UNITED STATES - CANADA

MEMORANDUM OF INTENT
ON
TRANSBOUNDARY AIR POLLUTION

Atmospheric Sciences Review

Working Group 2

2-14

INTERIM WORKING PAPER
JULY, 1981

ATMOSPHERIC SCIENCES REVIEW

by the

Atmospheric Sciences Sub-group

of

Work Group 2

Atmospheric Sciences and Analysis

REPORT NO. 2-14

July 10, 1981

Submitted to the Coordinating Committee in Fulfillment of the
Requirements of the Memorandum of Intent Signed by
United States and Canada on August 5, 1980.

Mr. Howard Ferguson, Director
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Dr. Lester Machta, Director
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Dear Mr. Ferguson and Dr. Machta:

We are pleased to transmit under cover of this letter the interim report of the Atmospheric Sciences Review as provided for in the Phase II Work Plan. We believe that this report satisfies, in a scientifically responsible manner, our Phase II objectives.

Sincerely,

John W. Miller
John Miller
U.S. Atmospheric Science
Review Coordinator

for Peter Summers
Canadian Atmospheric Science
Review Coordinator

PREFACE

This is a "Working Report" prepared by the Atmospheric Sciences Subgroup of Work Group 2. This group is one of five established under the Memorandum of Intent signed by the governments of Canada and the United States on August 5, 1980.

This "working report" is one of a set of eleven Work Group 2 reports in Phase 2 which represents the drawing together of currently available information relevant to transboundary air pollution.

This information will be used by both governments to develop a consensus on the nature of transboundary pollution.

These reports contain some information and analyses that are still preliminary in nature; however, they accurately reflect the current state of knowledge as of July 3, 1981 on the issues considered, given the resources available to prepare these reports. Any portion of these reports is subject to modification and refinement as peer review, further advances in scientific understanding, or the results of ongoing assessment studies become available.

More complete "final reports" dealing with a variety of transboundary air pollution issues are expected in early 1982. These reports will integrate the efforts of the present "working reports" and will also incorporate editorial revisions.

INTRODUCTION

At a Work Group 2 workshop meeting held in Washington, DC on December 16, 1980, a wide-ranging discussion occurred regarding the most important areas in the atmospheric sciences which were closely connected with the use of long range transport models. From that discussion emerged several topics on which Work Group 2 would prepare reviews for their May 15, 1981, Phase II report. The purpose of these reviews would be to highlight the state of knowledge in the particular topic areas, and to indicate how that knowledge is reflected in various models being used by this Work Group. The reviews were to be brief, comprehensive, reflect recent literature and work in progress, and written in a manner which is comprehensible to the educated layman.

The initial topics chosen are described briefly below, and the lead authors are identified. First drafts of the write-ups were to be distributed to all Work Group 2 members for discussion in the last half of February, 1981.

1) Sulfur and Nitrogen Chemistry in LRT Models

   (A.P. Altshuller) Homogeneous and heterogeneous reaction mechanisms will be reviewed. The degree to which models can treat sulphur chemistry as being first-order and independent of other atmospheric cycles (e.g., oxidants, nitrogen, particulates, visibility) will be discussed. Seasonal differences will be mentioned. The ways in which SO_2 is converted into sulphuric acid, as opposed to other sulfate products, will be emphasized in all parts of the report.

It is known that nitrogen chemistry is more complex than sulphur chemistry, and that in many situations it is not first order. Additionally, other key species involved in nitrogen chemistry are often not being measured. This discussion will review the above issues, as well as the aspects mentioned above for sulfur. Finally, the possibility of crudely modeling nitrogen reactions, in a psuedo-first order way in existing Lagrangian models will be discussed.

2) <u>Trends in precipitation composition and deposition</u> (J. Miller) What data sets are available which have not been discussed to date? Are the data sets reliable? Is there any way to relate trends, which these and newer sets of data may show, to estimates of past and present emissions of SO_2; should the comparison even be made in view of the different spatial distribution of the sources, the different release heights of the SO_2, etc.

3) <u>Deposition processes for sulphur and nitrogen compounds</u> (G. Van Volkenburg) Once atmospheric reactions have occurred, how does one measure and model the various

pathways of deposition, both wet and dry? Are the mechanisms and amounts of deposition radically different because of seasonal changes? What is the role of changing meteorological conditions (e.g., mixing height, temperature, type of storm, amount of precipitation) and surface conditions (wet, snow-covered, vegetation-covered, etc.)? How valid are the parameterizations of deposition being used in models currently?

4) Global and western North American measurements of precipitation pH

(P. Summers) The strength of the assumption of "unpolluted" rain having a pH of 5.6 will be compared to recent global background measurements, and these measurements will be interpreted in light of current assumptions about residence times of acid precursor compounds and scavenging mechanisms for these compounds over oceans, coastal regions, and over land. Recent measurements from western North American will be examined thoroughly.

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SECTION I

SULFUR AND NITROGEN CHEMISTRY IN LONG RANGE TRANSPORT MODELS

by

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Preface

Recently the chemistry of sulfur oxides, and to a lesser extent nitrogen oxides, has been critically reviewed and discussed in the U.S. Environmental Protection Agency External Review Draft of the Air Quality Criteria for Particulate Matter and Sulfur Oxides Document. Relevant sections in that document contributed by the authors have been reproduced herein for inclusion in the Work Group 2 Atmospheric Sciences Review Report. In a similar manner material has been reproduced in part from Chapter 6, U. S. Environmental Protection Agency External Review Draft of the Air Quality Criteria for Oxides of Nitrogen. (In the latter document, Durham and Demerjian were reviewers, not principal contributors). It should be noted that since this material is in draft form concurrently undergoing public comment, it is subject to change. It has not been formally released by EPA and should not at this stage be construed to present EPA Agency policy. The numbering system used in the Criteria Document was retained for this material.

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2. CHEMISTRY OF THE OXIDES OF SULFUR IN THE LOWER ATMOSPHERE

2.3.3 Gas-Phase Chemical Reactions of Sulfur Dioxide

The chemical transformation of sulfur dioxide in the atmosphere has been studied extensively over the past 20 years. Recent reviews, Calvert et al. (1978), Middleton et al. (1980) and Moller (1980), which consider analysis of laboratory and field data as well as theoretical studies, indicated that SO_2 oxidation may proceed through both gas and liquid phase reactions. The oxidation of SO_2 in the atmosphere is of considerable importance, in that it represents a major pathway for particle production through the formation of sulfates. The SO_2 oxidation process, though not completely understood mechanistically, has been demonstrated to proceed via four pathways: homogeneous gas phase reactions; heterogeneous gas-solid interface reactions; and catalyzed and uncatalyzed liquid phase reactions. Homogeneous gas phase reactions are by far the most extensively studied and best understood quantatively.

The homogeneous gas-phase chemistry of oxidation in the clean and polluted troposphere is reviewed in this section. The status of our knowledge is presented for the elementary oxidation reactions of SO_2 and the importance of volatile organic and nitrogen oxides as generators of free radical oxidizers. This review will show that the photochemical oxidation of SO_2 is potentially a significant pathway for tropospheric sulfate formation. The three most important oxidizers of SO_2 are: (1) hydroxyl radical HO; (2) peroxyl radical, HO_2, and (3) methoxyl radical, CH_3O_2. At this time, only the reaction rate constant for HO is well established. The pathways of formation of the oxidizer radicals for the unpolluted troposphere can be explained in terms of the photochemistry of the NO-CH-CO-O_3 system. In polluted atmospheres, volatile organics and oxides of nitrogen act together to produce additional radicals and accelerate overall radical production. There is also evidence that a dark reaction among O_3, alkenes, and SO_2 is effective in oxidizing SO_2.

2.3.3.1 Elementary Reactions - The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1965 have been critically reviewed by Altshuller and Bufalini (1971), and more recently by Calvert et al. (1978). The review of Calvert et al. (1978) systematically examined the rate constants and significance of SO_2 elementary reactions known to occur in the troposhere; identified as generally unimportant reactions were: photodissociation, photoexcitation, reaction with singlet delta oxygen [$O_2('\Delta g)$] reaction with oxygen atom [$O(^3P)$] reaction with ozone (O_3), reaction with nitrogen oxides (NO_2, NO_3, N_2O_5), reaction with tert-butylperoxyl radical [$(CH_3)_3CO_2$], and reaction with acetyl-peroxyl radical ($RCOO_2$). The only SO_2 reactions in the troposphere that were identified as important were those due to hydroxyl radical (HO), peroxyl radical

(HO_2), and methoxyl radical (CH_3O_2). The rate constants recommended by Calvert et al. (1978) for these three reactions are given in Table 2-4. More recent work is in conflict with the rate constants for HO_2 and CH_3O_2 that have been recommended by Calvert et al. (1978). Graham et al. (1979) and Burrows et al. (1979) have reported rate constants for the HO_2 reaction that are much lower than that recommended by Calvert et al. (1978); these more recent results are shown in Table 2-4. Also Sander and Watson (1981) have reported a rate constant for the CH_3O_2 reaction that is much lower than that recommended by Calvert et al. (1978); that value is given in Table 2-4. The reasons for the discrepancies for these two rate constants are unknown, and there is no basis to recommend preferred values.

Although the dark reaction of $SO_2 + O_3$ is too slow to be important in the troposphere, the addition of alkenes greatly enhances the oxidation rate. The experimental work of Cox and Penkett (1971a,b), Penkett (1972) and McNelis et al. (1975) has been reviewed and reevaluated by Calvert et al. (1978). The reaction system is too complex to discuss here, but Calvert et al. (1978) report results of their calcuations for total alkenes = 0.10 ppm, $[O_3]$ = 0.15 ppm, and $[SO_2]$ = 0.05 ppm; they estimated that the disappearance rate of SO_2 is 0.23 and 0.12% h^{-1} at 50 and 100% relative humidity (25°C), respectively. The reaction mechanism for the O_3 + alkene + SO_2 system is not known, but studies by Niki et al. (1977) and Su et al.

(1980) indicate that the reactive species may be the biradical, formed by the decomposition of the original monozonide.

Summary: The status of our knowledge of the gas-phase tropospheric oxidation reactions is:

1. Three reactions have been identified as being potentially important.
    a. HO radical. The rate constant appears to be well-established.
    b. HO_2 radical. The rate constant is not well-established.
    c. CH_3O_2 radical. The rate constant is not well established.
2. The $SO_2 + O_3$ + alkenes reaction may be an important dark reaction.

Table 2-4: Rate Constants for Hydroxyl, Peroxyl, and Methoxyl Radicals

Reaction	Second order rate constant, $cm^3 mole^{-1} s^{-1}$	Source
$HO + SO_2 \rightarrow HOSO_2 \rightarrow H_2SO_4$	$(1.1 \pm 0.3) \times 10^{-12}$	Calvert et al. (1978)
$HO_2 + SO_2 \rightarrow HO + SO_3 \rightarrow H_2SO_4$	$>(8.7 \pm 1.3) \times 10^{-16}$	Calvert et al. (1978)
	$<1 \times 10^{-18}$	Graham et al. (1979)
	$\leq 2 \times 10^{-17}$	Burrows et al. (1979)
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3 \rightarrow H_2SO_4$	$(5.3 \pm 2.5) \times 10^{-15}$	Calvert et al. (1978)
	5×10^{-17}	Sanders and Watson (1981)

2.3.3.2 Tropospheric Chemistry of SO_2 Oxidation -- The chemistry of the clean troposphere and its mathematical simulation have been studied extensively by Levy (1971), Wofsy et al. (1972), Crutzen (1974), Fishman and Crutzen (1977), Chameides and Walker (1973, 1976) and Stewart et al. (1977).

The photochemistry of the unpolluted troposhere develops around a chain reaction sequence involving NO, CH_4, CO and O_3. The photochemical reaction chain sequence in the troposphere is initiated by hydroxyl radicals (HO) formed from the interaction of $O(^1D)$, the product of photolysis of ozone in the short end portion of the solar spectrum, with water.

$$O_3 + h\nu(\lambda \leq 310\ nm) \rightarrow O(^1D) + O_2 \qquad (2\text{-}1)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (2\text{-}2)$$

The HO produced reacts with CH_4 and CO present in the clean troposhere, resulting in the generation of peroxyl radical species, HO_2, CH_3O_2.

$$HO + CH_4 \rightarrow CH_3 + H_2O \qquad (2\text{-}3)$$

$$HO + CO \rightarrow H + CO_2 \qquad (2\text{-}4)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (2\text{-}5)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (2\text{-}6)$$

The peroxyl radicals in turn participate in a chain propagating sequence which convert nitric oxide (NO) to nitrogen dioxide (NO_2) and in the process produces additional hydroxyl and peroxyl radical species.

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (2\text{-}7)$$

$HO_2 + NO \rightarrow HO + NO_2$ (2-8)

$CH_3O + O_2 \rightarrow HO_2 + H_2CO$ (2-9)

$H_2CO + h\nu(\leq 370\text{ nm}) \rightarrow H + HCO$ (2-10)

$HCO + O_2 \rightarrow HO_2 + CO$ (2-11)

The major chain terminating steps include:

$HO + NO_2 + M \rightarrow HONO_2 + M$ (12-12)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (12-13)

$H_2O_2 + HO \rightarrow H_2O + HO_2$ (12-14)

The reaction sequence for O_3 production involves converting NO to NO_2 at a rate sufficiently high to maintain a NO_2/NO ratio to sustain the observed background levels of O_3.

$HO_2 + NO_2 \rightarrow NO_2 + HO$ (2-8)

$NO_2 + h\nu \rightarrow NO + O$ (2-15)

$O + O_2 + M \rightarrow O_3 + M$ (2-16)

$NO + O_3 \rightarrow NO_2 + O_2$ (2-17)

$HO + CO \rightarrow H + CO_2$ (2-4)

In general, reactions (15) through (17) govern the ozone concentration levels present in the sunlight irradiated well-mixed atmosphere at any instant and to a first approximation the steady state relationship, Leighton (1961).

$$\frac{(NO_2)\ k_{15}}{(NO)\ k_{17}} = (O_3)$$

provides an accurate estimate of ozone given the ratio of $(NO_2)/(NO)$ and k_{15}/k_{17}. The photolytic rate constant k_{15} is directly related to the integrated actinic solar flux over the wavelength range 290 - 430 nm.

The paths for ozone destruction in the troposphere include the reactions sequence

$$HO_2 + O_3 \rightarrow HO_2 + 2O_2 \qquad (2\text{-}18)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (2\text{-}19)$$

Hydroxyl radical abundances predicted by the tropospheric photochemical models, 10^5 to 10^6 molecules cm^{-3}, are in qualitative agreement with recent measurements by Davis et al. (1976), Perner et al. (1976), and Campbell et al. (1979) and inferred HO levels based on measured trace gas abundances in the troposphere by Singh (1977).

In the case of the chemistry of polluted atmospheres, extensive discussions on the mechanism of photochemical smog and its computer simulation have been presented by Demerjian et al. (1974), Calvert and McQuigg (1975), Niki et al. (1972), Hecht et al. (1974) and Carter et al. (1979).

Perturbations introduced by man's emissions on the photochemical oxidation cycle within the atmosphere are predominately due to two classes of compounds, volatile organics and nitrogen oxides. The reaction chain sequence discussed earlier for the clean troposphere has now been immensely complicated by the addition of scores of volatile organic compounds which participate in the chain propagating cycle. Figure 2-4 depicts a schematic of the polluted atmospheric photooxidation cycle (Demerjian, 1981). The addition of volatile organic compounds (VOC) in the atmosphere introduces a variety of new peroxyl radical species.

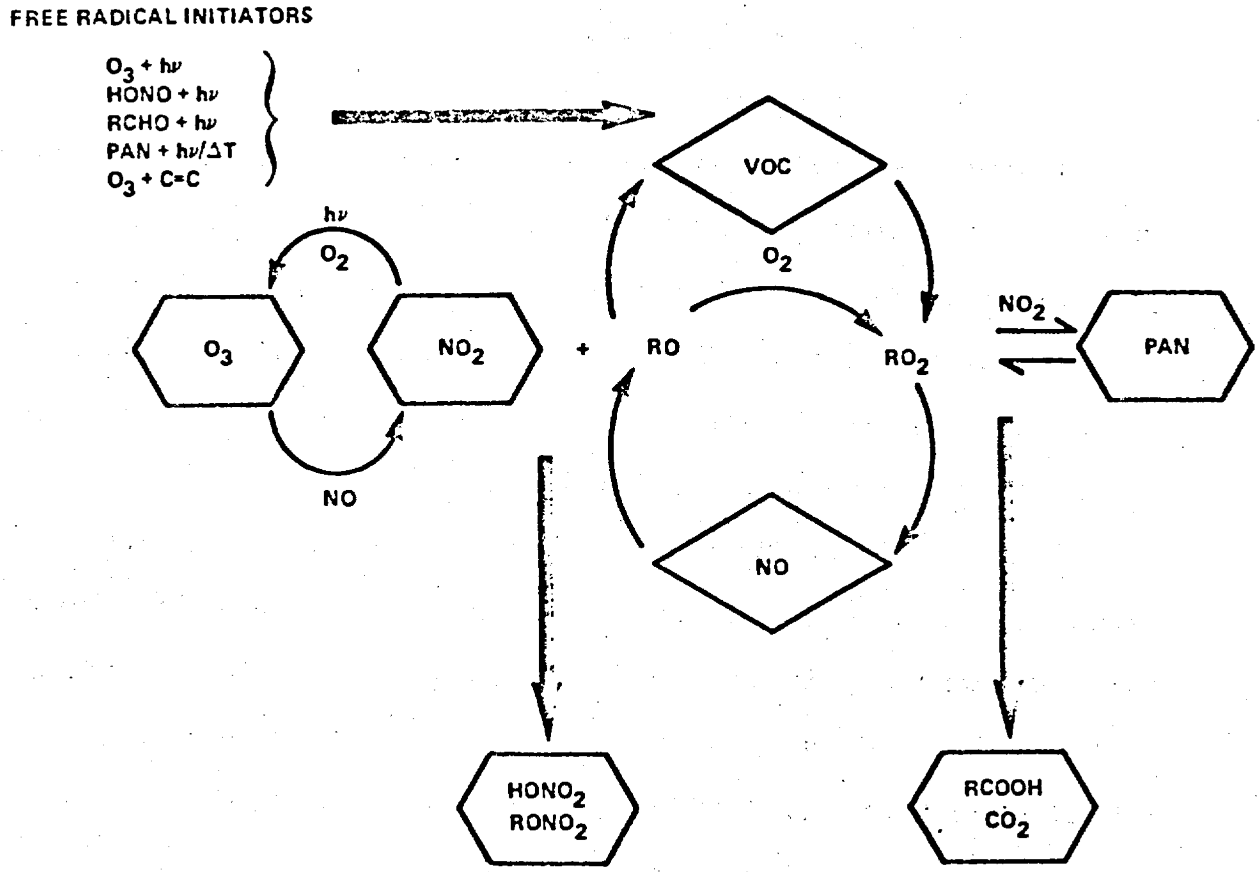

Figure 2-4. Schematic of the Polluted Atmospheric Photo-oxidation Cycle. Source: Demerjian (1981)

In its simplest form the photochemical oxidation cycle in polluted atmospheres is governed by the following basic features. Free radical attack on atmospheric VOCs is initialized by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After initial free radical attack, the VOCs decompose through paths resulting in the production of peroxyl radical species (HO_2, RO_2, $R'O_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds. The peroxyl radicals react with NO, converting it to NO_2, and in the process produce hydroxyl/alkoxyl radical species (OH, RO, R'O, etc.). Alkoxyl radicals can be further oxidized, forming additional peroxyl radicals and partially oxidized products, thereby completing the inner cyclical loop reaction chain process illustrated in Figure 2-4; or they may attack, as would be the major path for hydroxyl radical, the VOC pool present in the polluted atmosphere, thereby completing the outer loop reaction chain process. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon.

