements on a single galvanized steel sheet. The life of a coating is generally proportional to its thickness; thus, rusting of the substrate steel will occur first at the thinnest spots and last at the thickest spots. The American Society for Testing and Materials (ASTM) as reported in Haynie (1980) has observed rusting at thin spots on galvanized steel wire, fencing, and sheet exposed to various types of atmospheres over many years. Some of their exposures were started in 1916 and were continued until the test could reveal no

TABLE 10-3. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE SITES

Study	Time-of-wetness coefficient, μm/yr	SO_2 coefficient, (μm/yr)/(μg/m^3)	Number of data sets
CAMP (Haynie and Upham, 1970)	1.15 ± 0.60	0.081 ± 0.005	37
ISP (Cavender et al., 1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman, 1968	1.79	0.024	>400
Guttman and Sereda, 1968	2.47 ± 0.86	0.027 ± 0.008	136
Chamber study (Haynie et al., 1976)	1.53 ± 0.39	0.018 ± 0.002	96
St. Louis (Mansfeld, 1980)	2.36 ± 0.13	0.022 ± 0.004	153

additional information. In the case of sheet, the product was completely rusted and showed perforations. In general, the amount of corrosion at each site varied linearly with time. Corrosion rates at each site were calculated on the basis of time to first rust and time to complete rust for various zinc thicknesses, assuming ±40 percent thickness variability.

Originally, State College, Pa., was selected by ASTM as a control site representing a "clean" rural environment; however, the corrosion was higher there than at five other rural locations including the rural-marine environment of Santa Cruz, Calif., where high relative humidities are expected to accelerate corrosion. ASTM made no pollution measurements but recognized the effects of "industrial" and "severe industrial" environments.

Zinc corroded nearly twice as fast on wire and fencing as it did on sheet, a finding that is consistent with the theoretically predicted effects of surface configuration on SO_2 deposition velocity. One would expect a greater deposition velocity onto fencing than onto sheet material. ASTM noted that fencing corrodes less near the ground than it does near the top because wind velocity increases with height, with a resultant increase in deposition velocity and similar variation of SO_2 concentration. Another factor may be the decrease in concentration near the ground, since both soil and vegetation are sinks for SO_2 (see Chapters 6 and 8).

The average corrosion rates in the Haynie (1980) study shown in Table 10-4 correspond to actual corrosion rates that are two to four times greater when the substrate is wet. Theoretical calculations indicate that the average SO_2 levels at the Pittsburgh site over the long period of exposure were between 350 and 700 $\mu g/m^3$. The average at the Altoona site could have been as high as 1000 $\mu g/m^3$.

From the relationships between theoretical and experimental studies, Haynie (1980) concluded the following:

1. Both short-term laboratory evidence and long-term exposure results for galvanized steel are consistent with theoretical considerations.
2. Damage functions for some materials can be calculated from theoretical relationships that consider factors controlling time of wetness and pollutant fluxes.

TABLE 10-4. CORROSION RATES OF ZINC ON GALVANIZED STEEL PRODUCTS EXPOSED TO VARIOUS ENVIRONMENTS PRIOR TO 1954

	Mean corrosion rate and estimated standard deviation, μm/year	
Site	Sheet	Wire and fencing
Altoona, PA	7.57 ± 0.54	
Pittsburgh, PA	5.63 ± 0.34	10.86 ± 1.02
Sandy Hook, NJ	2.74 ± 0.30	4.37 ± 0.45
Bridgeport, CT		4.25 ± 0.44
Lafayette, IN		2.94 ± 0.34
Ithaca, NY		2.68 ± 0.42
State College, PA	1.27 ± 0.29	2.48 ± 0.24
Ames, IA		1.68 ± 0.19
College Station, TN		1.22 ± 0.43
Santa Cruz, CA		0.83 ± 0.26
Manhattan, KS		0.79 ± 0.27
Davis, CA		0.76 ± 0.42

Source: Haynie (1980)

3. Wind speed and material geometry should be considered in evaluating atmospheric corrosion effects.

Harker et al. (1980) examined the variables controlling the corrosion of zinc by SO_2 and sulfuric acid. They used an aerosol flow reactor. Under steady-state conditions, they made the following measurements:

Environmental Measurements:

- Percent RH and temperature (at two points).
- Average flow velocity (Pitot tube).
- Flow velocity profile (recorded when a steady state had been established).

Aerosol Measurements:

- Aerosol size distribution and number concentration determined at intervals during test by TSI 3050 analyzer.
- Two total-mass filter samples collected.
- Total-deposition sample collected on aluminum foil throughout each experiment.
- TEM deposition grid samples collected continuously.
- X-ray photoelectron spectroscopy samples (both zinc plate and aluminum foil) collected continuously during experiment.

Corrosion rate measurements were recorded continuously by an atmospheric corrosion monitor (ACM), which had been pretreated with either 0.1 N sulfuric acid or ammonium sulfate. The ACM consists of galvanic cells of alternating plates of copper and zinc separated by sheets of plastic insulators. Experimental conditions were selected from the following ranges:

Temperature, °C	12-20
Relative humidity, percent	65-100
Mean flow velocity, m/sec	0.5-8
Sulfur dioxide concentration, ppb (volume)	46-216
Sulfate aerosol mass concentration, mg/m^3	1.2
Aerosol size distribution, μm diameter	0.1-1.0

The factors controlling the rate of corrosion in the Harker et al. study (1980) were RH, pollutant flux, and chemical form of the pollutant. Corrosion occurred only at RH high enough (more than 60 percent) to wet the surface; temperature did not appear to be a controlling factor within the range 12-20°C. The results indicate that on initial exposure SO_2-induced corrosion of zinc proceeds at a rate approximately a factor of two greater than that for the equivalent amount of deposited sulfuric acid aerosol.

The investigators noted deposition velocities of 0.07 cm/sec for 0.1-1.0 μm sulfate aerosols and 0.93 cm/sec for SO_2 at a friction velocity of 35 cm/sec. These factors indicate that the effects of SO_2 will dominate the effects of H_2SO_4 in most urban areas.

10.2.2.2 Paint Technology and Mechanisms of Damage--Compared with other environmental impacts such as sun and precipitation, paint damage due to air pollutants is considered less important. There are at present no standard ASTM procedures for evaluating the effect of SO_2,

nitrogen dioxide, and/or ozone on paints. Degradation by ultraviolet light has received the major emphasis; outdoor test stations have been located where SO_2 levels are low.

The erosion of paint can be measured by loss of thickness of the paint layer, which can result from the chemical action of SO_2 and the action of light and ozone. Film erosion rates are used by paint manufacturers to determine the fail point for their formulations.

In the formulation of paints, the ratio of pigments to film formers is of importance in the overall properties of gloss, hardness, and permeability to water. If the amount of film former is too low, soiling is increased and the paint may lose the film flexibility needed for durability and become brittle. The permeability of paints to water has been reported by Hay and Schurr (1971). High-permeability films are desirable for surfaces that must allow water to pass through, such as wooden exterior walls behind poorly ventilated kitchens. Low-permeability coatings are needed to protect surfaces that corrode when repeatedly moistened. The low permeability of chlorinated rubber is advantageous for use on concrete, a use this coating shares with styrene-acrylic.

Paint films permeable to water are also susceptible to penetration by SO_2 and sulfate aerosols. The absorption of SO_2 was observed by Holbrow (1962), who found sulfites and sulfates in paint, and by Walsh et al. (1977), who used radioactive SO_2 to determine rates and saturation values for SO_2 absorption.

Concentrations of SO_2 encountered in fogs or near industrial sites can increase the drying and hardening times of certain kinds of paints. Holbrow (1962) found that the drying time of linseed, tung, and certain castor oil paint films increased by 50 to 100 percent on exposure to 2620 to 5240 $\mu g/m^3$ (1 to 2 ppm) SO_2. The touch-dry and hard-dry times of alkyl and oleoresinous paints with titanium dioxide pigments were also reported to increase substantially; however, the exposure time of the wet films was not reported. Analysis of the dried films indicated that SO_2 had chemically reacted with the drying oils, altering the oxidation-polymerization process. No studies have been reported on the effects of SO_2 on the drying of latex paints.

Holbrow (1962) also studied the effects of sulfur dioxide on dried paint film. In these experiments, paint films were allowed to dry, were refrigerated, and then were exposed for 15 min to an atmosphere containing 1.2 percent SO_2. The paint films with condensed moisture were finally placed in an accelerated-weathering chamber. For all paints except a pentaerythritol alkyd paint, the gloss decreased significantly after 1 day in the accelerated-weathering chamber. Without the accelerated weathering, the actions of sulfur dioxide and moisture on the paint films produced only a slight reduction in gloss. Holbrow concluded that the sulfur dioxide had sensitized the film, permitting water to be absorbed during the weathering cycle.

Bluing of lead chromate pigment (green) paints has been observed during the early life of the film. Holbrow (1962) reproduced this effect in the laboratory by exposing the film to sulfur dioxide and moisture and then to warmth and moisture. The bluing was probably caused by conversion of the lead chromate pigment to lead sulfate. Holbrow did not attempt to

correlate moisture, temperature, and pollutant concentration, or to obtain dose-response data. Although very high levels of sulfur dioxide were used, this experimentation does indicate that condensation and moisture evaporation are critical in concentrating the pollutant on the surface of exterior paint films; under these conditions, deterioration of the film occurs.

Svoboda et al. (1973) compared pigmented and unpigmented paint film for SO_2 permeability and found that the rate of penetration of SO_2 into a paint film was related to the pigment content. Zinc oxide and titanium dioxide pigments caused a 50 to 70 percent decrease in the rate of penetration of SO_2 into the paint film.