The complex mixture of organic compounds present in the polluted atmosphere react at different rates depending upon their molecular structure, the result being varying yields of free radical species, ozone, NO_2, PAN and other partially oxidized organic products as a function of VOC composition and VOC-NO_x levels.

Hydroxyl radical (HO) reactions seem to be the dominant mechanism by which hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmospere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). Interestingly enough, this highly reactive transient specie, quite contrary to its organic free radical counterparts, does not show appreciable change in concentration with atmospheric VOC and NO_x variation, a result readily explainable upon review of the free radical production and consumption sources. In the case of hydroxyl radicals, ambient concentration conditions which enhance its production tend to also consume the radical at an equivalent rate. The result is a faster cycling in the VOC-NO_x oxidation chain (that is, increased chain lengths) but very little perturbation in the HO steady state concentration. In contrast, organic free radicals, mainly peroxyl species, are consumed by alternate pathways which are less competitive and result in increased steady state concentration.

Applying this basic knowledge of the photochemistry of the lower atmosphere, Calvert et al. (1978) determined theoretical rates of SO_2 oxidation via attack of various free radical species whose concentrations were estimated from computer simulations of the chemical reaction mechanisms for clean and polluted atmospheres.

Based on limited rate constant data for the SO_2 - free radical reactions, Calvert determined that the hydroxyl radical dominated the rate of SO_2 oxidation in the clean troposphere, while in polluted atmospheres the rate of SO_2 oxidation showed equivalent contributions from hydroxyl, hydroperoxyl (HO_2) and methylperoxyl (CH_3O_2) radicals. Figure 2-5 depicts the estimated time dependent rates of SO_2 oxidation by free radical species in a polluted air mass. Recent laboratory measurements suggest that the rate of reaction of SO_2 with HO_2 and CH_3O_2 may not be as great as estimated by Calvert et al. (1978) (see discussion in Section 2.3.3.1). Typical rates of SO_2 oxidation were of the order of 1.5 percent/h and 4.0 percent/h for clean and polluted atmospheres, respectively, during July at mid-northern latitudes. The major difference in rates are a result of higher concentration levels of free radicals in the hydrocarbon rich polluted atmospheres. In a similar manner, Altshuller (1979) predicted the rates of homogeneous oxidation of sulfur dioxide to sulfate in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen (1978). A sample result from this study showing the latitudinal and seasonal dependence of the rate of SO_2 oxidation is presented in Figure 2-6; the variability in rate being predominantly due to availability of u.v. solar intensity which drives the free-radical production process. The solar radiation

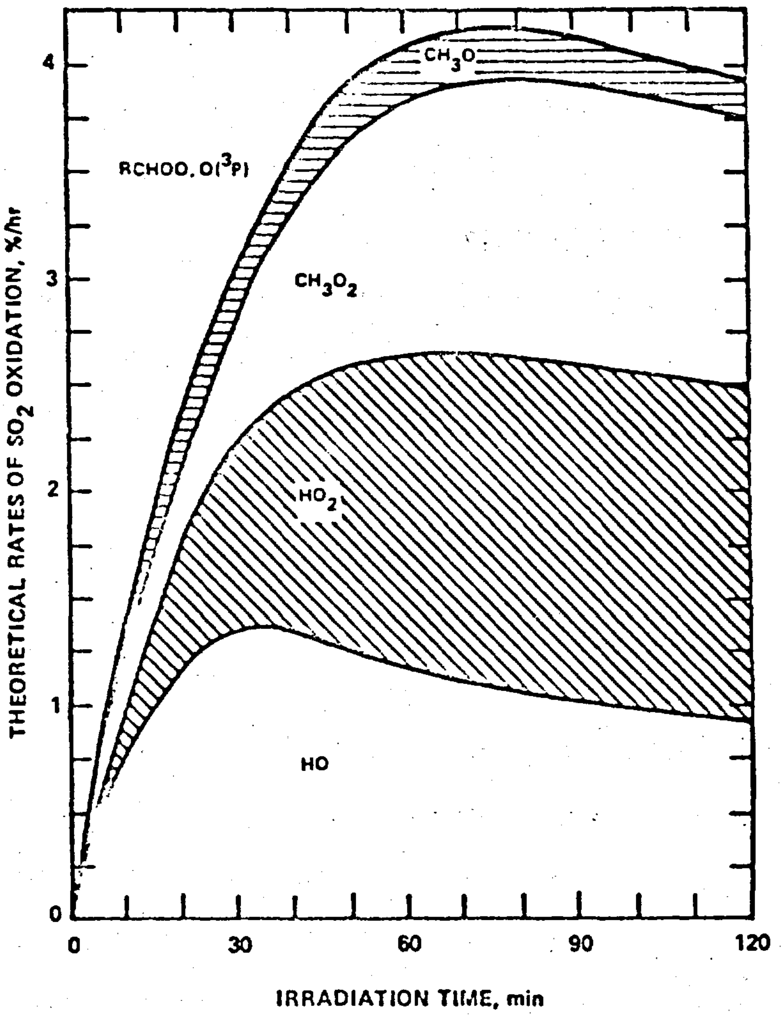

Figure 2-5. The Theoretical Rate of Reaction (percent per hour) of Various Free-Radical Species on SO_2 for a Simulated Sunlight-Irradiated (solar zenith angle of 40°) Polluted Atmosphere. Note- The initial concentrations (in ppm) were as follows: SO_2, 0.05; NO, 0.15; NO_2, 0.05; CO, 10; CH_4, 1.5; CH_2O, 0; CH_3CHO,0. The relative humidity was 50 percent, and the temperature was 25°C. The rate constants for HO_2 and CH_3O_2 radical reactions with SO_2 are not well established. See Table 2-4 and its discussion.
Source: Calvert et al. (1978).

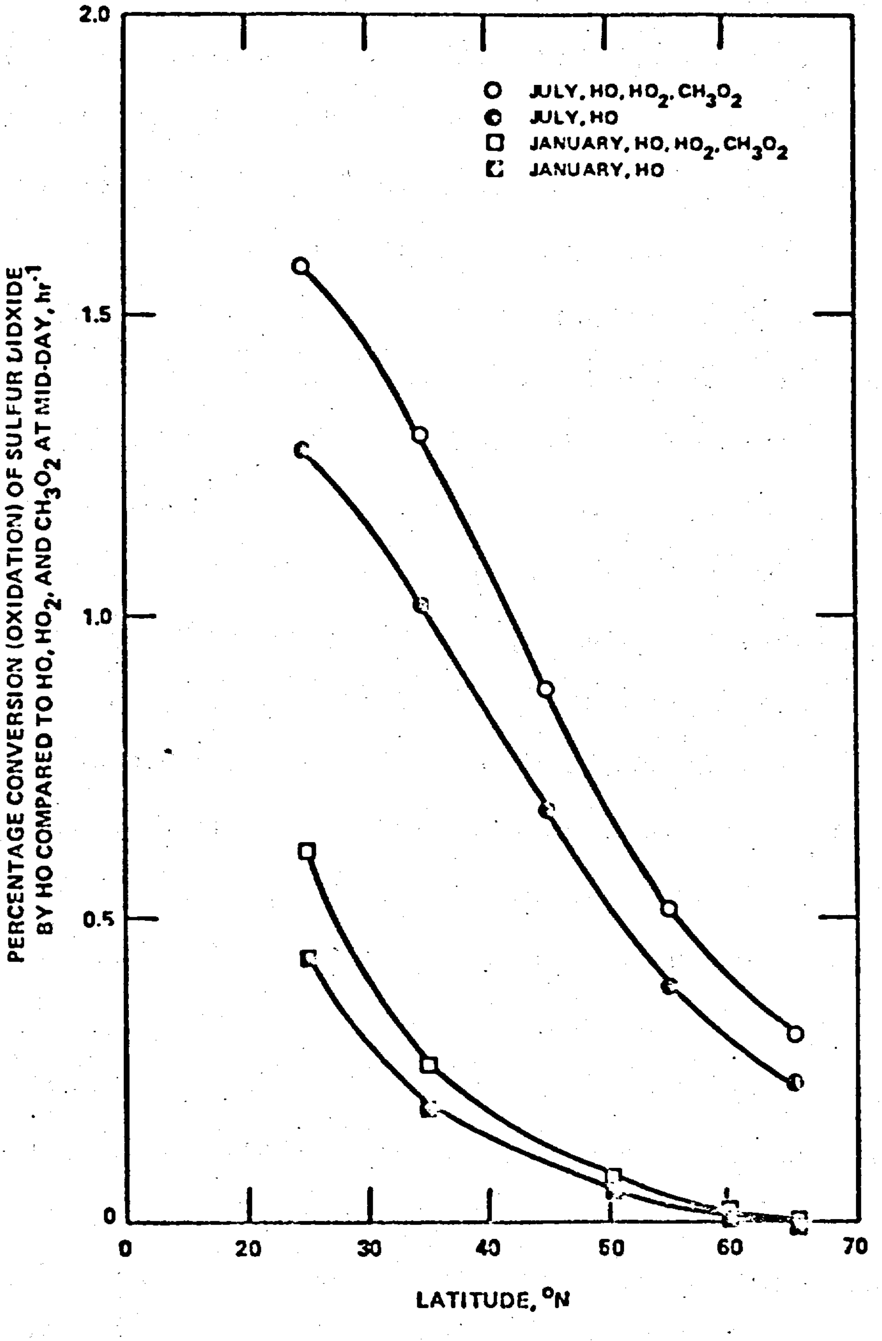

Figure 2-6. Percentage Conversion at Mid-Day of Sulfur Dioxide to Sulfate by HO and by HO, HO_2, and CH_3O_2 Radicals as a Function of Degrees N Latitude in Summer and Winter.
Source: Altshuller (1979).

dependence of SO_2 conversion rate has also been observed in field measurements within power plants plumes, Husar et al. (1978), but should be viewed cautiously in light of the complicating factors introduced by the dispersion and local chemistry of the primary source emissions.

The most important impact on SO_2 homogenous gas phase reactions has come from recent experimental determinations of the reaction rate constants of SO_2 with HO_2 by Graham et al. (1979) and by Burrows et al. (1979) and SO_2 with CH_3O_2 by Sander and Watson (1981). As a result of these recent determinations, HO_2 and CH_3O_2 must be considered as questionable contributing sources to oxidation of SO_2 in the atmosphere. Therefore, in the theoretical estimates of SO_2 oxidation rates, by Calvert et al. (1978), and by Altshuller (1979), only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established SO_2 oxidation rates of the order of 1.5 percent/h for both clean and polluted atmosphere during July at mid-northern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order 0.4 percent/hr. Field measurements on the rates of SO_2 oxidation, discussed in Section 2.3.7, indicate that maximum SO_2 oxidation rates of the order of 10 percent/h are typical of many atmospheric pollution scenarios. Our present knowledge of homogeneous SO_2 gas-phase reactions does not sufficiently account for the rates observed. Smog chamber studies have demonstrated that some spiecies other than HO radical oxidizes SO_2 (Kuhlman et al., 1975; McNelis et al., 1975). Alternate homogeneous gas reaction oxidation pathways are being studied (Su et al., 1980), but certainly the role of heterogeneous and liquid phase SO_2 oxidation pathways should not be overlooked in attempts to resolve this discrepancy.

Summary. The status of our knowledge of SO_2 oxidation in the troposphere is:

1. HO radical dominates the gas-phase oxidation of SO_2 in the clean troposhere. A typical rate is on the order of $1.5\%h^{-1}$ at noon during July at mid-northern latitudes.

2. HO radical accounts for about $1.2\%h^{-1}$ of the SO_2 oxidation in the polluted troposphere. The combined contribution of HO_2 and CH_3O_2 radical reactions may be as great as about $2.8\%h^{-1}$, but their rate constants are not well-established.

2.3.4 Solution-Phase Chemical Reactions of Sulfur Dioxide

The knowledge of the reactions of the aqueous $SO_2.H_2O$-HSO_3^- -and SO_3^{2-} system is important to understanding the processes of H_2SO_4 formation in tropospheric particles, mists, fogs and rain. This section reviews the oxidation reaction of dissolved SO_2 species, including the auto-oxidation, metal-ion catalyzed oxidation, carbon catalyzed oxidation, and reactions with the dissolved oxidants NO_2, O_3, and H_2O_2.

The state of knowledge of aqueous oxidation rates of dissolved SO_2, HSO_3^-, and SO_3^{2-} is inadequate for simple systems and is extremely poor (or non-existent) for complex systems that include dissolved nitrogen and carbon compounds. Unfortunately, most of the studies are not definitive because the investigators: (1) did not provide sufficient descriptions of experimental procedure (especially the purification of the water and reagents), (2) did not select a proper reactor design, and (3) worked at concentration levels that were orders of magnitude greater than possible for ambient atmospheric aqueous systems. Trace quantities (at the part-per-billion level) of catalytic metal ions are capable of enhancing the reaction velocities by orders of magnitude over the auto-oxidation rate, while similar trace quantities of organics inhibit the rate. The characteristics of the chemical reactor govern the range of the half-life that can be investigated and may influence the observed rate of oxidation. Two-phase air-water reactors (e.g., bubblers and supported droplets) may have reaction characteristics that are dependent upon: (1) the mass transfer rate of the reactants through the air-water interface, and (2) the mixing rates within the gas and water phases (Carberry, 1976; Freiberg and Schwartz, 1981). Unless an adequate characterization of the two-phase reactor was performed, it is not recommended that the implied elementary rate constant be accepted. Supported droplets may suffer from an additional problem: radical chains are efficiently terminated at liquid-solid interfaces, thereby reducing the observed rate. Therefore, supported droplet measurements are not defensible unless it is established that the oxidation is not a free-radical mechanism. Notable reviews of the oxidation of dissolved SO_2 and its hydration products in simple systems have been published (Schroeter, 1963: Hegg and Hobbs, 1978).

This review will show that:

1. The auto-oxidation (uncatalyzed) reaction is very slow compared to the other reactions.
2. Mn(II) and Fe(III) are significant catalysts for the oxidation. The kinetic rate expression is in doubt for the Mn(II) reaction, but that for Fe(III) is in agreement among several independent investigators.
3. The catalytic effectivenss of these ions is unknown: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).
4. Elemental carbon (soot) with a water film is a potentially effective oxidation catalyst.
5. Dissolved HNO_2 and O_3 oxidation rates are known and appear to be too low to be effective.
6. The kinetics of the dissolved H_2O_2 oxidation of dissolved SO_2 species are known and appear to be effective for forming sulfate in particles, mists, fogs and rain.

2.3.4.1 $S(IV)-O_2 - H_2O$ System-- The simple $S(IV) - O_2$ auto-oxidation has been the subject of numerous investigations, most of which are listed in Table 2-5. The mechanism for the auto-oxidation is not firmly established. However, the behavior of the system is best explained as a modification to the scheme of Bäckström (1934), taking into account the recent results of Schmidkunz (1963) and Hayon et al. (1972):

Chain initiation

$$SO_3^{2-} + M^+ \rightarrow .SO_3^- + M \qquad (2\text{-}20)$$

(M^+ = trace concentration of metal ion or reactive wall)

Chain propagation

$$.SO_3^- + O_2 \rightarrow .SO_5^- \qquad (2\text{-}21)$$

$$.SO_5^- + SO_3^{2-} \rightarrow .SO_4^- + SO_4^{2-} \qquad (2\text{-}22)$$

Oxidation

$$.SO_4^- + SO_3^{2-} \rightarrow .SO_4^{2-} + SO_3^- \qquad (2\text{-}23)$$

Termination

$$.SO_4^- + \text{inhibitor} \rightarrow \qquad (2\text{-}24)$$

$$\text{radical} + \text{radical} \rightarrow$$

Brimblecombe and Speeding (1947b) propose an alternative scheme that does not include the $.SO_4^-$ radical-ion; in their scheme, equation (2-22) is replaced by:

$$.SO_5^- + SO_3^{2-} \rightarrow .SO_3^- + SO_5^{2-} \qquad (2\text{-}26)$$

$$.SO_5^{2+} + SO_3^{2-} \rightarrow 2\ SO_4^{2-} \qquad (2\text{-}27)$$

and equation (2-24) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table 2-5, and they summarized the rate expressions, rate constants, and important features of the studies. The observations can be classified into three types of rate expressions:

TABLE 2-5. Investigations of $SO_2 - O_2$ Aqueous Systems

Investigators	Type of System	Comment*
Bigelow (1898)	Bubbler	1,2,3
Titoff (1903)	Bulk	2,3
Lumiere and Seyewetz (1905)	Bulk	2,3
Milbaur and Pazourek (1921)	Bulk	2,3
Reinders and Vles (1925)	2-phase bulk	2,3
Haber and Wansbrough-Jones (1932)	Bulk	2,3
Vol'fkovick and Belopol'skii (1932)	Bulk	2,3
Backstrom (1934)	Theoretical	
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2,3
Abel (1951)	Theoretical	
Winkelmann (1955)	Bulk	2
van den Heuvel and Mason (1963)	Supported droplet	1,3
Schroeter (1963)	Bubbler	1
Schwab and Strohmeyer (1965)	Bulk	2
Rand and Gale (1967)	Bulk	2,3
Scott and Hobbs (1967)	Theoretical	
McKay (1971)	Theoretical	
Miller and de Pena (1972)	Supported droplets	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Bielke et al. (1975)	Supported droplet	1,3
Horike (1976)	Bubbler	1,3
Larson (1976)	Bubbler	1
Huss et at. (1978)	Bulk	1,3
Larson et al. (1978)	Bubbler	1

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*1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Purity of water is uncertain; results cannot be considered to be reliable.
3. Rate expression not reported.

1. The type first reported by Fuller and Crist (1941)

$$\frac{d\,[SO_4^{2-}]}{dt} = (k_1 + k_2\,[H^+])^{0.5}\,[SO_3^{2-}] \qquad (2\text{-}28)$$

2. The type first reported by Winkelman (1955),

$$\frac{d\,[SO_4^{2-}]}{dt} = k_1\,[SO_3^{2-}] \qquad (2\text{-}29)$$

3. The type observed by Beilke et al. (1975)

$$\frac{d\,[SO_4^{2-}]}{dt} = k_1\,[H^+]^{-0.16}\,[SO_3^{2-}] \qquad (2\text{-}30)$$

It is presently unresolved as to which type of rate expression is correct. Doubt is cast on "type 3" found by Beilke et al. (1975) because of the use of a plastic vessel that could have introduced trace organic inhibitors into the system. All of the other studies (yielding "types 1 and 2") were performed with two-phase systems whose mass transfer properties were insufficiently reported.

The auto-oxidation is inhibited by trace concentrations of organic species. The classes of organic species capable of serving as inhibitors include alcohols, glycols, aldehydes, ketones, phenols, amines, and acids. Bäckström (1934) first demonstrated that the inhibition of sulfide oxidation can be expressed as:

$$\frac{d\,[SO_4^{2-}]}{dt} = [A/(B + m)]\,k_1\,[SO_3^{2-}] \qquad (2\text{-}31)$$

where

k_1 = the uninhibited rate constant

A,B = constants that are functions of the inhibitor

m = molar concentration of the inhibitor

The influence of inhibitors on the rate has been extensively studies by Schroeter (1963), and more recently by Altwicker (1979). According to Schroeter (1963), A and B are usually on the order of 10^{-5} molar, which means that inhibitor concentrations greater than 10^{-6} molar are effective. The form of the rate equation (Equation 2-31) suggests that the mechanism involves a bimolecular reaction between an inhibitor molecule and a radical in the chain.

In summary, our status of knowledge of the auto-oxidation reaction is:

1. The reaction is very slow.
2. The rate is extremely sensitive to the presence of catalysts and inhibitors.
3. The rate is first order in sulfite.
4. No reaction mechanism has been satisfactorily demonstrated to account completely for the observations of the more reliable studies (e.g., the dependence of the rate on $[H^+]^{0.5}$ found by Fuller and Crist, 1941 and by Larson et al., 1978).

2.3.4.2 S(IV) - catalyst - O_2 - H_2O System -- It is well-established that some metal cations catalyze the oxidation of HSO_3 and SO_3^{2-}. Of particular interest to the issue of atmospheric sulfur formation in particles, mist, fog, and rain is possible catalytic activity of: Mn(II), Fe(III), Cu(II), Ni(II), and V(IV). General features of the catalyzed reaction include: (a) inhibition by oxidizable organic molecules, (b) inhibition by metal ion-complexing molecules (inorganic and organic), (c) exhibition of an induction time of several seconds to several minutes, (d) detection of metal ion - S(IV) complexes, (e) no dependence of rate on dissolved O_2 concentration, (f) dependence of the rate of the inverse of the initial H^+ concentration (i.e., the rate is independent of pH change after the reaction has been initiated). While the catalytic reaction mechanisms are unknown, they are thought to be a modification of the initiation step of the auto-oxidation free radical mechanism (Equations 2-20 through 2-25); instead of M^+ being a trace concentration ($<10^{-9}M$) of metal ion or a reactive wall, it is a reagent present at concentrations $>10^{-6}M$. The rate expressions for the various catalysts have different forms, suggesting different types of initiation mechanisms (e.g., simple redox reactions or the formation of stable, reactive complexes). The agreement between independent investigators is generally poor, indicating the likelihood of mass transfer limitations of the rate or the presence of contaminants. A large percentage of the investigations were conducted with two-phase reactors for which the mass transfer characteristics were not adequately reported; therefore, those results must be considreed to be unreliable for estimating the elementary rate constant and for determining the reaction order. Also, the results for investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years, the studies pertinent to the formation of sulfate in the troposphere are presented in Table 2-6. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "in Bigelow"s (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen". Unfortunately, that comment applies to all but three of the Mn studies in Table 2-6, which are: Hoather and Goodeve (1934), Neytzell-de Wilde Taverner (1958), and Coughanowr and Krause (1965). It is odd that each of these investigators did not present rate expressions and rate constants derived from their data, and instead left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table 2-7. There is agreement that the Mn(II) catalyzed rate is independent of dissolved O_2, SO_2, HSO_3, and $SO_3{}^{2-}$ concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in good agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on $\lbrack Mn(II) \rbrack$. There appears to be no basis to discount any of the three investigations, yet it appears that serious errors may have been made. There is a slight preference for the expression for the results of Neytzell-de Wilde and Taverner (1958) because: (1) they measured the rate of disappearance of S(IV) by direct chemical means, and (2) the period of observation

TABLE 2-6. Investigations of SO_2 - Manganese - O_2 Aqueous Systems

Investigators	Type of System	Comment
Titoff (1903)	Bulk	2
Johnstone (1931)	Bubbler	1,2
Hoather and Goodeve (1934)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Coughanowr and Krause (1965)	Bulk and flow	2
Bracewell and Gall (1967)	Bubbler	1
Matteson et al (1969)	Free and supported droplets	3
Cheng et al. (1971)	Supported droplets	1

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.
3. Results are biased due to continued reaction (supported) droplets on filter sampler; rate expression cannot be considered to be reliable.

TABLE 2-7. Rate Expression for the Manganese-Catalyzed Oxidation

Expression[a,b,c]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} = 44\ [Mn(II)]^{1.7}\ [S(IV)]^0\ [H^+]^0$	3,4	Adapted from Hoather Goodeve (1934)
$\frac{d[SO_4^{2-}]}{dt} = 1.7 \times 10^{-5}\ [Mn(II)]\ [S(IV)]\ [H^+]_0^{-1}$	~2.2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 8[Mn(II)]^2\ [S(IV)]^0$	~ 3-4	Adapted from Coughanowr and Krause (1965); dependence on pH not reported

[a] The units are: liter, mole, second.

[b] Concentrations shown with zero power (e.g., $[S(IV)]^0$) indicate that the investigators found the rate to be independent of those species. Note that any concentration to the zero power is equal to unity.

[c] The term $[H^+]_0^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

(10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radial chains, and not during the induction period.

The Fe(III) catalyzed reaction studies that are pertinent to the formation of sulfate in the troposphere are identified in Table 2-8. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958), Karraker (1963), Brimblecombe and Spedding (1974a), and Fuzzi (1978). Hegg and Hobbs (1978) have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved O_2 is the oxidant, but instead the redox system associated with the couple Fe(III) + e^- -> Fe(II) in an oxygen-free system. Thus, Karraker's work is not considered applicable. Neytzell-de Wilde and Taverner (1958) reported that the sulfate formation rate was second order for [S(IV)], but Karraker (1963) has re-analyzed their data and has shown instead that the order is unity. As noted for the Mn(II) system, Neytzell-de Wilde and Taverner (1958) did not present a rate expression and constant for the Fe(III) system; an estimate derived from their paper is presented in Table 2-9. Brimblecombe and Spedding (1974a) have reported a rate expression and constant measured at a constant pH = 4; unfornately, they used a plastic reaction vessel, which could have released organic inhibitors into the system, causing the rate to be diminished. (At pH = 4, their rate is 0.25 of that of Neytzell-de Wilde and Taverner, 1958, and 0.1 of that of Fuzzi, 1978) Fuzzi (1978) did not note the similarity of his observations and those of Neytzell-de Wilde and Taverner (1958), especially the dependence of the rate on the initial inverse H^+ concentration for $pH \leq 4.0$. Fuzzi's (1978) rate expression has been modified by incorporating the dependence on $[H^+]_o^{-1}$ and is presented in Table 2-9. Note that Fuzzi's (1978) modified rate constant is 2.5 times greater than that of Neytzell-de Wilde and Taverner (1958), which is good agreement for this type of measurement; these two studies appear to be the most definitive for the Fe(III) system, and there is no basis to prefer one over the other. Fuzzi (1978) has clearly demonstrated the change in kinetics is due to the formation of colloidal $Fe(OH)_3$ for pH > 4, which provides an explanation for the disagreement among earlier investigators. Because of the formation of the $Fe(OH)_3$ colloid, it is unlikely that a meaningful Fe(III) catalyzed rate expression for use in tropospheric sulfate formation can be stated for conditions in which pH > 4.

The Cu catalyzed reaction kinetics have been described in the early work of Titoff (1903). The pertinent investigations are identified in Table 2-10. As with the Mn and Fe studies, most of the Cu studies were performed with incompletely characterized systems. Fuller and Crist (1941) point out that the prior work is unreliable because of the likely presence of contaminants. However, the investigations of Fuller and Crist (1941) were carried out in a two-phase reactor whose mass transfer characteristics are not completely described; no one has since conducted a study that is more definitive of this system. The reagent concentrations used by Barron and O'Hern (1966) are orders of magnitude too large, and the pH range (>8) used by Mishra and Srivastava (1976) is not applicable. For that reason, no rate expression can

Table 2-8 Investigations of SO_2 - Iron - O_2 Aqueous Systems

Investigators	Type of System	Comment
Reinders and Vles (1925)	Bulk	2
Basset and Parker (1931)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Danilczuk and Swinarski (1961)	Bulk	2
Karraker (1963)	Bulk	3
Bracewell and Gall (1967)	Bubbler	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Brimblecombe and Spedding (1974b)	Not reported	4
Freiberg (1974)	Theoretical	
Lunak and Veprek-Siska (1975)	Flow	5
Barrie and Georgii (1976)	Supported droplet	1
Fuzzi (1978)	Bulk	

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.
3. O_2 -free system; results not applicable to tropospheric SO_2 oxidation.
4. Insufficient details reported to determine if the results should be considered to be reliable.
5. Photochemical initiation.

TABLE 2-9. Rate Expression for the Iron-Catalyzed Oxidation

Expression[a],[b]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} = 0.04\ [Fe(III)][S(IV)][H^+]_o^{-1}$	~ 2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 100\ [Fe(III)][S(IV)]$	4	Brimblecombe and Spedding (1974a)
$\frac{d[SO_4^{2-}]}{dt} = 0.1\ [Fe(III)][S(IV)][H^+]_o^{-1}$	≤ 4	Adapted from Fuzzi (1978)

[a] The units are: liter, mole, second.

[b] The term $[H^+]_o^{-1}$ indicates that the rate is dependent on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

Table 2-10 Investigations of SO_2 - Copper - O_2 Aqueous Systems

Investigators	Type of System	Comment
Titoff (1903)	Bulk	2
Reinders and Vles (1925)	Bulk	2
Alyea and Backstrom (1929)	Bulk	2
Johnstone (1931)	Bubbler	1
Albu and Grof von Schweinitz (1932)	Bulk	2
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al (1949)	Bulk	2
Basset and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1
Barron and O'Hern (1966)	Flow	
Bracewell and Gall (1967)	Bubbler	1
Cheng et al. (1971)	Supported droplet	1
Veprek-Siska and Lunak (1974)	Flow	2
Barrie and Georgii (1976)	Supported droplet	1
Huss et al. (1978)	Bulk	2
Mishra and Srivastava (1976)	Flow	

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.

be recommended as reliable for use in calculating sulfate formation rates due to CU catalysis in the troposphere.

Vanadium catalysis has been reported in only one study (Bracewell and Gall, 1967); a bubble reactor was used, and its mass transfer characteristics were inadequately reported. Therefore, no rate expression can be recommended as reliable. However, Bracewell and Gall (1967) did observe qualitatively that V(V) was orders of magnitude less effective that Mn and Fe. Most likely, V(V) catalysis is unimportant for sulfate formation in the troposphere. Likewise, there are no definitive studes for Cr(III), Ni(II), Zn(II), and Pb(II), but it appears from the qualitative work of Bracewell and Gall that these catalytic reactions are unimportant.

Barrie and Georgii (1976) have demonstrated qualitatively that Mn(II) and Fe(III) exhibit a synergistic rate for the catalysis of S(IV) oxidation. Their rate expression cannot be considered to be reliable since they used a supported droplet.

In summary, our status of knowledge of the homogeneous metal ion catalysis systems is:

1. S(IV) oxidation rates are significantly increased by Mn(II) and Fe(III). There is serious doubt regarding the rate expression for Mn(II), but the agreement among independent studies is much better for Fe(III).

2. These systems are presently inadequately characterized: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).

3. There are no quantitative studes of metal ion-metal ion synergism.

4. The ability of atmospheric organic compounds to inhibit the catalysis is unknown.

5. All studies have been performed in the absence of HCO_3^-; however, the reactions

$$\cdot SO_4^- + HCO_3^- \rightarrow HCO_3 + SO_4^{2-}$$

$$\cdot OH + HCO_3^- \rightarrow HCO_3 + OH^-$$

may be important. It is possible that such reactions may occur, and if so, they would prevent the oxidation radical chain from establishing since HCO_3 is not a powerful oxidizer (Hoigné and Bader, 1978).

6. In general, the rate expressions for catalytic oxidation to form sulfuric acid are not well-established.

2.3.4.3 S(IV) - Carbon Black $-O_2 - H_2O$-- The catalysis of the oxidation of dissolved SO_2 by carbon particles suspended in the water has been studied by Chang et al. (1979) and by Eatough et al (1979). It was found by Chang et al. (1979) that the oxidation rate of dissolved SO_2 species was:

$$-\frac{d[S(IV)]}{dt} = k[C\ ][O_2]^{0.69}[S(IV)]^0 \exp.(-E_a/RT) \qquad (2\text{-}32)$$

with an activation energy of E_a = 11.7 kcal/mol over the pH range of 1.45 to 7.5 for the carbon studied, which was Nuchar-190. (The investigators demonstrated that Nuchar-190 behaved similarly to soot from acetylene and natural gas flames.) An average value of $k = 1.17 \times 10^5$ $mol^{0.3} \times liter^{0.7}$/g-sec was reported. The kinetics have been interpreted in terms of the rate-limiting step being the formation of an activated complex between molecular oxygen and the carbon surface (Chang et al., 1979; Eatough et al. 1979).

Chang et al. (1979) have estimated that for 10 ug of their fine carbon soot suspended in 0.05 g of liquid water and dispersed in 1 m^3 of air, the atmospheric sulfate production would be 1 ug/hr. Heavy hydrocarbons are adsorbed on the surfaces of atmospheric soots and may inhibit the carbon-surface catalyzed oxidation of dissolved SO_2. At this time, it remains to be demonstrated that the laboratory soots used by Chang et al. (1979) correspond to those present in the atmosphere or that the suspension of soot at ambient levels ($<10\ \mathrm{ug/m^3}$) in aerosols, cloud droplets or rain is similar to the laboratory system.

2.3.4.4 S(IV) - Dissolved Oxidants - H_2O-- Hydrogen peroxide, ozone, and nitrogen dioxide may be important in the oxidation of SO_2 in aqueous aerosols and fogs. Although these compounds do not demonstrate high reactivity toward SO_2 in air, their reactivity is enhanced in the liquid phase. Again, caution is advised in accepting the results of studies of two-phase systems in which the investigators have not completely accounted for the possibility of the mass transport limitation of the oxidation rate. Therefore, only the recent results for single-phase systems are discussed here.

Martin et al. (1981) have used a stopped-flow reactor to investigate the kinetics of oxidation of aqueous SO_2 species by aqueous NO, NO_2^-, and NO_3^-. Over the pH range of 0.6 to 3.2, they found for NO and NO_3^- that the disappearance of S(IV) species is:

$$\frac{d[S(IV)]}{dt} = k\ [\mathrm{NO\ or\ \underline{N}O_3^-}][S(IV)] \qquad (2\text{-}33)$$

$$k \leq 0.01\ \mathrm{mole\ l^{-1}sec^{-1}}$$

However, for the same conditions, the reaction with NO_2^- is rapid and the formation of SO_4^{2-} can be expressed as:

$$-\frac{d[SO_4^{2-}]}{dt} = k_1[H^+]^{0.5}\ [HNO_2 + NO_2]\ [SO_2.H_2O + HSO_3]$$

$$k_1 = 142\ (\mathrm{liter/mole})^{1.5}\mathrm{sec}^{-1} \qquad (2\text{-}34)$$

The NO_2^- is reduced quantitatively in this reaction to N_2O. Martin et al. (1981) also observed that this reaction is not catalyzed by Fe(III), Mn(II), or VO^{2+}. It is unlikely that tropospheric nitrous acid (HNO_2) concentrations are high enough for this reaction to be important for H_2SO_4 formation.

The oxidation of dissolved SO_2 by ozone has been investigated with stopped-flow systems. Penkett (1972) and Penkett et al. (1979) have interpreted their work in terms of a decomposition of ozone to initial a free-radical chain reaction involving OH, HSO_3, and HSO_5 radicals, after Backstrom (1934). Penkett et al. (1979) suggested that the rate expression is

$$\frac{d[SO_4^{2-}]}{dt} \simeq k[HSO_3^-]\ [O_3]\quad [H^+]^{-1} \qquad (2\text{-}35)$$

where k - 71 sec^{-1}. Erickson et al. (1977) reported the fractional contributions to the oxidation of the three sulfur oxide species by ozone at various pH values; their rate expressions are

$$\frac{d[SO_4^{2-}]}{dt} = k_1[SO_2.H_2O]\,[O_3] \qquad (2\text{-}36)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_2[HSO_3^-]\,[O_3] \qquad (2\text{-}37)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_3[SO_3^{2-}]\,[O_3] \qquad (2\text{-}38)$$

where $k_1 = 590$ liter mol.$^{-1}$sec^{-1}, $k_2 = 3.1 \times 10^5$ liter mol.$^{-1}$ sec^{-1}, and $k_3 = 2.2 \times 10^9$ liter mol.$^{-1}$sec^{-1}.