Spence et al. (1975) carried out a chamber study of the effects of gaseous pollutants on four classes of paints formulated for exterior exposure: oil-base house paint, vinyl-acrylic latex house paint, and vinyl and acrylic coil coatings for metals. The house paints were applied to aluminum panels by spraying. The coil coating panels were cut from commercially painted stock. The oil-base paint film was 58 μm thick; the acrylic latex, 45 μm; the vinyl coil coating, 27 μm; and the acrylic coil coating, 20 μm. The exposure chambers controlled temperature, humidity, SO_2, nitrogen dioxide, and ozone. Each exposure chamber had a xenon arc lamp to provide ultraviolet radiation. A dew/light cycle was included; light exposure time was followed by a dark period wherein coolant circulated through racks holding the specimens, thereby forming dew on the panels. Each dew/light cycle lasted 40 min and consisted of 20 min of darkness with formation of dew, followed by 20 min under the xenon arc. The total exposure time was 1000 hr. Damage was measured after 200-hr, 500-hr, and 1000-hr intervals by loss of weight and by loss of film thickness. In evaluating the data, loss of weight was converted to equivalent loss of film thickness.

Visual examination of the panels coated with oil-base house paint revealed that all exposure conditions caused considerable damage. The erosion rate varied from 28.3 to 79.1 μm/year, with an average of 60 μm/year. The investigators concluded that SO_2 and RH markedly affected the rate of erosion of oil-base house paint. The presence of nitrogen dioxide increased the weight of the paint film. A multiple linear regression on SO_2 concentration and RH yielded the following relation:

$$E = 14.3 + 0.0151\ SO_2 + 0.388\ RH,$$

where

E = erosion rate in μm/year,

SO_2 = concentration of SO_2 in $\mu g/m^3$, and

RH = RH in percent.

The authors reported the 95 percent tolerance limits on 99 percent of the calculated rates to be ± 44 μm/year.

The formation of blisters on acrylic latex house paint was noted at the high SO_2 levels. The blisters resulted from severe pitting and buildup of aluminum corrosion products on the substrate. The paint acted as a membrane retaining moisture under the surface and excluding

oxygen which would passivate the aluminum. The vinyl coating and the acrylic coating are resistant to SO_2. The visual appearance of the vinyl coil coating showed no damage. The average erosion rate was low, 3.29 μm/year. The average erosion rate for a clean air exposure was 1.29 μm/year. The acrylic coil coating showed an average erosion rate of 0.57 μm/year.

A study of the effects of air pollutants on paint was conducted by Campbell et al. (1974). The paints studied included oil and acrylic latex house paints, a coil coating, automotive refinish, and an alkyd industrial maintenance coating. These coatings were exposed to clean air, SO_2 at 262 and 2620 μg/m^3, and ozone at 196 and 1960 μg/m^3 (i.e., equivalent to 0.1 and 1.0 ppm of each pollutant). Other controlled study variables included light, temperature, and RH. In addition, one-half of the coatings were shaded during the laboratory exposures. Similar panels (half facing north) were exposed at field sites in Leeds, North Dakota; Valparaiso, Indiana; Research Center, Chicago, Illinois; and Los Angeles, California.

The laboratory exposure chamber operated on a 2-hour light-dew cycle (i.e., 1 hour of xenon light at 70 percent RH and a temperature of 66°C followed by 1 hour of darkness at 100 percent RH and a temperature of 49°C). Coating erosion rates were calculated after exposure periods of 400, 700, and 1000 hours. Estimated erosion rates and statistical characterizations of the results are summarized in Table 10-5. Erosion rates at O_3 or SO_2 concentrations of 0.1 ppm were not significantly different from values for clean air exposures due to high variability of the data. The erosion rates on the shaded specimens were significantly less than the unshaded panel results shown in Table 10-5; panels facing north were also less eroded. At 1 ppm pollutant concentrations erosion rates were significantly greater than controls with oil-base house paint experiencing the largest erosion rate increases, latex and coil coatings moderate increases, and the industrial maintenance coating and automotive refinish the smallest increases (Yocom and Grappone 1976; Yocom and Upham 1977; and Campbell et al., 1974). Coatings that contained extender pigments, particularly calcium carbonate, showed the greatest erosion rates from the SO_2 exposures. Results of field exposures also support these conclusions (Campbell et al., 1974).

10.2.3 Fabrics

Fibers that suffer destructive action upon exposure to acids derived from SO_2 include (1) cellulosic fibers such as cotton and its close relative viscose rayon, a regenerated cellulose, and cellulose acetate; and (2) polyamide fibers such as nylon 6 and 66. Polyester, acrylic, and polypropylene fibers are not damaged directly by SO_2. However, sulfur dioxide concentrations can be a source of absorbed acid which can accelerate the fading of dyes and result in fabric deterioration through chemical reactions. The possibility of higher acid content due to oxidation of sulfur dioxide to sulfur trioxide must be considered (Salvin, 1963).

Brysson et al. (1967) exposed cotton fabrics at 12 different environmental sites in St. Louis, MO. and Chicago, IL, for a period of up to one year (1963-64). The seven sites in the St. Louis metropolitan area represented industrial, urban, suburban, and rural-suburban

TABLE 10-5. PAINT EROSION RATES AND T-TEST PROBABILITY DATA

TABLE 10-5a. PAINT EROSION RATES AND PROBABILITY DATA (T-TEST) FOR CONTROLLED ENVIRONMENTAL LABORATORY EXPOSURES

Type of paint	Mean erosion rate (mil loss X 10^{-5}/hour with 95 percent confidence limits) for unshaded panels and percent probability that differences exit in parentheses		
	Clean air control	SO_2 (1.0 ppm)	O_3 (1.0 ppm)
House paint			
oil	20.1 ± 7.2	141.0 ± 19.0 (99)	44.7 ± 10.5 (99)
latex	3.5 ± 1.5	11.1 ± 1.0 (99)	8.5 ± 5.9 (93)
Coil coating	11.9 ± 2.3	34.1 ± 4.7 (99)	14.9 ± 2.5 (94)
Automotive refinish	1.8 ± 0.8	3.1 ± 2.6 (75)	5.1 ± 1.3 (99)
Industrial maintenance	18.6 ± 5.1	22.4 ± 7.0 (66)	28.1 ± 14.0 (85)

TABLE 10-5b. PAINT EROSION RATES AND PROBABILITY DATA (T-TEST) FOR FIELD EXPOSURES

Type of paint	Mean erosion rate (mil loss X 10^{-3}/month with 95 percent confidence limits) for panels facing south and percent probability that differences exist in parentheses			
	Rural (clean air)	Suburban	Urban (SO_2 dominant, ≈60 μg/m^3)	Urban (oxidant dominant, ~40 μg/m^3)
House paint				
oil	4.3 ± 7.5	14.8 ± 4.9 (99.3)	14.2 ± 4.9 (98.1)	21.0 ± 6.2 (99.2)
latex	1.8 ± 0.5	3.0 ± 0.7 (99.2)	3.8 ± 0.3 (97.8)	6.5 ± 5.6 (94.3)
Coil coating	2.1 ± 0.8	10.0 ± 1.9 (99.9)	9.5 ± 0.8 (99.9)	8.8 ± 1.7 (99.9)
Automotive refinish	0.9 ± 1.1	2.3 ± 0.7 (97.6)	1.6 ± 0.4 (86.2)	1.7 ± 0.4 (91.6)
Industrial maintenance	3.6 ± 1.6	8.2 ± 4.2 (97.3)	6.6 ± 3.9 (91.2)	7.8 ± 2.4 (99.7)

Source: Adapted from Yocom and Upham, 1977.

environments. Four of the Chicago sites represented downtown, industrial, commercial, and rural environments. An additional site was 20 miles southwest of Chicago at Argonne National Laboratory.

Suspended particulate matter in the St. Louis area was measured using periodic 24-hour high volume air samplers. Sulfation values were determined by the lead peroxide candle method. Monthly dustfall measurements were also used. At the Chicago sites, a high volume air sampler measured 24-hour total particulate matter 3 days per week and SO_2 was monitored by bubbler type absorbers for 24 hours twice a week.

Two fabric types were exposed in this study, a desized and scoured cotton print cloth and scoured cotton army duck. Two samples were untreated, two dyed, and one resin treated. Study results indicate that there is a significant relationship between air pollution and both strength degradation and degree of fabric soiling. As shown in Figure 10-7, high pollutant levels (mean sulfation 5 mg SO_3/100 cm^2/day and/or SO_2 concentrations of 0.2 ppm or 520 $\mu g/m^3$) reduced effective fabric strength by one-sixth when compared with low pollution sites (0.5 mg SO_3/100 cm^2/day and/or 0.02 ppm or 60 $\mu g/m^3$ SO_2 concentrations). The relationship between suspended particulate matter and fabric strength degradation was not as good as that for SO_2. No correlation between dustfall and strength degradation/effective life was demonstrated and biological deterioration did not appear to be a major factor in this study (Brysson et al. 1967).

In a review of the Brysson et al. (1967) study, Upham and Salvin (1975) report a correlation coefficient of 0.95 was obtained for breaking strength versus sulfation for cotton duck cloth. The correlation coefficient for the thinner cotton print was 0.96. Of the pollutants measured, SO_2 was most responsible for causing fabric damage (Upham and Salvin, 1975).