Penkett et al. (1979) used a stopped-flow reactor to determine the kinetics of oxidation of dissolved SO_2 species by hydrogen peroxide. It was found that the rate of sulfate formation is given by

$$\frac{d[SO_4^{2-}]}{dt} = k[H_2O_2][HSO_3^-][H^+] + k_a[H_2O_2][HSO_3^-][HA] \qquad (2\text{-}39)$$

where $k = 2.6 \times 10^7$ liter^2 mol^{-2}.sec^{-1}, with k and k_a being the third-order rate constants for the catalysis by free protons and proton-donating buffers (HA), respectively. At pH ≤ 4, it is found that $k/k_a \geq 3200$. Therefore, the second term is probably not important for acid aerosols and fogs. It is of great significance that the reaction rate increases as the solution becomes more acidic, which is in contrast to aqueous oxidation by metal ions and by ozone. The activation energy and the effect of ionic strength on the reaction have been measured by Penkett et al. (1979). Dasgupta (1980) has criticized the presentation of Penkett et al. (1979); use of the rate expression (equation 2-39) takes into account Dasgapta's (1980) points. Martin and Damschen (1981) have found that

$$\frac{d[SO_4^{2-}]}{dt} = k[H_2O_2][SO_2.H_2O] \;/(0.1 + [H^+]) \qquad (2\text{-}40)$$

where $k = 7.2 \times 10^4$sec^{-1}; their expression is applicable over the range $0<pH<5$ and is in good agreement with Penkett et al. (1979).

In summary, our status of knowledge of the formation of H_2SO_4 by dissolved oxidants is:

1. The oxidation rates are known for NO and NO_3^- and are too low to be important.

2. The oxidation rate is known for NO_2^-, but the tropospheric concentration of HNO_2 is probably too low for this reaction to be important.

3. The oxidation rate is known for O_3, but it is usually expected to be unimportant.

4. The oxidation rate for H_2O_2 is known and appears to be potentially a highly effective reaction for formation of H_2SO_4 in the troposphere. This rate could possibly be enhanced by metal ions, but no studies have been reported.

5. Organic oxidizers may be important, but no studies have been reported.

2.3.4.5 The Influence of NH_3-- It has been recognized for several decades that NH_3 may influence the formation rate of H_2SO_4 in aqueous particles, mist, fog, and rain. Hegg and Hobbs (1978) have reviewed the studies of the NH_3 influence. They have called attention to a misunderstanding in the literature. NH_3 is commonly reported incorrectly to be a "positive catalyst" for the oxidation of dissolved SO_3. In the strict sense of the definition of "catalyst," the term cannot be applied to the role of NH_3. The observed enhancement by NH_3 of the oxidation rates of the auto-oxidation, metal -ion oxidation, and the O_3 oxidation is due to its action to raise and maintain a high pH. The following process occurs to raise and maintain a higher pH through the conversion of HN_3 to NH_4^+:

1. Ambient gaseous $NH_{3(g)}$ dissolves in the water, $NH_{3(g)} \rightleftarrows HN_{3(aq)}$
2. The dissolved $NH_{3(aq)}$ reacts with H^+, which raises the pH $NH_{3(aq)} + H^+ \rightleftarrows NH_4^+$.

Therefore, the ambient pathways of auto-oxidation, Mn(II)- and Fe(III)- catalyzed oxidation, and O_3 oxidation would have their rates enhanced by absorption of NH_3. However, the ambient pathways of H_2O_2 and HNO_2 would have their rates retarded by NH_3 absorption. The rate for soot would not be influenced.

NH_3 can play other important roles. Reinders and Vles (1925) observed qualitatively that Cu(II) was complexed by NH_3 and rendered non-catalytic. At high pH's (>9) such that $NH_{3(aq)}$ is the dominant form, NH_3 is explained in terms of its influence on the pH of the water system; NH_3 is not a catalyst.

2.3.5 Surface Chemical Reactions

Industrial emissions of solid particles (e.g., fly ash) and fugitive dust (e.g., windblown soil and minerals) provide a solid-surface that may chemisorb SO_2 and yield sulfate ions. The work reviewed in this section will include investigations of the SO_2 oxidation on the surfaces of: metal oxides, fly ash, charcoal, and soot. Although reaction kinetics have not been identified, two general types of processes have been: a capacity-limited reaction for SO_2 removal and a catalytic SO_2

oxidation process. The inital contact of SO_2 with the solid produces a rapid loss of SO_2 from the gas phase; the reaction rate decreases with time. for the capacity-limited reaction, the rate approaches zero; for the catalytic process, the rate levels off for a time and them approaches zero. The latter phenomenon is attributed to a pH decrease caused by sulfuric acid formation.

Urone et al. (1968) and Smith et al. (1969) found a number of solids to be effective in removing SO_2. In Urone's studies, SO_2 was admitted to a flask containing a powder that was allowed to react with no mixing, and the product and remaining SO_2 were determined. Only the average reaction rates can be calculated from these experiments; more importantly, with this experimental procedure the rates may be diffusion-limited. The highest rate determined was for SO_2 with ferric oxide; the value was >75 percent per minute. Other materials found to be slightly less reactive than ferric oxide were magnetite, lead oxide, lead dioxide, calcium oxide, and aluminum oxide. The rate for the ferric oxide experiment was for 20 mg of ferric oxide in a 2-liter flask, the ferric oxide concentration would thus be 10^7 ug/m^3. Assuming a direct proportionality between rate and particle concentration, the SO_2 removal rate in the atmosphere would be calculated to be 0.04 percent per hour for 100 ug/m^3 of particles with the same reactivity as ferric oxide. However, since the mass transfer characteristics of the reactor were not reported, these results cannot be considered reliable for estimating rates.

Smith et al. (1969) did not focus on sulfate formation kinetics; instead, they illustrated through a novel experiment the ability of solid particles to adsorb SO_2 and to release SO_2 during passage through a tube with a wall that adsorbes SO_2. They measured the number of SO_2 monolayers absorbed on suspended Fe_3O_4 as function of SO_2 partial pressure. (The monolayer coverage data reported in their Table I are in error by a factor of 100 too large; e.g., the number of monolayers at 1.13 ppm should be 0.38×10^{-2}.)

Chun and Quon (1973) measured the reactivity of ferric oxide to SO_2, using a flow system involving a filter containing suspended particles. They determined a removal rate constant of 9.4×10^{-3} ppm^{-1} min^{-1} $[-d(\ln \rho)dt]$, where ρ is the fraction of surface sites available for reaction. Extrapolating this to an atmospheric particle concentration of 100 ug/M^3 with an equivalent reactivity and an SO_2 concentration of 0.1 ppm, the data project an atmospheric removal rate of 0.1 percent per hour.

Stevens et. al. (1978) report total iron concentrations in six U. S. cities ranging between 0.5 and 1.3 ug/m^3. Other species such as manganese, copper, or vanadium had total concentrations usually below 0.1 ug/m^3. Thus actual ambient air concentrations are a factor of approximately 50 times less than that assumed by the authors in the above papers. A reactive particle concentration of 2 ug/m^3 would yield a predicted SO_2 removal rate of no more than 0.002 percent per hour. Therefore, surface reactions are probably not not important except in sources prior to or immediately after emission.

The most comprehensive study to date on SO_2 removal by pure solids was made by Judeikis (1974) and Judeikis et al. (1978), who used a tubular flow reactor in which solids were supported on an axial cylinder to measure reactivities of MgO, Fe_2O_3, Al_2O_3, MnO_2, PbO, NaCl, charcoal, and fly ash. They found that the rates of SO_2 removal diminished with exposure until the solids completely lost ability to react with SO_2. The relative humidity was important in determining the total capacity for SO_2 removal, but not the initial rate of uptake; total capacity increased as relative humidity increased. The capacity for SO_2 could be extended by exposure to NH_3. This type of behavior is consistent with the formation of H_2SO_4 on the surfaces.

Because of the ubiquitous nature of carbonaceous matter in ambient air particulate samples, various workers have studied the SO_2 removal rate by carbon. A comparison of the results is rather difficult because of the varieties of carbon available for study, such as activated charcoal, graphite, acetylene flame products, and combustion products of diesel oil and heating oil. We cite here a few investigations that deal with the gas-solid reaction of SO_2 with carbon.

Novakov et al. (1974) performed laboratory experiments that showed that graphite and soot particles oxidize SO_2 in air.

The soot exposed to humidified air produced more SO_4^{2-} than that exposed only to dry air. They also observed for downtown Los Angeles a strong correlation between the concentration of ambient carbon and SO_4^{2-} formation. (See discussion in Section 2.3.4.3.)

Tartarelli et al. (1978) studied the interaction of SO_2 with carbonaceous particles collected from the flue ducts of oil burning power stations. They concluded that the amount of adsorption is increased by the presence of oxygen and water in the gas stream. Reaction rates were not determined in this study.

Liberti et al. (1978) studied the adsorption and oxidation of SO_2 on various particles, including soot from an oil furnace and various atmospheric particulate samples. They concluded that the main interaction between the SO_2 and particulate matter is adsorption, with most catalytic reactions occurring at high temperatures, near the combustion source. Their experiments with atmospheric particulate samples lead them to the conclusion that any heterogeneous nonphotochemical sulfate formation is strongly dependent on the reactivity of the particle surface, and hence the history (aged, freshly emitted), of the aerosol.

In summary, the status of our knowledge of surface reactions is:

1. The reactions are capacity-limited. Those that involve catalysis in liquid films can be extended by the absorption of NH_3.

2. The intial rates may be large, but quickly approach zero.

3. Except for the carbon (soot) reaction, solid surface reactions do not appear to be effective pathways for H_2SO_4 formation in the troposphere.

2.3.6 Estimates of SO_2 Oxidation

It is of interest at this point to compare the rates of SO_2 oxidation by the more important reactions identified in the previous sections of Chapter 2. The important reactions for gas-phase and aqueous-phase oxidation are listed in Table 2-11, and rates of SO_2 oxidation for an assumed set of conditions are present. These calculations ignore the non-homogeneous nature of the troposphere and assume that all of the reactants are well-mixed. (The more general case is treated in Section 2.3.7).

Table 2-11. Estimates of SO_2 Oxidation Rates in a Well-Mixed Troposphere

Reaction	Rate, % h^{-1}			Discussion Section	Comments
I. Gas Phase					
HO radical	0.3 - 1.3			2.3.3.2	1
HO_2 radical	0.4 - 2.0			2.3.3.2	1,2
CH_3O_2 radical	0.3 - 1.5			2.3.3.2	1,2
II. Aqueous Phase pH=	1	2	3		
Mn(II) catalysis	1E-1	1E+1	1E+3	2.3.4.2	2,3,4
Fe(III) catalysis	5E-5	5E-1	5E+3	2.3.4.2	3,5
C (soot) catalysis	3E+1	3E+1	3E+1	2.3.4.3	6
O_3 (40 ppb)	2E-8	2E-6	2E-4	2.3.4.4	3,7
O_3 (120 ppb)	6E-8	6E-6	6E-4	2.3.4.4	3,7
H_2O_2 (1 ppb)	2E-2	3E-2	3E-2	2.3.4.4	3,8
H_2O_2 (10 ppb)	2E-1	2E-1	3E-1	2.3.4.4	3,8

NOTE: "E" denotes "exponential to 10th power;" e.g., 3E-1 = 3×10^{-1}

1. Typical range for daytime at northern midlatitudes during the summer.
2. This reaction rate is not well established; see discussion section.
3. Assumed that liquid water volume of aerosol $= 50 \times 10^{-12} m^3/m^3$, $[SO_2]_g = 10$ ppb (or 27 ug/m^3).
4. Assumed that Mn(II) mass concentration = 20 ng/m^3; also , the Mn(II) is assumed to be uniformly dissolved in the liquid water of the aerosol [Mn(II)] = 8.9×10^3M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-7.

5. Assumed that Fe(III) mass concentration = 2 ug/m^3; also, the Fe(III) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Fe(III]) = 0.9 M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-9.
6. Assumed that C mass concentration = 10 ug/m^3 and behaves as the soots studied by Chang et al. (1979), whose expression was used for this calculation (Equation 2-32).
7. Rate calculation was based on Equation 2-35.
8. Rate calculation was based on Equation 2-39.

For this comparison, it has been assumed that the SO_2 concentration is 10 ppb for all of the reactions, and that the liquid water content of the aerosol is 50 x 10^{-12} m^3/m^3.

The gas-phase rates have been calculated based on the discussion material presented in Section 2.3.3.2. The aqueous-phase rates have been calculated based on the discussion material presented in Sections 2.3.4.2-4. Several of the assumptions made do not have any basis, namely:

1. The ambient mass concentration of 20 ng/m^3 for Mn is reasonable, but: (a) it is not known if the predominant form is Mn(II), and (b) it is unlikely that Mn is uniformly distributed and dissolved.

2. Likewise, the ambient concentration of 2 ug/m^3 for Fe is reasonable, but: (a) it is not known if Fe(III) is the predominant form, and (b) it is unlikely that Fe is uniformly distributed and dissolved.

3. There is no basis to assume that the rate equation observed for laboratory-generated carbon (soot) applies to atmospheric carbon.

4. The rates for the HO_2 and CH_3O_2 reactions recommended by Calvert et al. (1978) are not well established.

It is very likely that the rates estimated for Mn(II) catalysis, Fe(III) catalysis, and C (soot) catalysis are gross over-estimates. Also, the HO_2 and CH_3O_2 rates may be too high.

Uncritical acceptance of all of the rates, at a pH = 3, and $[H_2O_2]$ = 10 ppb, would lead to the SO_2 conversion rate exceeding 40% h^{-1}. However, if only the well-established rates are considered, the SO_2 conversion rate becomes $\sim$1.1% h^{-1}.

2.3.7 Field Measurements on the Rate of SO_2 Oxidation

The majority of SO_2 oxidation studies in the atmosphere have been only carried out in recent years and of those, most have involved power plant plumes. One reason for the late start in this research area has been the lack of adequate measurement technology for particulate sulfur, but recent developments Huntzicker et al. (1978), Cobourn et al. (1978) seem to have alleviated this problem. A summary of SO_2 oxidation rates based on field measurements in power plant, smelter and urban plume studies carried out from 1975 to the present is given in Table 16-1. The rates of SO_2 oxidation in industrial plant plumes consistently range from 0 to 10%/h, with urban plumes showing only a slightly greater maximum rate of 13%/h. The pre-1975 studies, Gartrell et al. (1963), Dennis et al. (1969), Weber (1970) and Stephens and McCalden (1971), which observed conversion rates an order of magnitude larger than more recent observations, must be considered suspect due to possible artifact formations in the sulfate analysis technique and limitations in the analytical methods in general.

Newman (1980) recently reviewed the majority of the power plant and smelter plume studies presented in Table 2-12 and arrived at the following conclusions.

1) The diurnal average oxidation rate of sulfur dioxide to sulfate is probably less than 1% per hour.
2) Little or no oxidation of sulfur dioxide occurs from early evening through to early morning.
3) Maximum oxidation rates of sulfur dioxide to sulfate of 3% per hour can occur under midday conditions.
4) The contribution of homogeneous and heteorogeneous mechanisms to sulfur dioxide oxidation in plumes cannot be elucidated from the present studies.

It should be noted that the reported SO_2 oxidation rates are estimates based on analyses of measured physical and chemical parameters and in many instances have incorporated within them certain simplifying assumptions which are not totally substantiated. Typically uncertainties in reported values are 50%, but may be greater if inappropriate assumptions have been used. Even with these uncertainties in mind, the overall consistency in the observed range of SO_2 oxidation rates is gratifying.

TABLE 2-12. Field Measurements on the Rates of SO_2 Oxidation in Plumes*

Plume Type Location	SO_2 Oxidation Rate (%h^{-1}	Method	Reference
Power Plant			
Keystone (Pennyslvania)	0-10	$^{32}S/^{34}S$ ratio, change with oxidation	Newman et al. (1975)
Labadie (Missouri)	0.41-4.9	Total change in particle volume	Cantrell and Whitby (1978)
Four Corners (New Mexico)	0.27-0.84	Sub-micron suflate and SO_2 - change of ration with time	Ursenbach et at. (1977)
Labadie and Portage des Sioux (Missouri)			
Muscle Shoals (Alabama)	0-5	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977a)
Kyger Creek (Ohio)			
Labadie (Missouri)	0-3	Particulate sulfur to total sulfur ratio	Gillani et al. (1978)
Four Corners (New Mexico)	2-8	CCN production (CCN to SO_2 ratios)	Pueschel and Van Valin (1978)
Labadie (Missouri)	0-4	Particulate sulfur to total sulfur ratio	Husar et al. (1978)
Cumberland (Tennessee)	0-7	Particulate sulfur to total sulfur ratio	Meagher et al. (1978)
Great Canadian Oil Sands (Alberta, Canada)	0-3	Particulate sulfur to total sulfur ratio	Lusis et al. (1978)
Keystone (Pennyslvania)	0-5	Particulate sulfur to total sulfur ratio	Dittenhoefer and de-Pena (1978)

Table 2-12 (Continued)

Plume Type Location	SO_2 Oxidation Rate (%h^{-1}	Method	Reference
Central (Washington) Four Corners (New Mexico)	0-6	Total change in particle volume	Hobbs et al. (1979)
Four Corners (New Mexico)	0.15-0.5	CCN production (CCN to SO_2 ratios)	Mamane and Pueschel (1980)
Leland-Olds (North Dakota) Sherburne County Minnesota Big Brown (Texas)	0-5.7	Total change in particle volume	Hebb and Hobbs (1980)
<u>Smelter</u>			
INCO Nickel (Copper Cliff, Canada)	0-7	Particulate sulfur to total sulfur ratio	Lusis and Wiebe (1976)
INCO Nickel (Copper Cliff, Canada)	1.2-5.2	Particulate sulfur to total sulfur rates	Forrest and Newman (1977b)
Mt Isa Mines (MT. ISA, Australia)	0.25†	Particulate sulfur to total sulfur ratio	Roberts and Williams (1979)
<u>Urban</u>			
Los Angeles (California)	1.2-13	Particulate sulfur to total sulfur ratio	Roberts and Friedlander (1975)
St. Louis (Missouri)	7-12.5	Particulate sulfur to total sulfur ratio	Alkezweeny and Powell (1977)
St. Louis (Missouri)	3.6-4.2	Particulate sulfur to total sulfur ratio	Chang (1979)

*Adapted in part from Hegg and Hobbs (1980)

†diurnal average rate

2.4 Summary and Conclusions

Present understanding of the homogeneous gas phase reactions of SO_2 indicates that the rate of SO_2 oxidation in the atmosphere is dominated by free radical reaction processes. The free radical species identified as important contributors to the SO_2 oxidation process are hydroxyl (HO), methylperoxyl (CH_3O_2) and other organic peroxyl species (RO_2, $R'O_2$, etc.). The concentration of these radicals in the atmosphere are dependent on many factors, the more important of which are the concentration of volatile organic compounds and nitrogen oxides (NO and NO_2) in the atmosphere, temperature and solar intensity. Theoretical estimates have shown that maximum SO_2 oxidation rates of 4.0% h^{-1} are possible in polluted atmospheres. However, recent experimental rate constant determinations for the HO_2 and CH_3O_2 reactions with SO_2 indicate that these processes may not be as important as previously thought and that the maximum possible homogeneous SO_2 oxidation rate under optimum atmospheric conditions may only be of the order of 1.5% h^{-1}. This rate is result of SO_2 reaction with hydroxyl radical only.

Present knowledge of heterogenous pathways to SO_2 oxidation in the atmosphere indicates that the liquid phase catalyzed oxidation of SO_2 by Mn^{+2} ion and carbon are potentially important processes, as is oxidation by hydrogen peroxide. Theoretical estimates of atmospheric SO_2 oxidation rates via these processes are of the order of 10% h^{-1}. Unfortunately, a great deal of uncertainty surrounds the actual availability of these catalyzing substances in ambient fine particulate matter. The quantitative determination of rates of SO_2 oxidation via these processes has never been demonstrated under actual atmospheric conditions.

Organic and nitrate particulate matter forming processes are presently thought to be dominated by homogeneous gas phase reactions. In the case of atmospheric nitrates, a particularly significant production pathway is through reaction between hydroxyl free radical and nitrogen dioxide resulting in nitric acid ($HONO_2$) formation. The fate of nitric acid in the atmosphere is not well understood, though a portion of gaseous nitric acid is known to enter into an equilibrium with ammonia (NH_3) to form particulate ammonium nitrate (NH_4NO_3). Present knowledge provides little support for liquid phase oxidation as an important pathway to NO_x transformation.

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6.1 CHEMISTRY OF THE OXIDES OF NITROGEN IN THE LOWER ATMOSPHERE

Solar radiation triggers a series of reactions in the atmosphere between gaseous organic molecules and nitrogen oxides, producing a wide variety of secondary pollutants. The totality of primary and secondary pollutants involved in these photochemical reactions is known as photochemical smog. To understand the chemistry of the oxides of nitrogen in the lower atmosphere, it is necessary to consider the interactions that take place between the oxides of nitrogen and organic constituents. Several reviews of atmospheric chemistry are available, [1-3] as are detailed discussions of reaction mechanisms [4-8] and rate constants.[9] In this section the chemistry of the oxides of nitrogen in the lower atmosphere is briefly reviewed. The above-cited references should be consulted for more detail.

Most of the chemistry that occurs in a sunlight-irradiated urban atmosphere involves the interaction of a variety of unstable, excited molecules and molecular fragments that have only a transitory existence. These species include: the unexcited and first excited electronic states of the oxygen atom, triplet-P oxygen atoms [$O(^3P)$], and singlet-D oxygen atoms [$O(^1D)$]; ozone (O_3); symmetrical nitrogen trioxide (NO_3); dinitrogen pentoxide (N_2O_5); hydroxyl radicals (HO); alkylperoxyl radicals (RO_2); acylperoxyl radicals $RC(O)O_2$; and less important species. In the formulas, R represents a methyl (CH_3), ethyl (C_2H_5), or another, more complex hydrocarbon radical. The paths by which these intermediates are formed and destroyed are important keys in explaining the chemical changes that occur in the polluted atmosphere.

6.1.1. Reactions Involving Oxides of Nitrogen

The major portion of the total oxides of nitrogen emitted by combustion sources is nitric oxide (NO). The rate at which NO is converted to nitrogen dioxide (NO_2) through oxidation by molecular oxygen in air:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (6\text{-}1)$$

is proportional to the square of the nitric oxide concentration since two molecules of NO are required for the oxidation; it is, therefore, very sensitive to changes in nitric oxide concentration. Reaction 6-1 can be important in the vicinity of sources in converting up to 25 percent of the total NO_x to NO_2 during the initial stages of dilution with air when the concentration of NO is still quite high. Reaction 6-1 is much too slow, however, to account for the high conversion rates of nitric oxide to nitrogen dioxide observed in the atmosphere under typical ambient concentrations.

Since sunlight triggers the phenomenon of photochemical smog formulation, it is important to recognize those constituents that will absorb light energy. In some cases, these constituents decompose or become activated for reaction. Nitrogen dioxide, a dominant sunlight absorber in the urban atmosphere, photodissociates upon absorbing wavelengths of light <430 nm. This photolytic reaction results in the formation of the ground state, triplet-P oxygen atom, and a nitric oxide molecule. The efficiency of this process is wavelength-dependent:

$$NO_2 + \text{sunlight (290-430 nm)} \rightarrow O(^3P) + NO \quad (6\text{-}2)$$

The highly reactive triplet-P oxygen atom predominantly reacts with oxygen molecules in the air, resulting in the formation of ozone.

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (6\text{-}3)$$

M in this equation represents a nitrogen, oxygen, or other third molecule that absorbs the excess vibrational energy released, thereby stabilizing the ozone produced. For most concentration conditions common in polluted atmospheres, ozone molecules regenerate nitrogen dioxide by reaction with nitric oxide:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (6\text{-}4)$$

To a much lesser extent, ozone can react with nitrogen dioxide to form the transient species, nitrogen trioxide:

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (6\text{-}5)$$

The nitrogen trioxide can further react with nitrogen dioxide to form dinitrogen pentoxide, the reactive anhydride of nitric acid.

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad (6\text{-}6)$$

Dinitrogen pentoxide which is in equilibrium with nitrogen trioxide and nitrogen dioxide can dissociate or react with water to form nitric acid ($HONO_2$):

$$N_2O_5 \rightarrow NO_3 + NO_2 \qquad (6\text{-}7)$$

$$N_2O_5 + H_2O \rightarrow 2HONO_2 \qquad (6\text{-}8)$$

Additional reactive pathways which can take place between oxygen atoms and NO_2 and NO include:

$$NO_2 + O(^3P) \rightarrow NO + O_2 \qquad (6\text{-}9)$$

$$NO_2 + O(^3P) + M \rightarrow NO_3 + M \qquad (6\text{-}10)$$

$$NO + O(^3P) + M \rightarrow NO_2 + M \qquad (6\text{-}11)$$

Also, NO and NO_3 can react to regenerate NO_2:

$$NO_3 + NO \rightarrow 2NO_2 \qquad (6\text{-}12)$$

Nitrous acid is produced by:

$$NO + NO_2 + H_2O \rightarrow 2HONO \qquad (6\text{-}13)$$

and may react bimolecularly to regenerate the original reactants:

$$HONO + HONO \rightarrow NO + NO_2 + H_2O \qquad (6\text{-}14)$$

The unexcited and first excited electronic state of the oxygen atom are produced by ozone photolysis in sunlight:

$$O_3 + \text{sunlight} \begin{array}{ll} (290\text{-}350 \text{ nm}) \rightarrow O_2 + O(^1D) \text{ or } O(^3P) & (6\text{-}15a) \\ (450\text{-}700 \text{ nm}) \rightarrow O_2 + O(^3P) & (6\text{-}15b) \end{array}$$

The singlet-D oxygen [$O(^1D)$] atom is much more reactive than the ground state triplet-P oxygen [$O(^3P)$] atom. For example, it reacts efficiently during collision with a water molecule to form an important transient species in the atmosphere, the hydroxyl radical:

$$O(^1D) + H_2O \rightarrow 2HO \qquad (6\text{-}16)$$

This radical is also formed through the photodecomposition of nitrous acid (HONO):

$$\text{HONO} + \text{sunlight (290-400 nm)} \rightarrow \text{HO} + \text{NO} \qquad (6\text{-}17)$$

The hydroxyl radical can react with nitric oxide to give back nitrous acid:

$$\text{HO} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \qquad (6\text{-}18)$$

or form nitric acid by reacting with nitrogen dioxide:

$$\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \qquad (6\text{-}19)$$

Demerjian et al.[106] have shown through computer simulations of the reaction sequence 6-1 through 6-19 that these reactions cannot explain the rapid conversion of NO to NO_2 observed in the ambient atmosphere. In fact, if these reactions alone occurred, the original supply of nitrogen dioxide in our atmosphere would be slightly depleted under irradiation with sunlight, and a small and near constant level of ozone would be created in a few minutes. The key to the observed nitric oxide to nitrogen dioxide conversion lies in a sequence of reactions between the transient species present and other reactive molecules such as the hydrocarbons and aldehydes present in the polluted atmosphere.

In the presence of hydrocarbons the number of reactions greatly increases. Thus, the hydroxyl radicals produced by reactions 6-16 and 6-17 can react with a hydrocarbon (paraffin, olefin, aromatic, or any compound having C-H bonds):

$$\text{OH} + \text{Hydrocarbon} \rightarrow \text{R} \quad + \text{H}_2\text{O} \qquad (6\text{-}20)$$

Reaction 6-20 produces an alkyl radical (R) which contains a free electron. This radical quickly picks up an oxygen molecule from the air to form a peroxyl radical RO_2 :

$$R + O_2 \xrightarrow{M} RO_2 \qquad (6\text{-}21)$$

Typically, the next reaction in the series converts NO to NO_2 and produces an oxyl radical, RO :

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6\text{-}22)$$

A hydrogen abstraction by molecular oxygen may then produce a hydroperoxyl radical, HO_2 . The rest of such an RO radical typical forms a carbonyl compound, OHC:

$$RO + O_2 \rightarrow OHC + HO_2 \qquad (6\text{-}23)$$

Finally, the hydroperoxyl radical (HO_2) can react with a second NO to form NO_2 to complete the cycle:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (6\text{-}24)$$

Although this description is very simplified, these series of reactions contain the essential features of NO to NO_2 oxidation and subsequent ozone formation.

The initial source of radicals is very important; although the rate and yield of oxidant formation depend on many other factors, the length of the induction period before accumulation of oxidant depends strongly on the initial concentration of radicals. (The length of the induction period is important primarily in constant light intensity smog chambers. Diurnally varying radiation tends to lessen the importance considerably.) In smog chambers and possibly in the ambient atmosphere, the photolysis of nitrous acid, reaction 6-17, may be the most important initial source of radicals. Nitrous acid has been detected in smog chambers in concentrations sufficient to explain the observed induction time for smog chemistry, but the concentrations necessary to initiate smog chemistry in the atmosphere are below the limits measured by most modern instruments.

Another possible source of radicals in the atmosphere is the photolysis of aldehydes:

$$RCHO + h\nu \rightarrow HCO + R \qquad (6\text{-}25)$$

Aldehydes are emitted from many sources, including automobiles. They are also formed in smog.

During the course of the overall smog formation process, the free radical pool is maintained by several sources, but the dominant one appears to be photolysis of the aldehydes formed from the initial hydrocarbons. Since the reactions of free radicals with NO form a cyclic process, any additional source of radicals will add to the pool and increase the cycle rate. Conversely, any reaction that removes free radicals will slow the cycle rate. For example, a primary radical sink and a primary sink for oxides of nitrogen is reaction 6-18 to form nitric acid.

The hydrocarbon classes important in the chemistry of the polluted troposphere are alkanes, olefins, and aromatics. In addition, the oxygenated hydrocarbons, such as aldehydes, ketones, esters, ethers, and alcohol are also important. A great variety of chemical reactions take place among these organic species and the free radicals cited above. The reactions of typical hydrocarbon species are now discussed briefly. Throughout the discussion references to more extensive coverages are given.

The most important atmospheric reaction involving alkanes is with the HO radical. For n-butane, for example, the reaction is

$$CH_3CH_2CH_2CH_3 + HO \rightarrow CH_3CH_2CH_2CH_2 + H_2O \qquad (6\text{-}26a)$$

and

$$\rightarrow CH_3CH_2CHCH_3 + H_2O \qquad (6\text{-}26b)$$

The alkyl radicals will rapidly add O_2 to form the corresponding peroxyalkyl radicals, e.g.

$$CH_3CH_2CH_2CH_2 + O_2 + M \rightarrow CH_3CH_2CH_2CH_2O_2 + M \qquad (6\text{-}27)$$

(subsequently the third body M will not be indicated). A reaction of substantially lesser importance is with oxygen atoms,

$$CH_3CH_2CH_2CH_3 + O(^3P) \xrightarrow{O_2} HO + CH_3CH_2CH_2CH_2O_2 \qquad (6\text{-}28a)$$

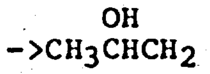
and

$$\xrightarrow{O_2} HO + CH_3CH_2\overset{OO}{\dot{C}}HCH_3 \qquad (6\text{-}28b)$$

The importance of both the HO and $O(^3P)$ reactions with alkanes is the generation of the peroxyalkyl radical RO_2 , which plays a substantial role in the conversion of NO to NO_2. Rate constants for alkane reations are summarized by Baulch et al.[9]

The atmospheric chemical reactions involving olefins have been widely studied.[4,5,10] The most important reactions in which olefins participate are with HO radicals, ozone, and atomic oxygen, in that order. The reaction of HO with an olefin, such as propylene, may proceed by addition of OH to the double bond or by abstraction of a H-atom from the olefin. For propylene, for example, the reaction paths with HO are:

$$CH_3CH = CH_2 + HO \rightarrow CH_3CHCH_2OH \qquad (6\text{-}29a)$$

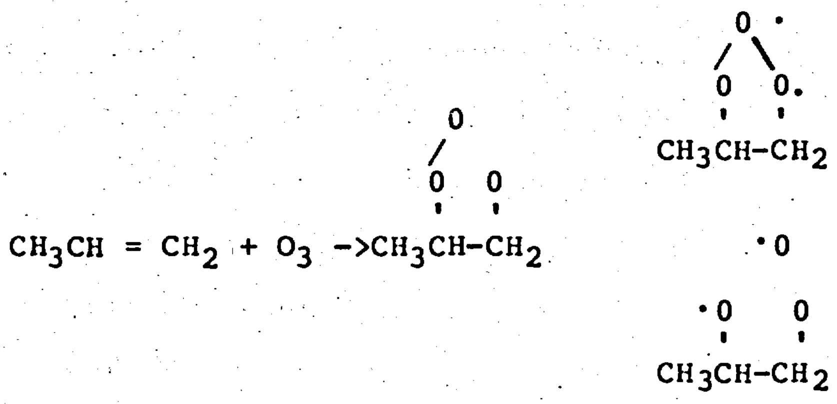


$$\rightarrow \overset{OH}{CH_3CHCH_2} \qquad (6\text{-}29b)$$

$$\rightarrow CH_2CH = CH_2 + H_2O \qquad (6\text{-}29c)$$

In each case the free radical product will quickly react with O_2 to produce a peroxyalkyl radical that is capable of converting NO to NO_2.

Ozone-olefin reactions are a source of free radicals and stable products in air pollution chemistry. The initial attack of O_3 on an olefin produces an unstable intermediate, which may decompose by several pathways.[10,11] For propylene, for example, the initial step in the reaction with O_3 is believed to be:



$$CH_3CH = CH_2 + O_3 \rightarrow \overset{\overset{O}{/}}{\overset{O\quad O}{CH_3CH-CH_2}} \qquad \overset{\overset{O\cdot}{/\ \backslash}}{\overset{O\quad O.}{CH_3CH-CH_2}} \qquad \cdot O \qquad \overset{\cdot O\quad O}{CH_3CH-CH_2} \qquad (6\text{-}30)$$

Subsequent de-composition of the products leads to a variety of free radicals and stable products.[12,13] The mechanisms of ozone-olefin reactions are still under considerable study, although most of the potential paths have been delineated.

The reaction of olefins with atomic oxygen plays a minor role in olefin consumption and radical and product formation. Again, for propylene the reaction is:

$$CH_3CH = CH_2 + O(^3P) \rightarrow CH_3CH_2 + HCO \qquad (6\text{-}31a)$$

or

$$\rightarrow CH_3CO + CH_3 \qquad (6\text{-}31b)$$

or

$$\rightarrow CH_3CH_2CHO \qquad (6\text{-}31c)$$

The mechanism of photooxidation of aromatic species in the atmosphere is perhaps the area of greatest uncertainty in atmospheric hydrocarbon chemistry. The principal reaction of aromatics is with the hydroxyl radical.[14,15] For aromatic-OH reactions, the initial step can be either addition to or abstraction from the aromatic ring.[103] The free radical addition products may then react, most likely with either O_2 or NO_2, leading to the cresols or nitrotoluences, respectively. The abstraction route probably leads to benzaldehyde. The mechanism of aromatic-hydroxyl radical reactions is yet to be clarified.