Zeronian (1970) carried out laboratory exposures in which cotton and rayon fabrics were exposed for seven days to clean air with and without 250 mg/m^3 (0.1 ppm) sulfur dioxide. Both controlled environments included continuous exposure to artificial light (xenon arc) and a water spray turned on for 18 minutes every two hours. Loss in strength for all fabrics exposed to clean air averaged 13 percent, while the fabrics exposed to sulfur dioxide averaged 21 percent. Zeronian et al. (1971) also exposed fabrics made from manmade fibers--nylon, polyester, and modacrylic--to controlled conditions similar to the cotton exposures, except that the sulfur dioxide level was 486 mg/m^3 (0.2 ppm). They found that only the nylon fabrics were affected, losing 80 percent of their strength when exposed to sulfur dioxide and only 40 percent when exposed in clean air.

In a study designed to determine effects of air pollution on dye fading on fabrics, 67 dye-fabric combinations were tested. The test samples were exposed in the dark at eleven sites representing climatic regimes and urban/rural conditions. High temperatures and humidities appeared to increase fading in the presence of air pollutants. Urban sites

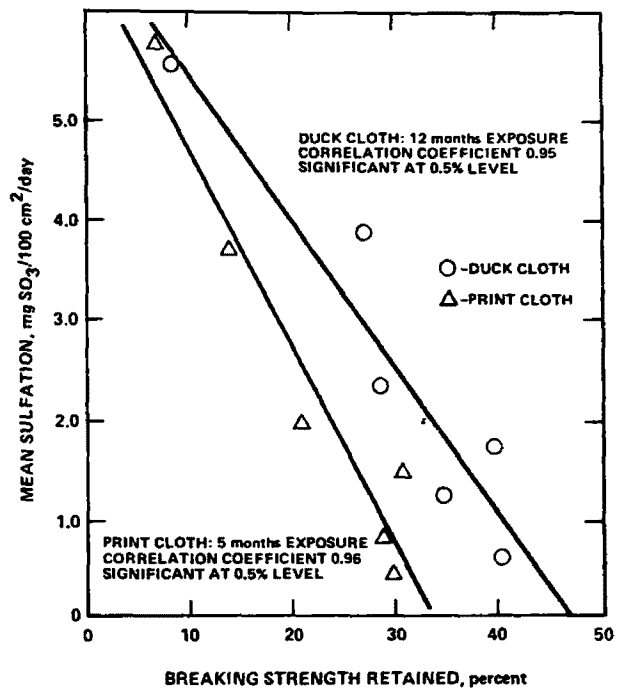

Figure 10-7a. Relationship between retained breaking strength of cotton fabrics and corresponding mean sulfation rate measured at selected sites in St. Louis area.
Source: Brysson et al. (1967).

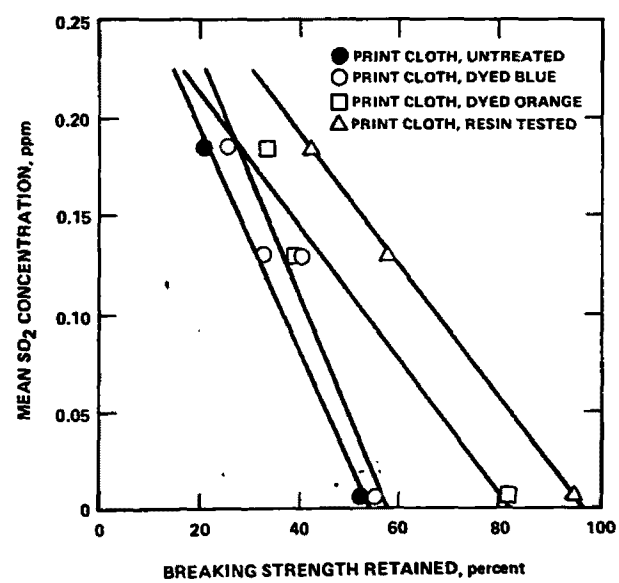

Figure 10-7b. Relationship between retained breaking strength of cotton print cloth samples and mean SO_2 concentration for 5-month exposure at three Chicago sites.
Source: Brysson et al. (1967).

produced significantly higher fading than rural sites. Fading was highest at the site which had the highest SO_2 and TSP concentrations (Beloin, 1972).

10.2.4 Building Materials

The deterioration of inorganic building materials occurs initially through surface weathering. Moisture and salts are considered to be the most important factors in building material damage. Many researchers believe that the mechanism of damage from air pollution involves the formation of salts from reactions in the material. Subsequently, these surface salts dissolve in moist air and are washed away by rainfall. The components of inorganic building materials can react with SO_2 and sulfates (Luckat, 1972; Winkler, 1975; Arnold et al. 1976). Other researchers believe that the role of air pollutants in stone and concrete damage has frequently been overestimated (Riederer, 1974; Niesel, 1979). These authors report that inorganic building material damage is dominantly associated with RH >65 percent and freeze/thaw weathering. Some researchers indicate that microorganisms must also be considered in order to quantify damage to building materials due to ambient pollutant concentrations (Winkler, 1966; Riederer, 1974; Krumbein and Lange, 1978; Eckhardt, 1978; Hansen, 1980). Sulfur chemoautotrophs are well known for the damage they can cause to inorganic materials. These microorganisms (e.g., Thiobacillus) convert reduced forms of sulfur to sulfuric acid (Anderson, 1978). However, the relative importance of biological, chemical, and physical mechanisms have not been systematically investigated. Thus, damage functions definitely quantifying the relationship of pollutant concentrations to stone and concrete deterioration are not available in the literature. Air pollution damage to glass is also not presently quantifiable (Newton, 1974).

10.2.4.1 Stone--Niesel (1979) has recently completed a literature review concerning the weathering of building stone in atmospheres containing sulfur oxides, which includes references from 1700 to the present. In brief, he reports that weathering of porous building stone containing lime is generally characterized by accumulation of calcium sulfate dihydrate in the near surface region. The effect of atmospheric pollutants on the rate of weathering is believed dominantly controlled by the permeability and moisture content of the stone. Migrating moisture serves primarily as a transport medium. SO_2 is sorbed and thus can be translocated internally while being oxidized to sulfates. Reacting components of the building stone are thus leached, the more soluble compounds inward and the less soluble toward the surface, often forming a surface crust.

Sengupta and DeGast (1972) also report that SO_2 sorption causes physical changes in stone involving changes in porosity and water retention characteristics. Removal of calcium carbonate changes the physical nature of the stone surface. The hard, nonporous layer that forms as a result of alternate freezing and thawing may blister, exfoliate, and separate from the surface. If the stone contains some substances that are unaffected by SO_2, the surface can deteriorate unevenly. The conversion of calcium carbonate into calcium sulfate results in a type of efflorescence termed crystallization spalling.

Acidic precipitation also contributes to the weathering process of building stone, according to Gauri (1979). He reported that marble that is directly exposed to rainfall undergoes nearly continuous erosion as the acid dissolves the calcium carbonate, allowing calcite granules to break away and wash off.

10.2.4.2 Cement and Concrete--Portland cement, the major active constituent of concrete, is manufactured by the high-temperature reaction of a mixture of limestone, alumina, silicates, and iron salts found in clay. Cement, the binding agent in concrete, is an alkaline material that reacts with SO_2 and thus also suffers erosion and spalling effects; it can be protected by paint. Concrete is also subject to damage by sodium sulfate. Sulfate-resistant cement can be prepared by reducing the calcium aluminate content. Concrete can also be protected by nonporous paint.

The chemical action of SO_2 or sulfates on cement or concrete can be described as a dual nature mechanism. Calcium hydroxide in cement and concrete can be converted to calcium sulfate, which reacts to form calcium sulfate aluminum hydrate (ettringite), with a substantial increase in volume. Cement for dams and culverts requires special formulation for sulfate resistance when exposed to sulfate concentrations > 200 ppm in water (Nriagu, 1978).

Litvin (1968) examined concrete samples containing Portland cement and marble aggregate with sand at an industrial site in Buffington, Indiana. Some changes were noted in the marble aggregate, but a more observable change was found in the cement portion. Sealants were evaluated as protective coatings; their use was accompanied in some cases by surface efflorescence.

10.2.5 Electrical Equipment and Components

Robbins (1970) and ITT Electro-Physics Labs (1971) studied the damaging effects of SO_2 and particles on electronic components and estimated the cost of this damage. The report by ITT Electro-Physics Labs considered damage to 11 categories of electronic components for which a literature survey indicated that sulfur dioxide pollution would be mainly responsible. However, information gained directly from manufacturers indicated that particles were the major factor in degradation and failure of electronic components and equipment. (See Section 10.3.1) Reduction of SO_2 and particulate concentrations would have little effect on costs for the prevention of corrosion; low concentrations of pollutants would still require essentially the same protective measures. Corrosion-resistant metals are used even in environments where air pollution is minimal, since their cost is far outweighed by the expense of equipment failure.

10.2.6 Paper

Modern papers are manufactured from cellulose. On exposure to acids, paper is hydrolyzed and loses strength. Spedding et al. (1971), in work with radioactive labeling techniques, determined that SO_2 is readily absorbed by paper and oxidized to sulfuric acid by the metallic impurities in the paper. The reaction may also involve the lignins in the paper, resulting in the formation of lignosulfonic acids. Walsh et al. (1977) showed that SO_2 is rapidly absorbed

by uncoated wallpaper and less rapidly absorbed by vinyl-coated paper. Although most paper is used in objects with a short service life, the preservation of documents has been of concern in museums and archives. Coating paper with polymers impervious to gases is an established process. The preservation of books in libraries is of major concern. The extent of the problem is emphasized by the estimate that 50 percent of the books printed between 1900 and 1940 are in need of conservation. The New York Public Library conserves books by microfilming, lamination, and electrostatic reproduction (Kingery, 1960). The library spent $900,000 between 1952 and 1967 to microfilm books that had deteriorated (Waddell, 1974).