Aldehydes, both aliphatic and aromatic, occur as primary and secondary pollutants and are direct precursors of free radicals in the atmosphere.[16] Consequently, aldehyde chemistry represents an important subject area in atmospheric chemistry. Although aldehydes are the main oxygenated hydrocarbons generally considered with respect to their role in atmospheric chemistry, other classes of oxygenated hydrocarbons, such as ketones, esters, ethers and alcohols, are present and participate to a somewhat lesser extent. Major secondary sources of aldehydes include the reactions of ozone and OH radicals with hydrocarbons, and radical decomposition products. In addition, aromatic aldehydes can be formed as an ultimate consequence of the reaction of OH with aromatics, e.g. benzaldehyde. The aldehydic hydrogen-carbon bond in aldehydes is relatively weak (CH bond strength is 86 kcal/mol^{-1}). Consequently, this hydrogen atom will be susceptible under atmospheric conditions to attack by radical species, such as $O(^3P)$, $O(^1D)$, HO, and HO_2. Of these HO is by far the most dominant. Hydroxyl radicals are generally thought to abstract a H-atom from aldehydes -- chiefly the aldehydic H-atoms, i.e.

$$HO + RCHO \rightarrow H_2O + RCO \qquad (6\text{-}32)$$

If one assumes an atmospheric concentration of 10^6 radicals cm^{-3}, the rates of decay of HCHO and CH_3CHO by reaction with OH are approximately 4.2 percent and 5.8 percent per hour, respectively.[16]

The photodissociation of aldehydes is an important radical generation mechanism in the formation of photochemical air pollution. The reactions that are most significant can be generalized in terms of a radical and a molecular route:

$$RCHO + h\nu \rightarrow R + HCO \qquad (6\text{-}33a)$$

and

$$\rightarrow RH + CO \qquad (6\text{-}33b)$$

(Reaction 6-33a was previously given as reaction 6-25.) The radical route is the more important one from the point of view of atmospheric chemistry. Considerable attention has been given to formaldehyde photolysis in recent years. There appears to be general agreement that the primary paths are:

$$HCHO + h\nu \rightarrow H + HCO \qquad (6\text{-}34a)$$

and

$$\rightarrow H_2 + CO \qquad (6\text{-}34b)$$

In order to compare the rates of photolysis with the depletion of formaldehyde by HO reaction, one can calculate a photolysis rate of approximately 13 percent per hour for a solar zenith angle of 20° using the value of the photodissociation rate given by Horowitz and Calvert.[17]

The interaction with NO and NO_2 of the organic free radicals produced by hydrocarbon oxidation represents an extremely important aspect of the chemistry of the oxides of nitrogen in the polluted atmosphere. The radicals can be classed according to:

R	alkyl	$R\overset{O}{\overset{\parallel}{C}}$	acyl
RO	alkoxyl	$R\overset{O}{\overset{\parallel}{C}}O$	acylate
ROO	peroxyalkyl	$R\overset{O}{\overset{\parallel}{C}}CO$	peroxyacyl

In air it can be assumed that combination with O_2 is the sole fate of alkyl (R) and acyl (RCO) radicals and that the reaction is essentially instantaneous. Consequently, in reactions with alkyl or acyl radicals as products, these products are often written as the corresponding peroxy radicals. Also, acylate radicals will decompose rapidly to give an alkyl radical and CO_2. Therefore, only alkoxyl, peroxyalkyl, and peroxyacyl radicals need to be considered explicitly in terms of NO_x chemistry. Table 6-1 shows the various raction combinations that are important between these radicals and NO and NO_2.

The reactions of HO with NO_2 and NO are reasonable well understood and have been previously listed as reactions 6-18 and 6-19. Rate constants for these two reactions are available.[9]

The rate constant for the reaction of HO_2 and NO has recently been determined by direct means and is substantially larger than previously calculated indirectly.[19] The HO_2-NO reaction, as noted earlier, is a key reaction in the atmospheric conversion of NO to NO_2.

The reaction of HO_2 and NO_2 has the following two possible mechanisms.[20] Reaction 6-35b is not considered to be important in atmospheric chemistry:

$$HO_2 + NO_2 \rightarrow HO_2NO_2 \qquad (6\text{-}35a)$$

and

$$HO_2 + NO_2 \rightarrow HONO + O_2 \qquad (6\text{-}35b)$$

In addition, the peroxynitric acid formed in reaction 6-35a thermally decomposes as follows:[21]

$$HO_2NO_2 \rightarrow HO_2 + NO_2 \qquad (6\text{-}36)$$

At the present time it appears that, at the temperatures prevalent in summer smog episodes (>20°C), peroxynitric acid

Table 6-1. REACTIONS OF ALKOXYL, ALKYLPEROXYL AND ACYLPEROXYL RADICALS WITH NO AND NO_2

	NO		NO_2	
Free Radical	Reaction	Reference	Reaction	Reference
OH	$OH + NO \rightarrow HONO$	Hampson and Garvin, 1978[9]	$OH + NO_2 \rightarrow HONO_2$	Tsang et al., 1977[18]
HO_2	$HO_2 + NO \rightarrow NO_2 + OH$	Howard and Evenson, 1977[19]	$HO_2 + NO_2 \rightarrow HONO + O_2$ $\rightarrow HO_2NO_2$ $(HO_2NO_2 \rightarrow HO_2 + NO_2)$	Howard, 1977[20] Graham et al., 1977[21]
RO	$RO + NO \rightarrow RONO$ $(RONO + h\nu \rightarrow RO + NO)$	Batt et al.[23]	$RO + NO_2 \rightarrow RONO_2$ $\rightarrow RCHO + HONO$	Wiebe et al.[24]
RO_2	$RO_2 + NO \rightarrow NO_2 + RO$ $\rightarrow RONO_2$		$RO_2 + NO_2 \rightarrow RO_2NO_2$ $(RO_2NO_2 \rightarrow RO_2 + NO_2)$	
RCO_3	$RCO_3 + NO \rightarrow NO_2 + RCO_2$	Cox and Roffey[25] Hendry and Kenley[26]	$RCO_3 + NO_2 \rightarrow RCO_3NO_2$ $(RCO_3NO_2 \rightarrow RCO_3 + NO_2)$	Cox and Roffey[25] Hendry and Kenley[26]

does not represent an appreciable sink for NO_2 because of the rapid thermal decomposition reaction 6-36. At lower temperatures HO_2NO_2 will achieve higher concentrations and its importance as a sink for NO_2 increases.

The reactions of RO, RO_2 and RCO_3 with NO and NO_2 represent key reactions in the conversion of NO to NO_2 and the formation of organic nitrites and nitrates.

The main alkoxyl radical reactions with NO and NO_2 are:

$$RO + NO \rightarrow RONO \qquad (6\text{-}37a)$$

or

$$\rightarrow RCHO + HNO \qquad (6\text{-}37b)$$

and

$$RO + NO_2 \rightarrow RONO_2 \qquad (6\text{-}38a)$$

or

$$\rightarrow RCHO + HONO \qquad (6\text{-}38b)$$

The reaction of alkylperoxyl radicals with NO is generally assumed to proceed by the oxidation of NO to NO_2 with formation of an alkoxyl radical:

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (6\text{-}22)$$

Reaction 6-22 is believed to be an important route for the oxidation of NO to NO_2 in the atmosphere (the alkoxyl radical may react further to produce HO_2, which also converts NO to NO_2).

It has been postulated that longer chain peroxyalkyl radicals ($n>4$) from alkane photooxidation will add to NO to form an excited complex that can be stablized to produce an alkyl nitrate:[22]

$$RO_2 + NO \rightarrow RONO_2 \qquad (6\text{-}39)$$

The peroxyalkyl-NO_2 reaction proceeds principally by

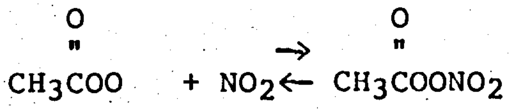
$$RO_2 + NO_2 \rightarrow RO_2NO_2 \qquad (6\text{-}40)$$

The peroxynitrate may thermally decompose according to

$$RO_2NO_2 \rightarrow RO_2 + NO_2 \qquad (6\text{-}41)$$

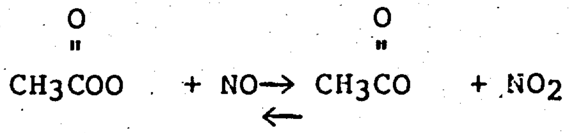
Measured rate constants for the RO_2-NO_2 reaction and the RO_2NO_2 decomposition are not currently available.

Peroxyacyl nitrates have been recognized as important components of photochemical air pollution.[27] Peroxyacetyl nitrate (PAN) exists in equilibrium with the peroxyacyl radical and NO_2:



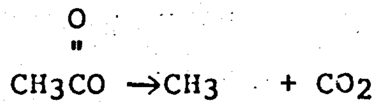
$$CH_3\overset{\overset{O}{\|}}{C}OO + NO_2 \rightleftarrows CH_3\overset{\overset{O}{\|}}{C}OONO_2 \qquad (6\text{-}42)$$

There exists a competition between NO and NO_2 for the peroxyacyl radical through:



$$CH_3\overset{\overset{O}{\|}}{C}OO + NO \rightleftarrows CH_3\overset{\overset{O}{\|}}{C}O + NO_2 \qquad (6\text{-}43)$$

The acetyl radical will rapidly decompose as follows:



$$CH_3\overset{\overset{O}{\|}}{C}O \rightarrow CH_3 + CO_2 \qquad (6\text{-}44)$$

followed by:

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad (6\text{-}21)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (6\text{-}22)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (6\text{-}23)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (6\text{-}24)$$

Thus, PAN chemistry is intimately interwoven in the NO to NO_2 conversion process. Rate constants for reactions 6-42 and 6-43 have recently been reported by two groups of investigators.[25,26]

The chemistry of the oxides of nitrogen in a hydrocarbon-containing atmosphere can be summarized as follows: the major observed phenomenon in the system is conversion of NO to NO_2 and formation of a variety of nitrogen-containing species, such as nitrites and nitrates. The conversion of NO to NO_2 is accompanied by accumulation of O_3. NO_2 serves as both as initiator and terminator of the chain reactions that result in conversion of NO to NO_2 and buildup of O_3. Termination of the chain reactions leads to nitric acid and organic nitrates. The nature of the system can be explained by considering its behavior as a function of the initial concentrations of NO_x and hydrocarbon in the irradiation of a static system, as well as the ratio of two reactants, i.e., the $[HC]/[NO_x]$ ratio.

At low $[HC]/[NO_x]$ ratios (usually ratios of less than about 1 to 2:1) the rate at which NO is converted to NO_2 is influenced by the availability of organic compounds. Therefore, the effects of reducing organic compounds are to slow the conversion of NO to NO_2, thereby lowering the NO_2/NO ratio. When this occurs, a larger proportion of the NO that is converted to NO_2 occurs through the destruction of ozone. This then has the overall effect of reducing the rate of ozone formation. If the oxidation of NO by organics is delayed sufficiently so that the sun has passed its zenith before significant amounts of NO_2 are created, photodissociation of NO_2 will be diminished and less ozone will accumulate on that date. At moderately high $[HC]/[NO_x]$ ratios (usually greater than about 5 to 8:1), the greater availability of organic radicals means that all of these radicals are not consumed as rapidly in reactions with NO, and more reactions between the radicals and NO_2 are able to occur. Thus, the amount of ozone formed and accumulated begins to become limited by the availability of NO_x, and becomes less sensitive to additional organic precursors. At very high $[HC]/[NO_x]$ ratios (greater than about 20 to 30:1), ozone cannot accumulate because either the ozone is consumed by reaction with hydrocarbons or radical-radical termination reactions occur which reduce oxygen atom and, hence, ultimate ozone concentration.

Identification of the nitrogen-containing products in atmospheric reactions has been under investigation for a number of years.[28-30] In general, the most important gaseous nitrogen-containing products in the NO_x-organic system are nitric acid and PAN. As noted, reactions of NO and NO_2 with free radicals produce, in addition to nitrous, nitric, and peroxynitric acids, a variety of organic nitrogen-containing species (Table 6-1). There currently exist important areas of uncertainty with regard to the formation of nitrogen-containing products in atmospheric reactions. The extent of formation and decomposition of peroxynitrates, RO_2NO_2, is unknown, and rate constants for the key reactions in the series, $RO_2 + NO$, are yet to be determined.

6.1.2 Laboratory Evidence of the NO_2-to-Precursor Relationships

In the previous section, the nature of chemical reactions involving oxides of nitrogen and hydrocarbons in the atmosphere was discussed. These reactions have traditionally been studied experimentally in laboratory vessels called smog chambers. These chambers characteristically employ radiation sources that closely approximate the UV portion of the solar spectrum as observed at the earth's surface and clean, chemically inert interior surfaces. It is believed that the chemical processes that take place in smog chambers are similar to those that take place in the atmosphere.

The presence of surfaces in a smog chamber may, however, be a source of difficulty in interpreting chamber results because of possible surface-catalyzed reactions or absorption of species on the walls. In addition, most chamber experiments have been conducted by initially injecting fixed amounts of reactants rather than simulating the continuous time-varying injection and dilution of reactants that characterize the ambient situation. Nevertheless, the behavior of irradiated mixtures of oxides of nitrogen and hydrocarbons in smog chambers has served as the foundation for our understanding of atmospheric chemical mechanisms.

Considerable effort has been devoted to the development of chemical reaction mechanisms that are capable of describing the processes observed in smog chambers.[4-8] Smog chambers have been used extensively to determine how concentrations of NO_x and other photochemical products respond to changes in the initial composition of nitrogen oxides and organics. A previous Criteria Document[27] discusses smog chamber evidence concerning the relationship between ozone/oxidant and the photochemical precursors. This section focuses on how NO_2 concentrations respond to changes in the input levels of organics and nitrogen oxides.

Several researchers have used smog chambers to investigate the dependence of nitrogen dioxide concentrations on the levels of precursor inputs:

- The University of North Carolina (UNC) study using an 11,000 cubic-foot (311 m^3) outdoor Teflon chamber, a simulated urban hydrocarbon mix, and twelve-hour irradiations[32]
- The Bureau of Mines study, using a 100 cubic-foot (2.8 m^3) aluminum-glass chamber, auto-exhaust hydrocarbons, and six-hour irradiations [33,34]
- The General Motors study, using a 300 cubic-foot (8.5 m^3) stainless steel-glass chamber, a simulated Los Angeles hydrocarbon mix, and six-hour irradiations[35]
- The Health, Education and Welfare (HEW) study using a

335 cubic-foot (9.5 m^3) chamber, auto-exhaust hydrocarbons, and up to ten-hour irradiation time[36] and

- The HEW study using a 335 cubic-foot (9.5 m^3) chamber, toluene and m-xylene, and 6-hour irradiations.[37]

Trijonis[38,39] has recently reviewed the results of these studies, as summarized in Table 6-2. As indicated in Table 6-2, the various chamber studies basically agree concerning the dependence of maximum NO_2 and average NO_2 on NO_x input. With other factors held constant, maximum NO_2 and average NO_2 tend to be proportional to initial NO_x. The minor deviations away from proportionality that sometimes occur tend to be in the direction of a slightly less than proportional relationship, i.e., a 50 percent reduction in NO_x input sometimes produces slightly less than a 50 percent reduction in NO_2.

There is less agreement among the chamber studies concerning the dependence of NO_2 on initial hydrocarbon concentrations. With respect to maximum NO_2, the Bureau of Mines study indicates essentially no dependence on hydrocarbons. However, two other studies suggest that hydrocarbon reductions decrease maximum NO_2 concentrations. The UNC results indicate that 50 percent hydrocarbon control tends to decrease maximum NO_2 by about 10 percent to 20 percent. The General Motors studies imply that 50 percent hydrocarbon control reduces maximum NO_2 by about 25 percent.

Table 6-2. Summary of Conclusions from Smog Chamber Experiments

CHAMBER STUDY	MAXIMAL NO_2 Dependence on NO_x	 Dependence on HC	AVERAGE NO_2 Dependence on NO_x	 Dependence on HC
University of North Carolina[32]	Proportional or slightly less than proportional	50% HC reduction reduces maximal NO_2 by 10% to 20%	Proportional or slightly less than proportional	Uncertain, 50% HC reduction may decrease average NO_2 by 20% or may increase average NO_2
Bureau of Mines[33,34]	Proportional	No effect	Proportional	50% HC reduction increases average NO_2 by 10% to 30%
General Motors[35]	Slightly less than proportional	50% HC reduction reduces maximal NO_2 by 25%	Proportional to slightly less than proportional	No effect
HEW, Auto Exhaust[36]	------------	-----------	Proportional	No consistent effect
HEW, Toluene[37]	------------	-----------	Proportional	No effect

With respect to average NO_2, the Bureau of Mines study indicates that hydrocarbon reductions would tend to increase NO_2 dosage. This result is consistent with the theoretical argument of Stephens,[40] who hypothesized that hydrocarbon reduction would increase average NO_2 because these reductions would delay and suppress the chemical reactions that consume NO_2 after it reaches a peak. However, the General Motors chamber study and the two HEW studies indicate that hydrocarbons produce no consistent effects on average NO_2 concentrations. The UNC experiments imply that a 50 percent reduction in hydrocarbons produces about a 20 percent decrease in average NO_2. There is some question about the UNC conclusion, however, because the UNC chamber runs were of a 10-hour duration and the NO_2 levels at the end of the experiments were greater when hydrocarbons were reduced. The extra NO_2 remaining after the 10-hour period could cause an increase in 24-hour average NO_2, even though average NO_2 was reduced during the first 10 hours.

Considering the results of all the chamber studies, Trijonis suggested a consensus based on existing chamber results which would appear to be as follows: fifty percent hydrocarbon reduction would have little effect on average NO_2 concentrations (a change of ± 10 percent) but would yield moderate decreases in maximal NO_2 (a reduction of about 10 to 20 percent). It should be noted that these conclusions are meant to apply to one basic type of ambient situation -- the situation of well-mixed urban air.

Some additional support for these conclusions was provided recently by studies of actual ambient data on NO_x and hydrocarbon levels from a number of cities in the U.S. Using empirical modeling and historical trend analysis, Trijonis[38,39] concluded that the ambient data were generally consistent with the consensus of chamber results. The exact form of the NO_2/precursor relationship, however, was found to vary somewhat from one location to another, presumably depending on local hydrocarbon/NO_x ratios, on the details of the hydrocarbon mix, and on specific meteorological conditions.

Reference is made also to another body of data due to Pitts et al.[55] (collected for a different purpose) which also contains potential information on the relationship between NO_x and its precursors. However, the data have not been analyzed to date for its pertinence to the NO_x/precursor question.

6.1.3 NO_x Chemistry in Plumes

The atmospheric chemistry involving oxides of nitrogen in plumes from major fuel burning installations is essentially that described earlier. However, the relatively high concentrations of NO and NO_2 in such plumes compared with those in the ambient urban atmosphere leads to certain chemical phenomena particularly characteristic of plumes. For example, ambient ozone is quickly scavenged in the plume by the large quantities of NO through reaction 6-4. Because the rate of the NO-O_3 reaction is fast relative to that of dilution of the plume, the rate of conversion of NO to NO_2 is controlled by the rate at which ambient O_3 is entrained into the plume by turbulent mixing.[41-44] There is some nitric acid produced in power plant plumes during the daylight hours through the oxidation of nitric oxide (reaction 6-1) and the subsequent photodissociation of NO_2 (reaction 6-2), then followed by the combination of NO_2 with NO_3 and H_2O (reactions 6-10 and 6-8). The generation of nitrous acid is also probable since the stack gases will contain NO, NO_2, and H_2O (reaction 6-13). Since nitrous acid will photodissociate to give hydroxyl radicals (reaction 6-17), more nitric acid can be produced by reaction 6-18. Thus, although the free radical concentration is expected to be low in power plant plumes, some NO_x will be converted to nitric acid. In addition, after sufficiently long travel times during which ambient hydrocarbons have been mixed with the plume constituents, the usual free radical reactions described earlier occur, possibly leading to O_3 production.

There are several studies in which measurements have been made of the concentrations of pollutants in power plant plumes.[43,45,46] The most difficult current problem is predicting the rate at which NO is converted to NO_2 in such a plume.

6.1.4 Computer Simulation of Atmospheric Chemistry

A key problem underlying the development and evaluation of kinetic mechanisms for atmospheric chemistry is determining the sensitivity of the concentration predictions to those uncertain aspects of the reaction scheme. Such a determination can serve as a valuable guide for future experimental studies and for identifying those parameters that, when varied within accepted bounds, will be most influential on the predictions of the mechanism.

Although the qualitative aspects of the chemistry of the polluted troposphere appear to be reasonably well understood, there are many important details that still need to be investigated before a complete quantitative understanding of the photochemical smog system is possible. Several groups [4-8] have formulated chemical reaction mechanisms for polluted tropospheric chemistry. Some of these are based on specific surrogate hydrocarbon chemistries; in others, attempts have been made to simulate the complex ambient atmospheric system by representing the general features of the hydrocarbon chemistry. All mechanisms contain aspects of uncertainty, whether in unknown rate constants, in the importance of competing reaction paths, or in the manner of representing the reaction of a generalized species. The measure of the accuracy of a mechanism is usually based on the extent of agreement between predicted concentration profiles and those generated experimentally in smog chambers. But here also, the inherent uncertainty of the experimental data base must be taken into consideration when comparing predictions to observations.

The chemistry of the inorganic portion of the photochemical smog mechanism is, by and large, well understood. Uncertainties remaining include:

- ° photolysis rates
- ° alkane-HO product distributions
- ° olefin-HO and olefin-O_3 product distributions
- ° aromatic chemistry
- ° alkoxyl radical reactions
- ° RO_x/NO_x reactions

Uncertainty in the model prediction can result from inappropriate specification of photolysis rate constants. In the case of computer simulations of smog chamber data, photolysis rate constants relative to the reported value for NO_2 are frequently used. While under real atmospheric conditions theoretical estimates are used corrected relative to empirical measurements, if available.

$$K_j = \int_0^\infty \sigma_j(\lambda)\phi_j(\lambda)I(\lambda)d\lambda \qquad (6\text{-}45)$$

where

K_j = photolysis rate constant for species j

$\sigma_j(\lambda)$ = absorption cross section of species j

$\phi_j(\lambda)$ = quantum yield for the photolysis of species j

$I(\lambda)$ = actinic irradiance

A recent review of theoretical estimates of photolytic rate constants in the lower troposphere by Demerjian, Schere and

Peterson[54] indicates that for species such as NO_2, HONO, H_2O_2, O_3, and formaldehyde, extensive experimental determinations of absorption cross sections and quantum yields are fairly reliable. However, since cross section and quantum yield data for higher aldehydes, alkyl nitrites and other carbonyl compounds are much less well characterized, these photolysis rate constants are subject to a large uncertainty. Of course, even if absorption cross sections and quantum yields could be determined accurately for all photo-sensitive species, uncertainties in atmospheric photolysis rate constants would still exist, as meteorological conditions, clouds, dust, and aerosols cause unknown variances in actinic irradiance.

Whereas rate constants in the inorganic portion of the mechanism are known fairly well, many more uncertainties, both in reaction rate constants and products, are associated with the organic reaction steps. Still to be determined are product distributions and reaction rate constants for the initial steps of the reactions of OH and hydrocarbon species, the largest uncertainties lying in the routes of the various radical species produced. For example, although rate constants for alkane-OH reactions are well established, the ratio of internal to external abstraction for all alkanes is not known. Addition to O_2 to form peroxyalkyl (RO_2) radicals can be considered as the sole fate of the alkyl radicals first produced in alkane-OH reactions, but after the formation of alkoxyl radicals through the conversion of NO to NO_2, the reaction mechanism becomes uncertain. Alkoxyl radicals can decompose, react with O_2, isomerize, or react with NO or NO_2, with the importance and rate of each reaction path depending on the nature of the alkoxyl group. Even for the most studied of the alkane-hydroxyl radical reactions, the relative rates between decomposition, isomerization, and reaction with O_2, NO, and NO_2 for alkoxyl radicals have not been measured, but must be estimated.[6]

Less well understood than alkane reaction mechanisms are olefin oxidation processes, primarily by HO. Olefin-hydroxyl radical reactions may proceed by addition or abstraction. For smaller olefins, the addition path predominates. However, the abstraction fraction increases with the size of the olefin. Along the addition path for terminally bonded olefins, there is uncertainty as to the ratio of internal to external addition. Similar to alkyl radicals, the hydroxy-alkyl radicals formed in the initial HO addition to olefins are thought to immediately add O_2 to form hydroxy-peroxyalkyl radicals and thereafter react with NO to give NO_2 and hydroxy-alkoxyl species. The fate of the hydroxy-alkoxyl radicals is subject to speculation, although the analogous alkoxyl reaction paths of decomposition, isomerization, and reaction with NO, NO_2 and O_2 are most likely possibilities.

The inherent uncertainty of the decomposition, reaction with O_2, and isomerization of the alkoxyl and hydroxy-alkoxyl radicals class can be presented by the generalized reaction step:

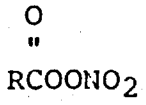
$$RO \rightarrow \alpha HO_2 + (1-\alpha)RO_2 + \beta HCHO + \gamma RCHO \qquad (6\text{-}46)$$

From the earlier discussions of alkoxyl radical behavior, RO always gives rise to either HO_2 or RO_2 in any of the decomposition, isomerization, or O_2 reaction pathways. Hence, the stoichiometric coefficients representing the fraction of HO_2 and RO_2 found in the lumped RO reaction should sum to one. Since the RO lumped species represents a large class of different-sized radicals and because splits between reaction paths for even specific radicals are not known, α can have a value in the range of 0 to 1. Many RO reaction routes produce aldehydes. Thus, $0 \leq \beta \leq 1$ and $0 \leq \gamma \leq 1$. Since the composition of the RO radical pool is continually changing during the course of a photooxidation, the actual values of α, β, and γ are functions of time. Thus, the selection of constant values of these coefficients introduces uncertainty.

A comprehensive sensitivity/uncertainty analysis of photochemical smog mechanisms has been carried out by Falls et al.[31] In this study the effects of rate constant and mechanistic uncertainties on predicted concentrations are illustrated.

6.2 NITRITE AND NITRATE FORMATION

The oxides of nitrogen are converted eventually to nitrites and nitrates by the reactions given in Section 6.1. In particular, the following gaseous nitrites and nitrates have been idenified:

$HONO$	nitrous acid
$HONO_2$	nitric acid
HO_2NO_2	peroxynitric acid
$RONO$	alkyl nitrite
$RONO_2$	alkyl nitrate
 $R\overset{O}{\overset{\Vert}{C}}OONO_2$	peroxyacylnitrate (PAN)
RO_2NO_2	peroxyalkyl nitrate

In addition to these gaseous species, particulate nitrites and nitrates may be formed. The object of this section is to present estimates of the importance of the various nitrites and nitrates. In most cases, estimates are necessary because ambient measurements of the concentration level of all but a very few of the species are lacking.

Typical ambient concentration levels of the gaseous nitrogen-containing species listed above can be estimated from simulations of smog chamber experiments using chemical mechanisms representing the hydrocarbon-NO_x chemistry. Table 6-3 lists calculated concentrations of $HONO$, $HONO_2$,

HO_2NO_2, RONO, $RONO_2$, $RC(0)OONO_2$, and RO_2NO_2 for smog chamber experiment EC-237 carried out at the Statewide Air Pollution Research Center of the University of California, Riverside, using the chemical mechanism of Falls and Seinfeld.[8] The conditions of the experiment are given in the footnote of Table 6-3. The simulated and predicted concentrations of the major measured species, such as NO, NO_2 O_3, PAN, and hydrocarbons, agreed well.

The concentrations of HONO, HO_2NO_2, and RONO are predicted to be small relative to those of NO and NO_2. Each of these species has decomposition reactions,

$$HONO + hv \rightarrow OH\cdot + NO \qquad (6\text{-}17)$$

$$HO_2NO_2 \rightarrow HO_2\cdot + NO_2 \qquad (6\text{-}36)$$

$$RONO + hv \rightarrow RO\cdot + NO \qquad (6\text{-}47)$$

that, at the temperatures and solar intensities prevalent in the experiment and in the summer atmosphere, are fast enough to insure that the concentrations of each of the three species are low. At lower solar intensities than those in the experiment, HONO and RONO can be expected to reach higher concentrations, and at lower temperatures, such as those in the stratosphere, HO_2NO_2 may accumulate.

Table 6-3. Predicted Nitrite and Nitrate Concentrations in Simuluation of Experiment EC-237 of the Statewide Air Pollution Research Center of the University of California, Riverside, Using the Chemical Mechanism of Falls and Seinfeld[8]

	Concentration, ppm		
	60 min.	180 min.	300 min.
HONO	0.0061	0.00040	0.00036
$HONO_2$	0.067	0.22	0.29
HO_2NO_2	0.00083	0.0019	0.0025
RONO	0.0030	0.00054	0.000080
$RONO_2$	0.0041	0.0070	0.0072
$R\overset{\overset{O}{\|}}{C}OONO_2$	0.025	0.089	0.13
RO_2NO_2	0.034	0.075	0.098

Conditions of the experiment: T = 303°K, $k_2 = 0.3\ min^{-1}$, $[NO_2]o = 0.106$, $[NO]o = 0.377$, $[H_2O] = 2.4 \times 10^4$, $[CO]^2 = 0.96$, [Aldehydes]o= 0.0012, [Alkanes]o = 1.488, [Non-ethylene Olefins]o= 0.15, $[C_2H_4]o = 0.875$, [Aromatics]o = 0.177, [HONO]o (assumed) = 0.1 (All concentrations in ppm). Dilution rate = $2.93 \times 10^{-4}\ min^{-1}$.

Under daytime conditions the reactions that govern the concentration of HONO are 6-17 and 6-18. At night, however, the only apparent destruction route for HONO is reaction 6-14. Depending on the relative importance of reactions 6-18, 6-13, and 6-14 HONO may reach substantial concentrations under nighttime conditions. A lower limit on the nighttime concentration of HONO can be estimated from the equilibrium HONO concentration based on reactions 6-13 and 6-14.

$$[HONO] = {\frac{k_{13}[NO]\,[NO_2]H_2O]}{k_{14}}}^{1/2} \qquad (6\text{-}48)$$

At $[NO] = [NO_2] = 0.1$ ppm, $[H_2O] = 2.4 \times 10^4$ ppm (50 percent relative humidity), the equilibrium HONO concentration calculated from equation 6-48 is 1.9×10^{-2} ppm.

Like HONO, HO_2NO_2 and RONO, PAN undergoes both formation and decomposition steps (reactions 6-42a,b). Unlike these former species, however, the balance between the formation and decomposition reactions is such that PAN may achieve appreciable concentration levels relative to those of NO and NO_2. Because the decomposition reaction for PAN is strongly temperature dependent, the steady state PAN concentration is highly dependent on the temperature. As temperature increases the role of PAN as an NO_2 sink decreases markedly; at low temperatures, on the other hand, steady state PAN concentrations can reach rather substantial levels.

Little is known about the existence and importance of peroxynitrates other than HO_2NO_2 and PAN. It is presumed in the mechanism on which the results of Table 6-3 are based that RO_2NO_2 thermally decomposes at a rate between those for HO_2NO_2 and PAN. Assessment of the importance of RO_2NO_2 as a sink for NO_x will depend on measurement of the rates of reactions 6-40 and 6-41.

In contrast to the other species of Table 6-3, nitric acid and alkyl nitrates apparently do not undergo appreciable decomposition reactions. Thus, these two species potentially serve as important atmospheric sinks for NO_2. Both nitric acid and alkyl nitrates may remain in the gas phase or react with other atmospheric constituents, such as ammonia, to produce low vapor pressure species that have a tendency to condense on existing particles or homogeneously nucleate to form particles.

Figure 6-1 depicts the potential paths by which particulate nitrate species may be formed from NO and NO_2. Path 1 involves the formation of gaseous nitric acid by reactions 6-8 and 6-19. Nitric acid concentrations resulting from these two reactions for the simulated smog chamber experiment have been given in Table 6-3. Comparisons of the individual rates of reactions 6-8 and 6-19 indicate that reaction 6-19

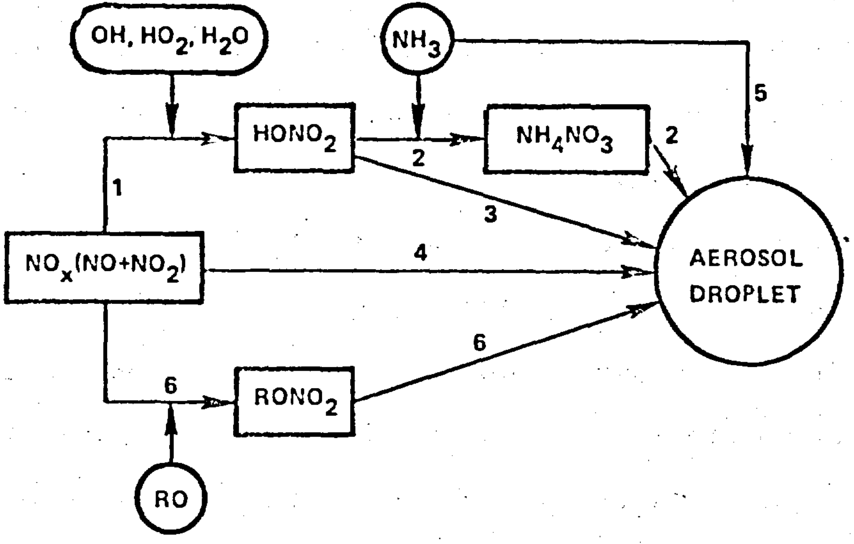


Figure 6-1. Paths of nitrate formation in thed atmosphere.
Source: Orel and Seinfeld (1977)

is the predominant route for gas-phase nitric acid formation under typical daytime conditions. Nitric acid vapor, once formed, may then react with NH_3, a ubiquitous atmospheric constituent with both natural and anthropogenic sources, to produce ammonium nitrate, NH_4NO_3 (path 2), which at standard temperature and pressure, exists as a solid. Alternatively, the nitric acid vapor may be absorbed directly onto a particle (path 3), although thermodynamic and kinetic considerations favor reaction with NH_3 to form NH_4NO_3 as the path of conversion of gaseous nitric acid to nitrate in particulate form.[48-50] Path 4 involves the direct absorption of NO and NO_2 into an atmospheric particle, a route that is likely for certain aqueous particles, particularly when accompanied by the absorption of ammonia (path 5).[51] Path 6 depicts the formation of organic nitrates through reactions such as 6-38a, followed by absorption of these nitrates into particles. At present little is known about the existence or importance of mechanisms such as that depicted by path 6.

There have been a limited number of measurements of nitric acid and particulate nitrate concentrations in ambient air, and of these measurements many have identified the particulate nitrate as NH_4NO_3, suggesting that the aerosol may consist of solid NH_4NO_3 or NH_4^+ and NO_3^- in solution in approximate stoichiometric balance. It is difficult to estimate the relative importance of the paths in Figure 6-1 for several reasons. First, the rate of reaction of nitric acid and ammonia is not well known, although the forward reaction is probably rapid and, in fact, can be presumed to be in equilibrium with the dissociation of solid ammonium nitrate.[48-50]

$$NH_{3(g)} + HONO_{2(g)} \rightleftarrows NH_4NO_{3(s)} \qquad (6\text{-}49)$$

Second, the rate of absorption of NO and NO_2 into existing particles depends on the composition and size of each particle and cannot generally be predicted a priori. In either case it is apparent that the presence of NH_3 is required, either to form NH_4NO_3 or to neutalize the acidity of a liquid droplet in which NO and NO_2 dissolve.

The current state of understanding of atmospheric inorganic nitrate formation can be summarized as follows. The principal gas-phase nitrate forming reaction is reaction 6-19. The nitric acid vapor formed in reaction 6-19 probably reacts rapidly with ammonia to form small particles of solid ammonium nitrate such that the equilibrium of reaction 6-49 is established. In competition with the nitric acid/ammonium nitrate path is the path consisting of direct absorption of NO and NO_2 into aqueous droplets. The relative rates of these two paths cannot be determined in general. Although measurements of particulate organic nitrate levels have been reported,[53] the mechanisms of formation of organic aerosol nitrates have not been fully identified.

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SECTION II

TRENDS IN PRECIPITATION COMPOSITION AND DEPOSITION

by

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1. Introduction

The establishment of trends in atmospheric chemistry parameters has been one of the major thrusts in evaluating man's influence on his environment. Trends in urban ozone concentration, regional sulfate values and global carbon dioxide levels are examples of measurements that show secular changes of possible anthropogenic origin. Scientists working in the precipitation chemistry field have also looked for possible trends in the chemical composition of precipitation. Unfortunately, no one consistent set of network data exists over a long enough period of time (>10 years) that can be used to give trends in wet depositions over an area. Because of this, workers have used a mix of data from networks that did not use comparable collection and analysis methods. Though definite changes could be seen in the period from 1955 to present, no clear cut trend can be established because of before mentioned data inconsistencies. In contrast to the past spotty performance of North American monitoring, a strong effort has been mounted in recent years that should go a long way to establish trends in the coming decade.

This paper reviews the historical data available, the new networks that have been established and the status of trend analysis in North America.

2. Data Bases in North America

The history of precipitation chemistry measurements in North America have been extremely erratic. National, regional, and local networks have been established and disbanded without thought of long-term considerations. In order to organize these efforts into a historical perspective, three major chronological thrusts can be recognized--agricultural (1875-1955), atmospheric (1955-1975) and ecological (1975-present). Though no one period can be identified by a single theme, they formed the major impetus in the given time period. To explain in more detail, each period is discussed in the following:

Agriculture (1875-1955)

Before the advent of commercial fertilizers, agricultural scientists both in Europe and North America were interested in the amount of substances such as nitrate and sulfate which were brought to the soils by rain. Throughout the western world, collection networks were established generally at agricultural research sites. The studies were generally limited to the measurement of only one or two ions. The method to measure pH was established generally after these studies were completed. Thus a full chemical balance could not be established. Also questions on collection methods, analysis techniques, site criteria and other important factors are not always clear from the references. It might be useful to look at this period in more detail, however no definitive results can be expected. A summary of the studies taken from Erikssen (1952) is given in Table 1.