10.2.7 Leather

Leather has a high capacity for absorbing SO_2. Spedding et al. (1971) reported that the rate of SO_2 diffusion to the leather surface is the controlling factor in SO_2 uptake. The formation, in the presence of water, of sulfuric acid is followed by hydrolysis of the protein (collagen) of which leather is principally composed. This weakening of leather causes cracking and ultimately results in reduction of the leather to a red-brown powder (Spedding et al., 1971; Yocom and Grappone, 1976).

The destruction of leather by absorption of SO_2 has long been known and was described in detail by Prenderleith (1946). The buildup of sulfuric acid in aged leathers correlates with deterioration, which can be reduced by inactivating the sulfate ion and by pH buffering. Deterioration of leather is important in bookbinding and in leather upholstery; the use of artificial leathers has reduced damage costs.

10.2.8 Elastomers and Plastics

The deterioration of natural rubber and synthetic elastomers under weathering conditions has been studied extensively. Heat, light, oxygen, certain metallic ions, and particularly ozone cause deterioration; but there is no mention in the literature of SO_2 damage to rubber. In fact, rubber is used as an acid-resistant coating. The problem of determining ambient air pollution effects on rubber is complicated by the presence of ozone, which attacks the double bonds in both natural rubber and the butadiene-styrene and butadiene-acrylonitrile synthetics.

Haynie et al. (1976) conducted a chamber study on rubber to determine the effects of ozone, SO_2, and nitrogen dioxide under controlled conditions of temperature, humidity, and light. Exposures were made at concentrations of 0.1 and 1.0 ppm for each pollutant (in $\mu g/m^3$; 262 and 2620 for SO_2, 196 and 1960 for O_3 and 188 and 1880 for NO_2). As expected, ozone was responsible for accelerated cracking of the rubber. Sulfur dioxide did not have any effect.

Verdu (1974) presented a theoretical study of the effect of air pollutants on the weathering of plastics. He attributed a direct deteriorating effect on plastics to ozone and suggested that air pollutants such as sulfur dioxide may form active compounds through photochemical reactions leading to oxidation chain reactions. In light-exposure trials, SO_2 increased the rate of degradation of polystyrene.

10.2.9 Works of Art

Although works of art are composed of materials already discussed in earlier section of this chapter, they are briefly treated here as a separate category because the cost of the materials involved does not represent the cost of the item.

The deteriorating effects of SO_2 and particles are well known to museum conservators whose function is to preserve and restore works of art. The rate of pollutant-related deterioration has increased markedly in the last 50 years. The damage is striking in Europe, where ancient buildings, paintings, frescoes, stained glass windows, bronze sculptures, and marble statuary have suffered deterioration.

Newton (1974) has investigated the cause of deterioration of medieval stained glass windows. He found that the main cause of decay is the leaching of potassium ions from the silicate glass by condensed water. Another cause is SO_2, which produces opaque white crusts containing $CaSO_4 \cdot H_2O$ and syngenate ($Ca \cdot CaSO_4 \cdot K_2SO_4 \cdot H_2O$). The poor durability of medieval glass is due to its high content of alkaline earths such as lime and magnesia.

Riederer (1974) conducted a study of the corrosion of bronze sculpture by air pollutants. Sulfates were found in the corroded surfaces.

The dome of the cathedral in Cologne, located in a highly polluted urban area, has suffered serious erosion of its sandstone due to the reaction of sulfur acids with calcium carbonate to form calcium sulfate, which is leached out by rain (Luckat, 1976). Decay and deterioration of the Taj Mahal in India has also been attributed to sulfur dioxide and other pollutants emitted from a nearly petrochemical complex (Gajendragakar, 1977).

Damage occurring in Venice, Florence, Rome, Athens, London, and Cologne has been attributed to the effect of SO_2 from industrial areas in these cities (Yocum and Upham, 1977). The United States is also concerned about the deterioration of public buildings and monuments. The National Bureau of Standards was asked by the National Park Service to investigate methods for preservation of stone after erosion was noted in the facade of the Lincoln Memorial in Washington, DC (Sleater, 1977).

Sleater (1977) investigated damage to stone from the action of SO_2, salt, sodium sulfate, and light. Conservation materials including epoxy resins, fluorosilicates, and silicone resins were evaluated. The conservation methods recommended to the National Park Service varied with the exposure conditions.

The damage to the Acropolis caused by SO_2 and SO_3 has resulted in a massive interdisciplinary effort by the Greek government to protect the ancient buildings from further deterioration (Yocom, 1979).

10.2.10 Review of Damage Functions Relating SO_2 to Material Damage

Even the most reliable damage functions must be used with caution. Those listed in Table 10-6 were selected on the basis of their treatment of independent variables and their inclusion in major literature reviews. Time-of-wetness (often expressed as RH above a critical value) is the most important variable in these damage functions.

TABLE 10-6. SELECTED PHYSICAL DAMAGE FUNCTIONS RELATED TO SO_2 EXPOSURE

Material	Reference	Dose-Response relationships	R^2
Zinc	Haynie and Upham, 1970	$Y = 0.001028\ (RH - 48.8)\ SO_2$	0.92
Galvanized steel	Haynie et al., 1976	$corr = (0.0187\ SO_2 + e^{41.85 - 23{,}240/RT})t_w$	0.91
Galvanized steel	Haynie, 1980	$corr = 2.32\ t_w + 0.0134 v^{0.781} SO_2 t_w$	
Oil-base house paint	Spence et al., 1975	$Y = 14.3 + 0.0151\ SO_2 + 0.388\ RH$	0.61
Enameling steel	Haynie and Upham, 1974	$corr = 325\ t^{\frac{1}{2}}\ e^{(0.00275\ SO_2 - 163.2/RH)}$	
Weathering steel	Haynie et al., 1976	$corr = [5.64\ \sqrt{SO_2} + e^{(55.44 - 31{,}150/RT)}]\ \sqrt{t_w}$	0.91

corr = corrosion, μm
Y = corrosion/erosion rate, μm/yr
SO_2 μg/m^3
R = gas constant (1.98 cal/gm mol/°K)
RH = percent average annual relative humidity
t_w = time-of-wetness in years
v = wind velocity in m/s
T ≡ °K
t ≡ time of exposure, years

Functions for zinc or galvanized steel appear to show the best fit, followed by the functions for oil-based house paint. The field studies by Haynie and Upham (1970) and Haynie (1980) and chamber study by Haynie et al. (1976) incorporated critical variables and provided relatively reliable damage functions for galvanized steel. The functions selected for weathering and enameling steel and for oil-based paint also utilized these critical environmental variables.

When these functions are used to estimate damage, other factors must be considered, such as the amount of exposed (uncoated) metal, the percentage of buildings with oil-based (not Latex) paint, and temperature and humidity variables (sites in the arid southwest compared with sites in the relatively humid northeast).

10.3 PARTICULATE MATTER

A report by the National Academy of Sciences (1977) on airborne particles notes that deposition of dust and soot on building materials not only significantly reduces the esthetic appeal of structures, but also, either alone or in concert with other environmental factors, results in direct chemical attack. Because of the paucity of data (see Chapter 5) regarding total suspended particulate matter (TSP) size distribution and composition, it is difficult to determine the specific types of particles and chemical constituents that have damaged or soiled a particular structure. As will be discussed in the following section, chemical composition of particulate matter is highly important to its corrosiveness; particle size may be important. Since information on both composition and size is spotty and incomplete, it is difficult to develop physical damage functions associating either TSP or any particular size function with materials damage or soiling. Research is under way to address the role of particle size in soiling of paint.

10.3.1 Corrosion and Erosion

Early studies indicated that suspended particulate matter played a significant role in metal corrosion. Sanyal and Singhania, writing in 1956, termed the influence of suspended particulate matter "profound." They ascribed the corrosive effects of particles to (1) electrolytic, hygroscopic, and/or acidic properties and (2) their ability to sorb corrosive gases, e.g., sulfur dioxide. It has been pointed out that it is quite difficult to predict corrosion rates separately for sulfur dioxide and particulate matter since they frequently coexist at high levels (Chandler and Kilcullen, 1968). Other field studies have established no conclusive correlation between total suspended particulate matter and corrosion (Mansfeld, 1980; Haynie and Upham, 1974; and Upham, 1967), though further analysis of recent data is still under way.

At an RH exceeding 60 percent, air polluted with SO_2 and PM results in a much more rapid corrosion rate than air polluted with SO_2 alone (Yocom and Grappone, 1976; Johnson et al., 1977). Kottori (1980) observed that zinc and galvanized steel corrosion rates appeared to be related to the sulfate content of TSP. Chloride content of dust also may contribute to accelerated corrosion of steels (Gibbons, 1970; Bresle, 1976).

Barton (1958) reported that dustfalls contribute to the initial stages of corrosion but that their influence becomes less important as a layer of rust forms. Two classes of particulate matter appear to be definitely associated with corrosion: hygroscopic salts (including those of natural origin such as sodium chloride) and acid smut.

A review of atmospheric factors affecting metal corrosion provides evidence of a relationship between salinity and corrosion (Guttman and Sereda, 1968).
Corrosion of metals can be accelerated by deposition of particles due to their hygroscopic nature. The influence of hygroscopic substances on metal corrosion rates has been previously discussed in section 10.2.1.1.4. As also discussed in section 10.2, particles can disrupt the protective oxide films formed on metal surfaces such as nickel, copper, aluminum and stainless steel resulting in pitting (Russell, 1976; NAS, 1977). Russell (1976) noted that airborne particles often play an important role on the attack by sulfur oxides on electrical contact surfaces by acting as points for the concentration of active ionic species.

Acid smut is highly corrosive, sticky material formed in and emitted mainly from furnaces burning liquid fuels containing sulfur, notably in power plants (Ireland, 1968). This material would not usually be considered suspended particulate matter, as it occurs as agglomerates of carbon, ash, and sulfuric acid up to 0.5 cm or more in diameter which fall close to the source (Rowden, 1968; Potter, 1971). According to one report, acid smut mainly settles out within 400 meters of the source under conditions of light wind (Hoshizawa and Koyata, 1970).

Japanese investigators analyzed a large (>10 drums [sic]) sample of acid smut and found the sulfuric acid content to be 30 percent (Oyama et al., 1974). Damage to painted surfaces, automotive finishes, and even agricultural crops can be substantial. As noted in a review of residual oil firing problems, "public reaction can be quite severe" (Exley, 1970). A report on the status of "public nuisances" in the electric power industry of Japan reported progress in determining the cause of acid smut and in developing preventive techniques (Overseas Public Nuisance Study Mission, 1965).

Finishes on automobiles parked near industrial sites have often been severely damaged. Staining and even pitting of auto finishes have been traced to iron particles from nearby industrial operations. Cars parked near brick buildings being demolished have been damaged by alkali mortar dust during humid weather. Repainting of damaged auto finishes was often required because color changes were not reversible by washing or polishing (Fochtman and Langer, 1957).

Parker (1955) reported that large numbers of black specks collected on freshly painted buildings in industrial areas. The exterior surfaces of these buildings became distinctly soiled and required cleaning or repainting in 2 or 3 years, depending on the particulate concentration in the air. When particulate matter became embedded in the paint film, the coating was both esthetically and physically damaged. Embedding of particles provides nucleation sites at which other pollutants can concentrate. Cowling and Roberts (1954)

suggest that particles promote the chemical deterioration of paint by acting as wicks to transfer the SO_2 corrosive solution to the underlying surface.

10.3.2 Soiling and Discoloration

Soiling is the accumulation of particulate matter on the surface of a material. As defined by Pfafflin and Ziegler (1976), soiling arises from the deposition of particles less than 10 μm by impingement on surfaces to thus mingle with settled dust. Soiling produces a change in reflection from opaque materials and reduces light transmission through transparent materials (Beloin and Haynie, 1975; NAS, 1977). Soiling due to airborne particles from manmade sources results in increased cleaning costs for building and other materials and reduction in the useful life of fabrics.

10.3.2.1 Building Materials--Under high wind conditions, large particles entrained in the windstream actually result in a slow erosion of surfaces similiar to sandblasting. Particles also fill surface pores of many sandstones causing them to become uniformly darkened. Particles can contribute to chemical decay of marble, limestone and dolomite stone work, and concrete structures if they carry acids and soluble salts (NAS, 1977). Dose-response relationships were developed for suspended particulate matter and various building materials by Beloin and Haynie (1975).

10.3.2.2 Fabrics--Although particulate matter obviously soils fabrics, researchers have noted that it is only damaging when the particles are highly abrasive and the fabrics are frequently flexed. Curtains hanging in open windows, serving as filters in polluted areas, provide a good example. Weakened as a result of such exposure, curtains often split in parallel lines along the folds. The more tightly woven the cloth, the more resistant it is to soiling (NAS, 1977).

Because of soiling, fabrics must be washed more often. Excessive washing may reduce fabric strength, leading to a poorer appearance and concomitantly to shortened life expectancy. However, sunlight, water vapor, SO_x, NO_x and ozone concentrations are believed to affect the service life of fabrics more significantly. Insolation decoloration is considered to be the most important service life reduction factor (NAS, 1977). Effects of elevated sulfur oxide concentrations have been previously discussed.

10.3.2.3 Household and Industrial Paints--Exterior paints can be soiled by liquids and by solid particles composed of soot, tarry acids, and various other constituents. Beloin and Haynie (1975) have compared the rates of soiling by different levels of TSP on six different building materials over a 2-year period. The mean annual PM concentrations at the five study sites ranged from 60 $\mu g/m^3$ for a rural residential location to 250 $\mu g/m^3$ for an industrial residential environment. The exposed materials included painted cedar siding, concrete block, brick, limestone, asphalt shingles, and window glass. As determined by reflectance measurements, the degree of soiling of painted surfaces was directly proportional to the square root of the PM dose, accounting for 74 to 90 percent of the measured variability. The results of regression for soiling of building materials as a function of TSP dose is included in Table 10-7. As one example, the linear regression results of soiling of acrylic emulsion

TABLE 10-7. RESULTS OF REGRESSION FOR SOILING OF BUILDING MATERIALS AS A FUNCTION OF TSP DOSE

Material	N	A	B	S_A^2	S_B^2	S_E^2	R^2
Oil base paint	400	89.43	-0.2768	0.0641	0.000069	7.6510	0.745
Tint base paint	400	86.13	-0.2618	0.0571	0.000061	6.8265	0.738
Sheltered acrylic emulsion paint	400	91.54	-0.593	0.1156	0.000123	13.8143	0.880
Acrylic emulsion paint	720	90.79	-0.4131	0.0497	0.000026	8.3791	0.902
Shingles	48	43.50	-0.199	0.5771	0.000258	7.6992	0.769
Concrete	160	41.75	-0.0458	0.1338	0.000080	7.5011	0.143
Coated limestone	80	44.57	+0.0779	0.2464	0.000164	6.9046	0.347
Uncoated limestone	80	46.99	-0.0503	0.1500	0.000089	4.2035	0.266
Coated red brick	80	12.95	-0.0296	0.0223	0.000013	0.6255	0.459
Uncoated red brick	80	14.88	-0.0374	0.0331	0.000020	0.9274	0.477
Coated yellow brick	80	45.05	-0.1133	0.5337	0.000317	14.9533	0.342
Uncoated yellow brick	80	43.21	-0.1133	0.2740	0.000168	7.6773	0.503
Glass	45	0.2806	+0.0314	0.008077	0.000007	0.6851	0.340

Note: Equation used in this regression analysis was reflectance = $B(\text{TSP} \times \text{months of exposure})^{\frac{1}{2}} + A$.

N, Number of data sets (dependent upon the number of controlled variables in the factorial experiment).

A, Intercept of linear regression.

B, Slope of linear regression.

S_A^2, Estimated variance of intercept.

S_B^2, Estimated variance of slope.

S_E^2, Residual variance (error).

R^2, Correlation index (fraction of variability accounted for by regression).

Source: Abstracted from Beloin and Haynie, 1975.

house paint by exposure to suspended particulate matter is shown below: (640 samples, R^2 = 0.896)

$$\ln(92.5 \quad Y) = -0.311 + 0.345 \ln(SP) + 0.612 \ln(t)$$

Where: 92.5 = Initial reflectance value (80 samples)

Y = Measured percent reflectance (Photvolt Model 625)

SP = Average TSP concentration ($\mu g/m^3$)

t = Exposure time (months)

Based on this equation, Figure 10-8 was prepared to summarize soiling of acrylic emulsion house paint as a function of exposure time and particulate concentrations. Although it is recognized that socio-economic factors control ability and motivation to maintain clean surfaces (Beloin and Haynie 1975), estimations of repainting frequencies can be formulated. Assuming an individual responds to a defined change in reflectance of house paint by repainting, that person will repaint a house twice as often in an environment with a TSP concentration of 260 $\mu g/m^3$ in comparison to 75 $\mu g/m^3$. Specifically, at a 35 percent change this houseowner would repaint every 4 years when TSP is 75 $\mu g/m^3$ and every 2 years when 260 $\mu g/m^3$.

10.4 SUMMARY, PHYSICAL EFFECTS OF SULFUR OXIDES AND PARTICULATE MATTER ON MATERIALS

Reviewing the facts presented in Sections 10.2 and 10.3, it should be clear that the best data base for association of sulfur oxides to materials effects is corrosion of metal and that the parallel case for particulate matter is soiling. Of the damage functions developed for corrosion of metals by sulfur oxides, the one for zinc appears to show the best fit. Slightly less well established are relationships for sulfur oxide exposure and corrosion of other metals. There is evidence that particulate matter aggravates corrosion, especially when coexistent with sulfur oxides. This is most likely due to the hygroscopic salt content of the particulate matter. However, no mathematical expression of the relative contribution of particulate matter to corrosion of metal has been established.

Both particulate matter and sulfur oxides have been shown to damage paint. Damage functions for erosion of various paint by sulfur oxides and for soiling of paint by particulate matter have been developed. The varying properties of the several types of paint employed for exposed materials make it difficult to construct mathematical expressions for effect of particulate matter and/or SO_2 on all paints.

Building materials also are eroded by sulfur oxides and soiled by particulate matter. That damage is attributable to both pollutants is established; quantitative general relationships between ambient concentration and effect are, however, lacking. For erosion of building materials, particularly stone and concrete, the contribution of sulfur oxides relative to other agents is not clear. As for soiling, though some damage functions have been developed, the lack of understanding of the role of particle size and composition makes it difficult to generalize about soiling effects of all suspended particulate matter on all building materials.

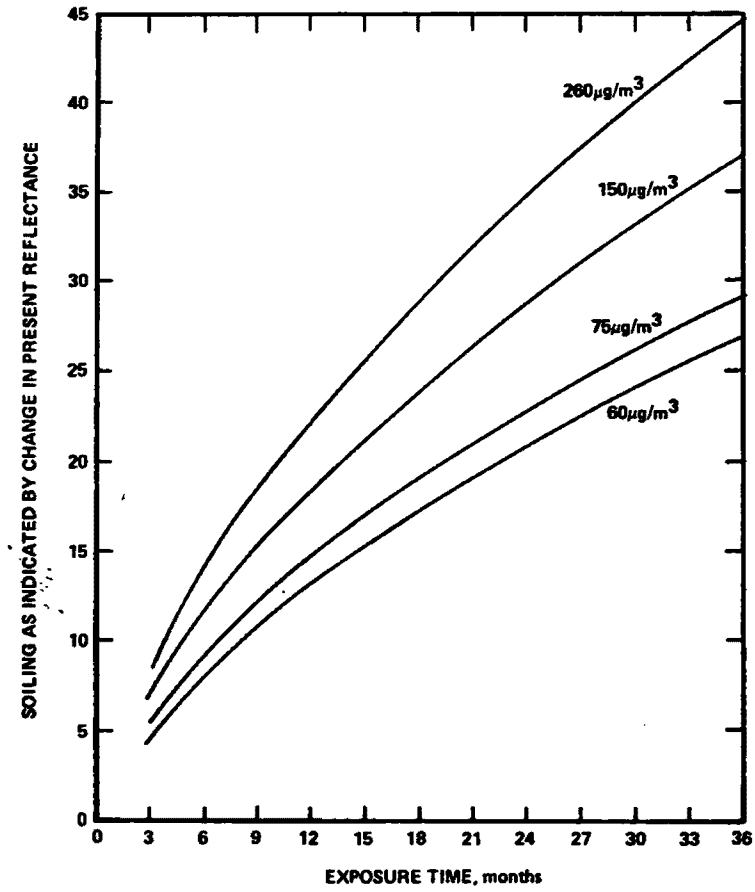

Figure 10-8. Representation of soiling of acrylic emulsion house paint as a function of exposure time and particle concentrations.

Source: Abstracted from Beloin and Haynie (1975).

Concerning effects of particulate matter and/or sulfur oxides on other materials, the data base is even less well established. There is evidence to show that damage occurs to fabrics, leather, paper, glass, and plastic, and to works of art composed of one or many materials. This evidence is mainly qualitative and spotty. For these materials, there are insufficient data to develop reliable estimates of effects attributable to specific ambient pollutant concentrations.

10.5 ECONOMIC DAMAGE OF AIR POLLUTION TO MATERIALS--SULFUR OXIDES AND PARTICULATE MATTER

10.5.1 Introduction

The task of estimating costs of air pollution effects on materials involves treatment of many variables, some of which are difficult to quantify and relate to other factors bearing on costs. Several approaches to the problem have been reported. These are: (1) the physical damage function approach, (2) the non-market approach, and (3) the indirect market approach.

The goal of all of the approaches is to estimate the total monetary damage caused by air pollution, in this instance, by particulate matter and/or sulfur oxides. Monetary damage, as defined by Maler and Wyzga (1976), is "the total compensating variation of a change that is detrimental to the environment." Monetary damage comprises two subsets of loss: financial loss is "that part of the monetary damage which is realized by changes in expenditure, while amenity loss is the difference between monetary damage and financial loss."

There are several types of financial losses resulting from damage to materials and soiling: (1) reduced service life of a material, (2) decreased utility of a material, (3) necessity for use of suitable substitute materials, (4) losses due to an inferior substitute, (5) protection of suspectible materials, and (6) additional required maintenance, including cleaning. The major losses of amenity, as defined by Maler and Wyzga, are "those of enduring and suffering soiled, damaged, or inferior products and materials because of pollution," in this case particulate matter and/or sulfur oxides. In addition, amenity losses are suffered when pollution damage repair or maintenance procedures results in inconvenience or other delays in normal operations. Some of these losses, such as effects on monuments and works of art, are especially difficult to quantify (Mäler and Wyzga, 1976).

In calculating monetary damage, the approach selected will vary depending upon whether financial losses or losses of amenity are to be emphasized, the type of damage being considered, and the availability of information. Regarding pollutant effects on materials, the literature has been dominated by calculations of financial loss based on the physical damage function approach. Sources of error in financial loss functions using this approach include the following: (1) present techniques do not reflect the recent introduction of resistant materials which last longer and require less maintenance; (2) estimates assume that galvanized steels are left uncoated; (3) many materials may wear out before they are significantly damaged by pollutants (Glass, 1978).

One area not dominated by the physical damage approach has been the estimation of monetary damage associated with soiling. In these studies, loss of amenity has been considered, since socioeconomic variables are heavily involved. The approaches employed

reflect the shift in emphasis. Non-market and indirect market approaches have been used to relate changes in air quality to changes in the amount of money people are willing to pay for improvement in air quality (reduction in air pollution). Documentation of this relationship may be sought through survey of affected individuals or through development of relationships between environmental quality and available data on price differentials. A major source of error in these approaches is that they demand that all factors other than air quality that affect cost must be accounted for. It is also very difficult to distinguish among the effects of many different air pollutants.

Recently, the nonmarket and indirect market approaches have been increasingly employed to estimate both financial loss and loss of amenity. To date, such studies have not been found more suitable for regulatory decision-making guidance than the body of literature resulting from employment of the more traditional (physical damage function) approach. All approaches are limited by the difficulty in quantification of the human response to damage based upon the ability and the incentive to pay additional costs. (Yocom and Grappone, 1976).

10.5.2 Economic Damage to Materials

10.5.2.1 Metals--Realistic estimation of the economic damage to metals attributable to sulfur oxides and particles must take into account several factors, including avoidance costs, such as the costs of specific protective treatment. For metals, these costs include the use of anticorrosive primers, the practice of sandblasting before painting, and the use of paints that are resistant to acid.

A recent report published by the U.S. Department of Commerce (Bennett et al., 1978) examined the cost of corrosion in the United States in 1975. Unfortunately, the developed damage costs were not pollutant-specific and were not associated with ambient concentrations of pollutants. A total annual metallic corrosion cost of $82 billion was estimated with a model which incorporated a broad range of cost items (e.g., materials, labor, energy, and technical capabilities). About 40 percent of this cost, or $33 billion, was considered avoidable. Within this avoidable cost is, of course, the cost of air pollution, a portion of which is in turn the cost of metallic corrosion resulting from particulate matter and/or sulfur oxides. The figure of $33 billion is thus only useful as an upper limit for present purposes.

Fink et al. (1971) estimated that corrosion of external metal structures caused by air pollution costs $1.45 billion annually in the United States, as shown in Table 10-8. As is the case for the extensive Bennett et al. (1978) Department of Commerce report, these studies also were not specific to single pollutants nor were the damage costs associated directly with ambient pollutant concentrations. Furthermore, in some cases material damage resulting from causes other than air pollution was included in cost estimates (e.g., the Fink et al. study included corrosion inside pipes of industrial systems). On the other hand, Haynie (1974) noted that within Fink's estimate of metal corrosion costs, damage to structural systems primarily constructed of galvanized steel accounted for more than 90 percent of the cost. Haynie reasoned that, based on Fink's data, the accelerated corrosion of zinc by sulfur dioxide accounts for more than 90 percent of corrosion caused by air pollutants.

TABLE 10-8. SUMMATION OF ANNUAL EXTRA LOSSES DUE TO CORROSION DAMAGE BY AIR POLLUTION TO EXTERNAL METAL STRUCTURES FOR 1970

Steel system or structure	Basis for calculation	Annual loss in $1000
Steel storage tanks	Maintenance	$ 46,310
Highway and rail bridges	Maintenance	30,400
Power transformers	Maintenance	7,450
Street lighting fixtures	Maintenance	11,910
Outdoor metal work	Maintenance	914,015
Pole-line hardware	Replacement	161,000
Chain-link fencing	Maintenance and replacement	165,800
Galvanized wire and rope	Replacement	111,800
Transmission towers	Maintenance	1,480
		$1,450,165

Source: Fink et al. (1971).

The economic damage from corrosion can also be estimated by determining the annual cost of industrial paints used for corrosion control. This cost is estimated by totaling the costs of surface preparation, paint, and labor. Coatings applied at this combined cost would protect metal structures against corrosion for about 10 years, whereas "ordinary" coatings of paint would provide protection for only 2 years. Painting of structural steel in bridges was investigated by Moore and O'Leary; (1975) the practice involves sandblasting the steel to produce a rust-free surface and to remove mill scale. Without such surface preparation, water is immediately absorbed and sets up a corrosion system, rusting occurs, and the paint surface deteriorates in 2 to 3 years. The metal surface is protected by primer that inhibits rust formation, and the primer coat is covered with two coats of SO_2-resistant paint, such as vinyl resin, which is substantially more expensive than household paint. Estimates have been developed by Banov (1973), Michelson and Tourin (1967), and others to reflect these preparation and painting costs for protection of metal structures. However, sound fractional allocation of these costs to sulfur oxide material damage is not available in the literature.

Damage from pollutants during the manufacture of electrical components must be controlled even in clean environments. To prevent such problems, parts are fabricated in "clean rooms" with filtered air. If equipment malfunctions in the plant or in service, additional maintenance costs are incurred for cleaning, repair, or replacement of defective equipment. ITT (1971) estimated $15.5 million per year in added costs for clean rooms and maintenance. Robbins (1970) conducted a survey of the effects of SO_2 and particles on electrical contacts such as in switches, relays, connectors, and computers. To reduce corrosion, contacts are electroplated with corrosion-resistant metals such as gold, platinum, palladium, and silver. Less expensive metals are susceptible to corrosion failure, mostly from the action of SO_2 and H_2S. Robbins estimated that 15 percent of the gold and platinum used in the United States for electrical contacts in 1970 was for the specific purpose of combating SO_2 corrosion, with the remainder going for protection against other environmental pollutants. However, protection against all deleterious environmental conditions is routinely provided in clean environments, due to high costs of replacement associated with electrical system downtime. Thus, costs for protection of electrical hardware cannot be allocated directly to ambient sulfur oxide and/or particulate matter concentrations.

10.5.2.2 Paints--Spence and Haynie (1972) presented a survey and economic assessment of the deterioration of exterior paints ("trade paints") caused by air pollution. Included in this category were both oil-base paints and latex paints containing polyvinyl acetate-acrylic as the binder. The total annual economic damage to exterior household paints was estimated at $540 million (1972 prices), including paint loss and a labor factor of three times the cost of the paint. Unfortunately, damage functions were not available for use in developing this estimate. Furthermore, the estimated damage cost reflects the impacts of all pollutants; no specific attribution of costs to particulate matter or sulfur oxides is possible.

Salmon (1970) estimated that the annual cost of soiling of household paint would be $35 billion if surfaces were maintained as clean as they are in a clean environment in this qualitative study. The annual cost of deterioration damage to paints was estimated to be $1.2 billion.

Michelson and Tourin (1967) investigated the frequency of house repainting as a function of suspended particulate concentration. Questionnaires were sent to residents of three suburbs of Washington, DC (Suitland, Rockville, and Fairfax) and two cities in the upper Ohio Valley (Steubenville and Uniontown). Data were compiled from the questionnaires to show maintenance intervals for exterior repainting in each of the five communities, but paint types were not reported. In Steubenville, where the mean annual particulate concentration was 235 $\mu g/m^3$, repainting occurred about every year. In Fairfax, where the mean annual particulate concentration was 60 $\mu g/m^3$, repainting occurred every 4 years. Thus, maintenance frequency increased as particulate concentration increased. The results of this investigation suggest that a significant relationship exists between frequency of repainting and particulate concentration. However, to establish a more definite correlation, additional maintenance data are needed, particularly for cities with mean annual particulate concentrations greater than 150 $\mu g/m^3$. Any correlation of frequency of repainting with concentration of particulate matter must take into account the fact that other pollutants are usually present in high concentration where particle counts are high. Socioeconomic factors also must be considered.

Booz, Allen and Hamilton (1970), in a study conducted for EPA, reported on painting maintenance frequencies in several zones of the Philadelphia metropolitan area with different population characteristics, climates, and types of industry. Socioeconomic factors were delineated by pollution zone; however, paint types were not reported. The percentage of households with incomes of less than $6000 increased with pollution level, a finding that may partially explain why there was no statistically significant correlation between painting frequency and particulate level.

10.5.2.3 Economic Cost of Soiling--Studies on soiling have in some approaches been limited to household cleaning costs. Other studies employ differences in property values or willingness to pay as the basis for cost estimates. In the study by Booz, Allen and Hamilton (1970), $5 billion for annual household cleaning costs was attributed to particulate pollution. This amount did not include laundering, dry cleaning, and personal care items (i.e., face and hair). The report has been criticized because it omits some sources of damage that might be responsible for extra maintenance. There is doubt as to which cleaning and maintenance operations are really sensitive to air particulate levels. Also, the labor of the homemaker was not added to the cost of the cleaning materials, and the number of urban homes surveyed was small.

Watson and Jaksch (1978) estimated physical soiling and frequency-of-cleaning functions using the study of Beloin and Haynie (1975) to establish the relationship between level of particulate matter and soiling rate and the work of Esmen (1973) to estimate various levels of

particulate soiling for rural, suburban, and industrial locations. Watson and Jaksch (1978) reported that the frequency of the low-cost cleaning operations depended on the level of airborne particles but that the frequency of professional house painting was unaffected by variation in airborne particle levels.

Watson and Jaksch (1978) concluded that 537 to 3816 million dollars (1971 dollars) can be saved per year in the United States in the form of net welfare benefits if the secondary TSP standard of 60 mg/m^3 can be met. Watson and Jaksch (1978) utilized data from a review report by Waddell (1974). Waddell utilized studies that were not specific to particulate matter pollution and do not contain dependable material exposure allocations (e.g., Gillette, 1975). Further, Watson and Jaksch (1978) determined frequency-of-cleaning functions from the Booz, Allen and Hamilton study (1970), which surveyed 1090 households in Philadelphia during 1969.

The Beaver Report (1954) suggested an annual total for damage by all forms of air pollution in Great Britain of 152 million pounds sterling in direct costs, of which 25 million was for laundry, 30 million for painting and decorating, and 20 million for cleaning and depreciation of buildings other than houses; thus, about half the total cost of pollution was attributed to soiling.

Michelson and Tourin (1967) compared the costs of air pollution in the highly polluted area of Steubenville, OH, with those in the relatively clean Uniontown, PA, area. The per capita costs for inside and outside maintenance of houses (painting and cleaning), laundry, dry cleaning, and personal care (hair and facial) were $84 higher in Steubenville than in Uniontown. Cost figures were based on data obtained from questionnaires, but the results have been questioned on the grounds that socioeconomic factors influenced responses and that there were insufficient statistically reliable data.

Narayan and Lancaster (1973) conducted a questionnaire survey in a rural area and a polluted area in New South Wales, Australia, to determine the difference in cost of household upkeep. The cost of maintaining a house in the polluted Mayfield area was about $90 per year higher than in the relatively unpolluted Rotar area. This cost differential was attributed to the higher levels of air pollution and airborne particulate matter in Mayfield; however, the accuracy of the cost data was considered questionable, since the attitude of the respondents could have introduced a biased point of view.

Waddell (1974), in his review of the economic damage of air pollution, noted that the Michelson and Tourin (1967) and Booz, Allen and Hamilton (1970) studies considered principally the costs of household cleaning and maintenance. He questioned the validity of extrapolating the Michelson and Tourin value of $84 per capita because of insufficient information and socioeconomic problems in obtaining defensible data. He further asserted that "intuitively, other than what is implicitly measured in property value differentials, it is difficult to conclude that there are not significant soiling-related costs." In particular, he stated that soiling costs should include laundering, dry cleaning, hair and facial care, washing of automobiles, and costs of cleaning commercial establishments and public structures. Waddell (1974) concluded that there are insufficient data to assess these soiling costs.

Waddell (1974) also reviewed the concept of property value as an estimator, noting the assumption that the inconvenience of living in a polluted area with soiling and odors leads to lower property values. He cited the Jacksch and Stoevener (1970) study in Toledo, Oregon, using dustfall measurements as the variable. Their hypothesis was that air pollution costs, though not quantitatively known, were reflected in the value of property. They found that reduction in property values from increasing air pollution was greater in the higher priced, newer sections of town than in low-cost housing.

Most property value approaches assume a direct and equal relationship between property values and air quality. In other words, "if two sites are similar in all respects except air quality, the difference in their values represents the market's willingness to pay for reduction in air pollution dosages. That is, all air pollution damages will be registered on differential site values (Crocker, 1970). However, using areas with similar socioeconomic characteristics Gillies and Youston (1976) found no statistical relationship between air pollution and property values.

In a more recent study of paired neighborhoods in the Los Angeles area employing both differences in property value and a willingness to pay survey, Brookshire et al. (1979a,b) found that the marginal willingness to pay for an approximate 30 percent improvement in air quality calculated from property values and the survey results ($950 million and $650 million respectively) were within a factor of 1.5. The study was, however, not pollutant-specific, and the authors noted that this approach to benefit analysis needs further refinement before the results "can even cautiously be applied to environmental decision making." They also cautioned that the study may well not be generalizeable to other situations.

The economic effects of soiling were examined by Liu and Yu (1976) in a Midwest Research Institute project undertaken for the EPA's Corvallis Environmental Research Laboratory. The objectives were to generate physical and economic damage functions, by receptor, for SO_2 and suspended particles and to establish cost/benefit relationships. The study included the effects of air pollution damage on health, household soiling, materials, and vegetation.

Liu and Yu (1976) used the data of Booz, Allen and Hamilton (1970) on soiling and maintenance operations to identify and quantify soiling damage. They surveyed costs of nine professional cleaning companies in Kansas City, and developed a methodology for use on a nationwide basis for estimating damage attributable to SO_2 and particulate matter. They calculated the gross cost of cleaning and the net (extra) cost from increases in suspended particles using a formula they derived. For these calculations, they chose a suspended particulate level of 45 $\mu g/m^3$ as the level necessitating extra cleaning.

Liu and Yu (1976) derived net and gross household cleaning costs for 65 large cities with populations greater than 500,000 and for 83 medium-size cities of 200,000 to 500,000. The extra costs for Chicago, New York, and Los Angeles in 1970 were $516 million, $418 million, and $388 million, respectively. Per capita costs for household maintenance activities ranged from $5 per person in San Antonio, Texas, to $104 per person in Cleveland, Ohio. The total net soilage cost for the urban areas was estimated as $5.033 billion.

10.5.2.4 Combined Studies--Salmon (1970) was one of the first to provide an estimate of material damage associated with ambient SO_2 concentrations. He calculated economic loss by determining the values of materials exposed to pollution and then multiplying by the estimated difference in useful lifetime between clean-rural and polluted-urban areas. The value of exposed materials was derived by multiplying annual production by a product lifetime estimate and then applying a labor-factor estimate and an exposure-factor estimate. Salmon cited economic damage from sulfur oxides in the United States to the following materials, listed in decreasing order of the extent of damage: metals, cotton, finishes and other coatings, building stone, paints, paper, and leather. Paint, zinc, and cement/concrete accounted for 70 percent ($2.647 billion) of the estimated annual economic loss of all major materials ($3.8 billion). Deterioration of paints alone was estimated at $1.2 billion. Salmon noted that it would cost $35 billion a year to keep household painted surfaces as clean as they would be in an unpolluted environment. Carbon steel, which has virtually no resistance to SO_2 and sulfate, accounted for $54 million of the total loss.

Gillette (1975) reported significant reductions in economic damage to materials from sulfur oxides attributable to improvements in existing air quality levels throughout the United States. Comparing annual SO_2 concentrations from more than 200 monitoring sites with the estimated inventory of materials exposed in the proximity of these sites, he estimated that nationwide material damage decreased from more than $900 million in 1968 to less than $100 million in 1972. These estimates were derived by carefully distinguishing between physical and economic losses and by attributing current estimates of losses to current exposure levels.

The distinction between physical and economic damage to materials was based upon the concept of normal or economic useful life of materials. Whereas physical deterioration to materials may occur at relatively low exposure levels, economic losses will occur only if the material requires early replacement or increased maintenance before its normal or economically useful life is spent. Given the prevailing ambient concentrations observed, Gillette reported that most materials were not adversely affected economically except for metallic products that were subjected to corrosion or paint damage. While material losses were much greater during the early 1960s, the losses in more recent years are substantially lower and reflect the considerable improvement in air quality (Gillette, 1975).

Waddell assumed that the Gillette study is more defensible than the Fink study, that it does not significantly overlap the Spence-Haynie study, and that it includes damage to electrical contacts and components. If the materials evaluated in these studies (zinc, paints, rubber, carbon and alloy steel, fibers, cement and concrete, plastics, building brick, paper, leather, wood, and building stone) plus those believed by Fink to be relatively unaffected by air pollution (aluminum, copper, stainless steel, and lead) are subtracted from the Salmon study, a total remainder from the Salmon study of $0.4 billion is obtained. Using these data and the assumptions outlined above, Waddell derived an estimate of 1970 air

TABLE 10-9. ESTIMATES OF TOTAL COSTS FROM AIR POLLUTION DAMAGE TO MATERIALS IN 1970

Source of information	Material category	Principal pollutants	Estimated cost, $ billion
Mueller-Stickney	Elastomers	Ozone	0.5
Gillette	General materials but principally metal corrosion	SO_2	0.4
Salvin	Textiles and dyes	NO_2, O_3	0.2
Spence-Haynie	Paints	Particulates, SO_2	0.7
Salmon	Remainder of important materials not accounted for above	Various, but probably mostly SO_2	0.4
Total			2.2

Source: Waddell (1974).

pollution damage costs of $2.2 billion. As shown in Table 10-9, $1.5 billion was directly attributed to PM and SO_x.

Yocum and Grappone (1976) also estimated that the economic costs of air pollution damage to materials for the United States was about $2.2 billion in 1970. They estimated the relative contribution to this total cost from SO_x at 41 percent (about $0.9 billion); particulate matter, 27 percent (about $0.6 billion); ozone, 26 percent; and NO_x, 6 percent.

10.5.3 Summary of Economic Damage of Air Pollution to Materials

The damaging and soiling of materials by airborne pollutants have an economic impact, but this impact is difficult to quantify. The accuracy of economic damage functions is limited by several factors. One of the problems has been to separate costs related to sulfur oxides and particles from those related to other pollutants, as well as those related to normal maintenance. Cost studies typically involve broad assumptions about the kinds of materials that are exposed in a given area and then require complex statistical analysis to account for a selected number of variables. Attitudes regarding maintenance may vary culturally, further confounding the problem of quantifying economic impact.

Studies have used various approaches to determine pollutant-related costs for extra cleaning, early replacement, more frequent painting, and protective coating of susceptible materials, as well as other indicators of the adverse economic effects of pollutants. No

study has produced completely satisfactory results, and estimates of cost vary widely (see selected examples in Figure 10-9). Studies of household maintenance costs in polluted and unpolluted areas have shown annual cost differentials of $100 or more, but the results of these various studies are difficult to compare because of differences in approach, methodology, and selection of variables. Damage functions indicate that reductions in pollutants will decrease physical and therefore economic damage, but the data base and methodology for attribution of costs to sulfur oxides and particulate matter are incomplete at this time.

10.6 SUMMARY AND CONCLUSIONS, EFFECTS ON MATERIALS

The nature and extent of damage to materials by sulfur oxides and particulate matter have been investigated by field and laboratory studies. Both physical and economic damage functions have been developed for specific damage/effect parameters associated with exposure to these pollutants. To date, only a few of these functions are relatively reliable in determining damage, while none have been generally accepted for estimating costs.

The best documented and most significant damage from sulfur oxides and particulate matter is the acceleration of metal corrosion, the erosion and soiling of paint and soiling of buildings and other structures. Erosion of building materials and stone due to sulfur oxides is also established, but the importance of sulfur oxides relative to other agents is not clear. Although evidence of damage to fibers (cotton and nylon), paper, leather and electrical components has been reported, reliable damage estimates have not.

Relatively accurate physical damage functions have been calculated for the effects of sulfur dioxide on the corrosion of galvanized steel. Determination of variables such as time of wetness and surface configuration affect the applicability of the functions. Similar, but less accurate, functions have also been developed for estimating erosion rates of oil-based paints from exposure to sulfur dioxide. The least reliable of the "significant" damage functions are those for soiling from particulate matter. The poorly understood deposition rates and poorly characterized chemical and physical properties make general application of the functions difficult, if not impossible.

The limitations of these and other physical damage functions hinder accurate estimates of total material damage and soiling. Coupled with these limitations is the lack of material exposure estimates. These problems presently preclude complete and accurate estimates of the costs of damage based on a physical damage function approach. Other approaches to cost estimation with lesser data requirements have been attempted, but the studies using these approaches to date have been inadequate for decision-making guidance.

POLLUTANTS	METALS	PAINT	MOST MATERIALS
MOST POLLUTANTS	1.45 FINK (1971)	0.54 SPENCE AND HAYNIE (1972)	2.2 WADDELL (1974) AND YOCOM AND GRAPPONE (1976)
SO_x AND TSP			1.5 WADDELL (1974) AND YOCOM AND GRAPPONE (1976)
TSP		1.2 SALMON (1970)	5.0 LIU AND YU (1976) AND BOOZ-ALLEN (1970) 0.54 - 3.8 WATSON AND JACKSCH (1978)
SO_x			0.1 - 0.9 GILLETTE (1975) 3.8 SALMON (1970)

MATERIAL TYPE

Figure 10-9. Summary of economic damage estimates of air pollution to materials. (in billions of dollars per year, early 1970's)

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GLOSSARY FOR VOLUME IV

Adsorption: Adhesion of a thin layer of molecules to a liquid or solid surface.

Aerosol: Solid particles or liquid droplets which are dispersed or suspended in air.

Albedo: That fraction of the total light incident on a reflecting surface, especially a celestial body, which is reflected back in all directions.

Anode: Positive electrode.

Austenite: Gamma iron with carbon in solution.

Austenitic steel: An alloy whose structure is typically that of austenite at room temperature.

Colloidal system: An intimate mixture of two substances, one of which, called the dispersed phase (or colloid), is uniformly distributed in a finely divided state through the second substance, called the dispersion medium (or dispersing medium); the dispersion medium or dispersed phase may be a gas, liquid, or solid. Also known as colloidal dispersion; colloidal suspension.

Convective mixing: Atmospheric motions that are predominantly vertical, resulting in vertical transport and mixing of atmospheric properties.

Crystalization spalling: The reduction of stone surfaces worn away by a crystalline-forming process.

Ecosystem: The interacting system of a biological community and its environment.

Efflorescence (mineral): A whitish powder, consisting of one or several minerals produced as an encrustation on the surface of a rock in an arid region. Also known as bloom.

Electrophoretic coating: A surface coating on a metal deposited by electric discharge of particles from a colloidal solution.

Exfoliate: Flake away or peel off in scales.

Ferrous (metals): Relating to or containing iron.

Hygroscopic: Pertaining to a marked ability to accelerate the condensation of water vapor.

Insolation decoloration: Removal or fading of color due to exposure to the sun.

Isopleth: A line on a map or chart connecting points of equal value.

Iterative bidding: A research technique for subjectively establishing value.

Mesoscale: Of or relating to meteorological phenomena from 1 to 100 kilometers in horizontal extent.

Nephelometer: A type of instrument that measures at more than one angle, the scattering function of particles suspended in a medium; information obtained may be used to determine the size of suspended particles and the visual range through the medium.

Nuclei (plural of nucleus): A central point, group, or mass about which gathering, concentration, or accretion takes place.

Particulate matter (particulates, particles, etc.): Fine liquid or solid particles within an aerosol such as dust, smoke, mist, fumes or smog.

Passivate (metal): To render passive; to reduce the reactivity of a chemically active metal surface by electrochemical polarization or by immersion in a passivating solution.

Rayleigh scattering: Coherent scattering in which the intensity of the light of wavelength g, scattered in any direction making an angle with the incident direction, is directly proportional to 1 + cos r and inversely proportional to g^4.

Sorb: To take up and hold by absorption or adsorption.

Sorbed: Past tense of "sorb."

Sorption: The process of being sorbed.

Spatial: Relating to, occupying, or of the nature of space.

Spectral: Relating to the electromagnetic spectrum.

Spectroscopy: The branch of physics concerned with the production, measurement, and interpretation of electromagnetic spectra arising from either emission or absorption of radiant energy by various substances.

Stoichiometry: The numerical relationship of elements and compounds as reactants and products in chemical reactions.

Sulfur dioxide (SO_2): Colorless gas with pungent odor released primarily from burning of fossil fuels, such as coal, containing sulfur.

Transmissometer: An instrument for measuring the extinction coefficient of the atmosphere and for the determination of visual range. Also known as hazemeter or transmittance meter.

Troposphere: That portion of the atmosphere in which temperature decreases rapidly with altitude, clouds form, and mixing of air masses by convection takes place. Generally extends to about 7 to 10 miles above the earth's surface.