Atmospheric (1955-1975)

In the late forties, atmospheric chemistry became a recognized branch of atmospheric studies. As a part of this interest in chemical cycles in the atmosphere, measurements of precipitation chemistry were begun in Europe under Professor Rossby. This interest spread to North America where the first continent-wide network was established by C. Junge. This network only lasted one year; other networks were established but soon were discontinued mainly because of the lack of support. Table 2 summarizes the work done during this period. Some of these efforts have continued through the present time. Initially precipitation chemistry had been studied mainly from the atmospheric viewpoint but as ecologists in the early seventies began to document the effects of acid deposition, the thrust of precipitation chemistry work began to change. This concern culminated in the first major international meeting on acid deposition in North America (Dochinger and Seliga 1976).

Ecological (1975-Present)

Though several of the networks mentioned in the previous section were aimed at evaluation of ecological effects, a major thrust in this area was begun with the establishment of the National Atmospheric Deposition Program (NADP). Though

Table 1. Agricultural Data Bases (1875-1955)

PERIOD	NUMBER OF STUDIES	LOCATIONS
1875 - 1895	3	MISSOURI, KANSAS, UTAH
1895 - 1915	7	OTTAWA, IOWA, TENNESSEE, WISCONSIN, ILLINOIS, NEW YORK, KANSAS
1915 - 1935	8	KENTUCKY, OKLAHOMA NEW YORK, ILLINOIS, TEXAS, VIRGINIA, TENNESSEE
1935 - 1955	6	ALABAMA, GEORGIA, INDIANA, MINNESOTA, MISSISSIPPI, TENNESSEE, MASSACHUSETTS

SOURCE: ERIKSSON, E., 1952

Table 2. Atmospheric Data Bases (1955-1975)

	NETWORK	PERIOD	SOURCE FOR ORIGINAL DATA	SUMMARIES & PUBLICATIONS
NATIONAL	AFCRC (JONES)	1955-1956	ILL. STATE WATER SURVEY	JUNGE'S PUBLICATIONS AND BOOK
	PHS-NCAR (NASN)	1956-1966	EPA/NOAA THROUGH 1964 1964-66 NOT AVAILABLE	LODGE, ET AL, REPORT LAZRUS, ET AL, UNPUBLISHED
	WMO/EPA/NOAA	1972-PRESENT	WMO PUBLICATION/EPA ARCHIVE NADP	EPA/NOAA REPORTS AND PUBLICATIONS
	CANADIAN WMO/ CANSAP	1973-PRESENT	CANSAP PUBLICATIONS EPA ARCHIVE	ATMOSPHERIC ENVIRONMENT (M.STILL)
REGIONAL	USGS EASTERN	1962-PRESENT	USGS PUBLICATIONS	PUBLICATIONS & REPORTS (FISHER, ET AL)
	CANADIAN CENTRE FOR INLAND WATERS (CCIW)	1969-PRESENT	CCIW PUBLICATIONS	PUBLICATIONS & REPORTS (CHAN)
	TVA	1971-PRESENT	TVA	PUBLICATIONS & REPORTS (PARKHURST)
LOCAL	HUBBARD BROOK	1963-PRESENT	NOT AVAILABLE	SEVERAL PUBLICATIONS (LIKENS)
	WASHINGTON, DC	1975-PRESENT	NOAA	TECHNICAL MEMORANDUM (MILLER)
	ONTARIO HYDRO	1975-PRESENT	EPA ARCHIVE	PUBLICATIONS & REPORTS

effects research gained nationwide recognition, event collection of precipitation under the MAP3S, EPRI, and SPN networks focused on providing data for atmospheric models though these data could also be used for ecological studies. Plans are now being made to coordinate networks on both a national and international level. A summary of these networks is given in Table 3. Reviews of precipitation chemistry activities have been documented in Miller and Wisniewski, 1976; Niemann et al., 1979; and Wisniewski and Kinsman, 1981.

3. Data Evaluation Criteria

Because different network objectives and monitoring techniques, it is difficult to evaluate one set of data with another. Networks with similar protocol such as EPRI and MAP3S have been shown to be compatible (Pack, 1980). How measurements of precipitation chemistry from diverse networks can be used to show trends and areal distributions is a difficult question. Some of the factors that must be taken into account are the following:

Collection Methods

- type of collectors, i.e., bulk or wet only
- materials used in collector
- aerodynamics of collector
- period of collection, i.e., event, daily, weekly, monthly
- reliability of collector

Table 3: Ecological Data Bases (1975 - PRESENT)

	NETWORK	PERIOD	SOURCE FOR ORIGINAL DATA	SUMMARIES AND PUBLICATIONS
NATIONAL	NADP	1978-PRESENT	NADP REPORTS	NADP REPORTS AND PUBLICATIONS (GIBSON)
REGIONAL	MAP3S	1976-PRESENT	MAP3S REPORTS	NUMEROUS PUBLICATIONS AND REPORTS (HALES, ET AL.)
	APN	1970-PRESENT	APN REPORTS	PUBLICATIONS (BARRIE)
	DOE/EML	1977-PRESENT	EML REPORTS	EML REPORTS (FEELY)
	EPRI	1978-PRESENT	EPRI DATA	PUBLICATIONS (PERHAC)
	MEXICO CITY	1980-PRESENT	NOT AVAILABLE	PRELIMINARY REPORTS (BRAVO)

NUMEROUS REGIONAL AND LOCAL STUDIES (>60)

Sitting Criteria

- purpose of site, i.e., atmospheric or ecological
- influence of local sources
- meteorological parameters availability
- gas and aerosol measurements

Chemical analysis methods

- analysis techniques and their limitation
- intercalibration
- priority and analysis

Shipment and storage

- time of storage and shipment
- method of shipping
- storage procedures

Quality assurance

- well define program
- outside reviewers

All of the above impinge to some degree on the final data a network produces.

4. Trends in Precipitation Chemistry Data

The obvious question that is asked in connection with the acid rain problem is whether we can see increasing (or decreasing) trends in precipitation acidity. Especially one would expect an increase of acidity with the corresponding increase in emissions of SO_2 and NO_2 (Figures 1 and 2). To evaluate the severity of the problem, researchers constructed areal acidity distributions from the historical data (Cogbill and Likens, 1979, Likens et al.,

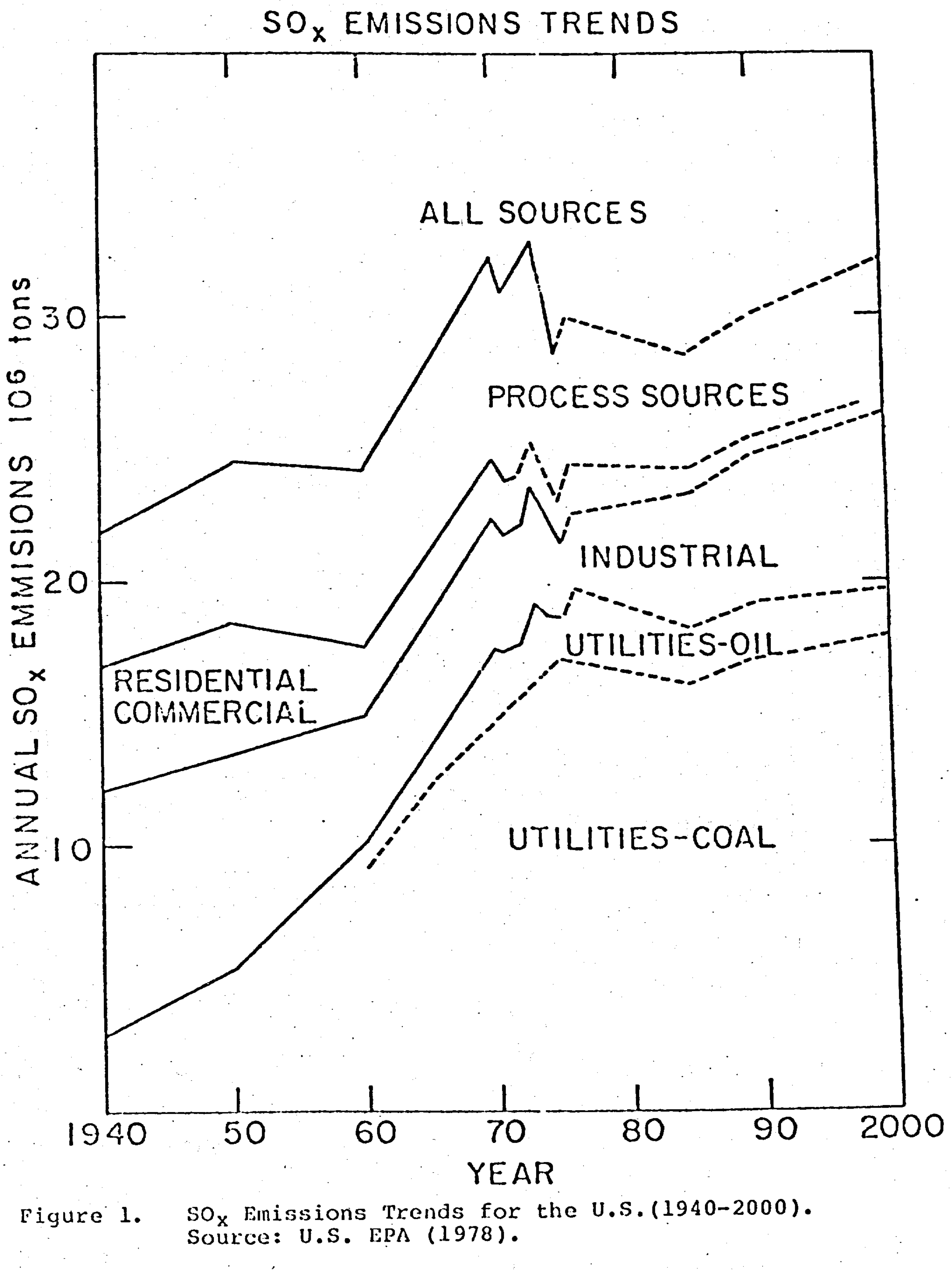


Figure 1. SO$_x$ Emissions Trends for the U.S.(1940-2000). Source: U.S. EPA (1978).

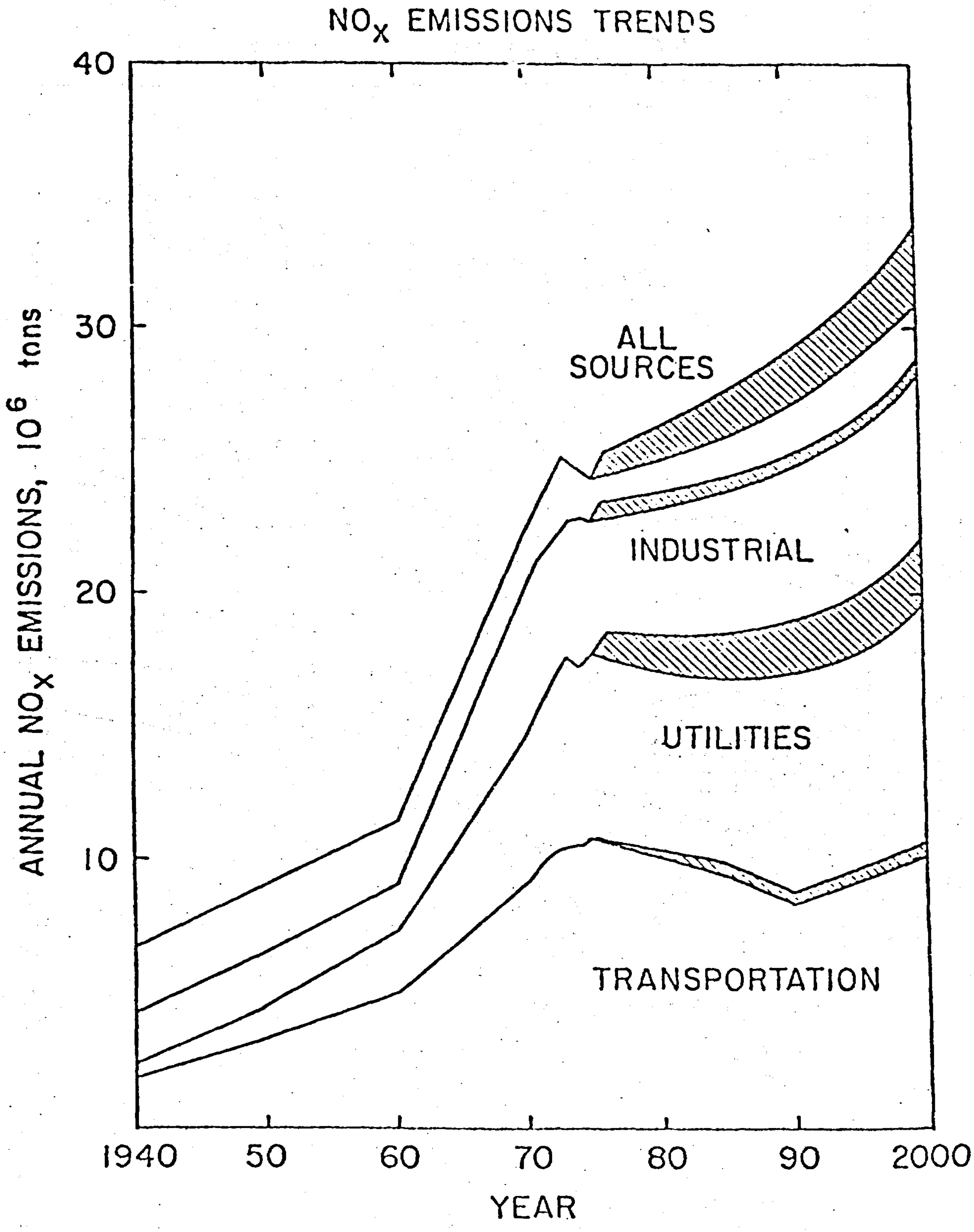


Figure 2. NO$_X$ Emissions Trends for the U.S. (1940-2000). Source: U.S. EPA (1978).

1979). The periods 1955-56, and 1975-76 were compared (Figure 3). Because of the uncertainties mentioned in Section 3, the implication of increasing acidity from the areal comparison has been criticized. Recent analysis by Butler and Likens (personal communication) has shown that the deposition of H ion has increased from the sixties to the seventies (Figure 4 and 5), at least when the two periods in the mid-sixties and mid-seventies are compared. However, the differences in amount of precipitation between the two periods was also significant and, of course, figures in the deposition calculations. The differences in precipitation amounts was, in some areas of the Northeast, over twenty inches(500 mm) between the dry sixties and the wet seventies. This trend cannot then be completely resolved.

Another set of data tht has been used to show either there has been a trend (Likens) or there has not been a trend (Perhac) is the USGC network in New York. Likens has reworked these data (Figure 6). However, because of the low priority given this network in the early years, the data may have some problems.

Two detailed reviews have been completed which discuss the question of trends in the historical data (Hansen et al., 1981; Wisniewski and Kinsman, 1981). A summary of their findings is as follows:

o It is difficult to justify a trend in acidity from 1955 to present because of the inconsistent data sets, questions of data validity and other factors cited in this paper.

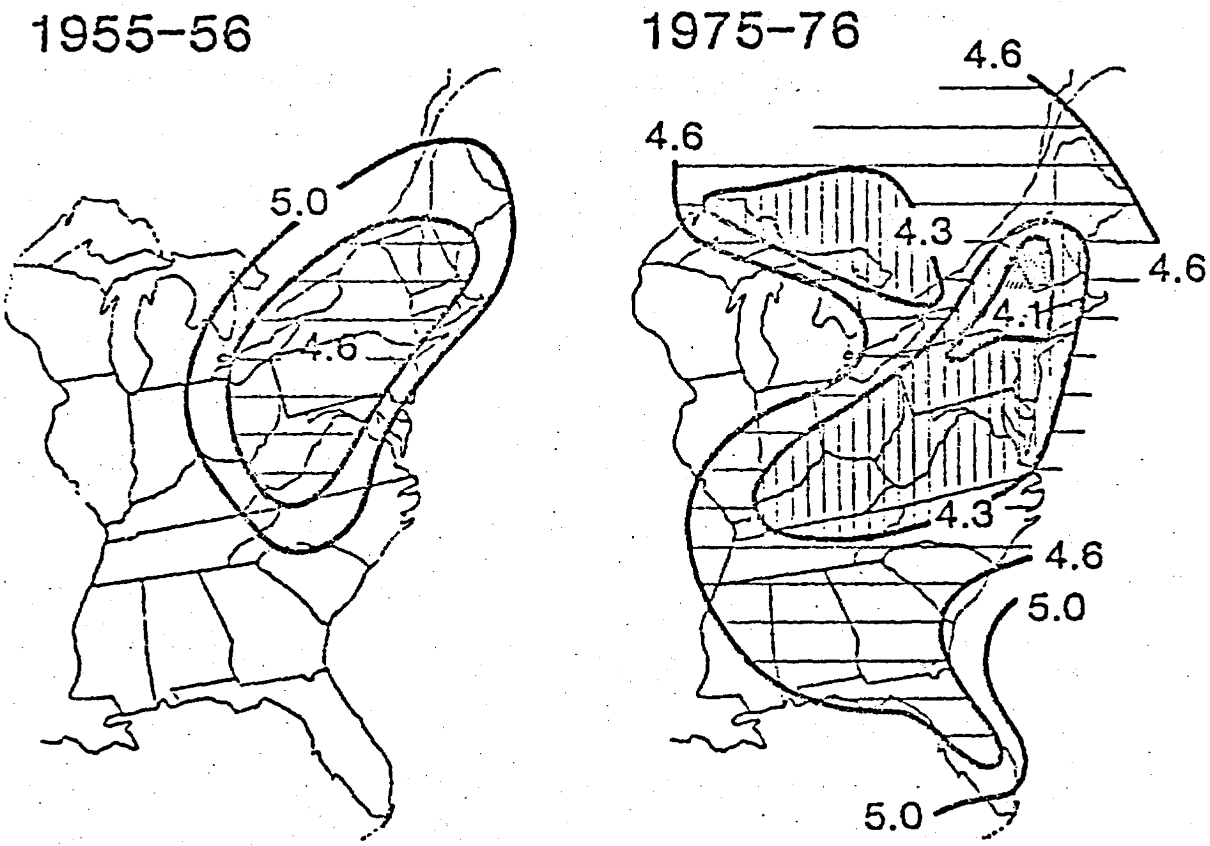


Figure 3. Deduced Weighted Annual Average pH of Precipitation in the Eastern United States in 1955-1956 and 1975-1976 (after Cogbill and Likens, 1974; Likens et al., 1979).

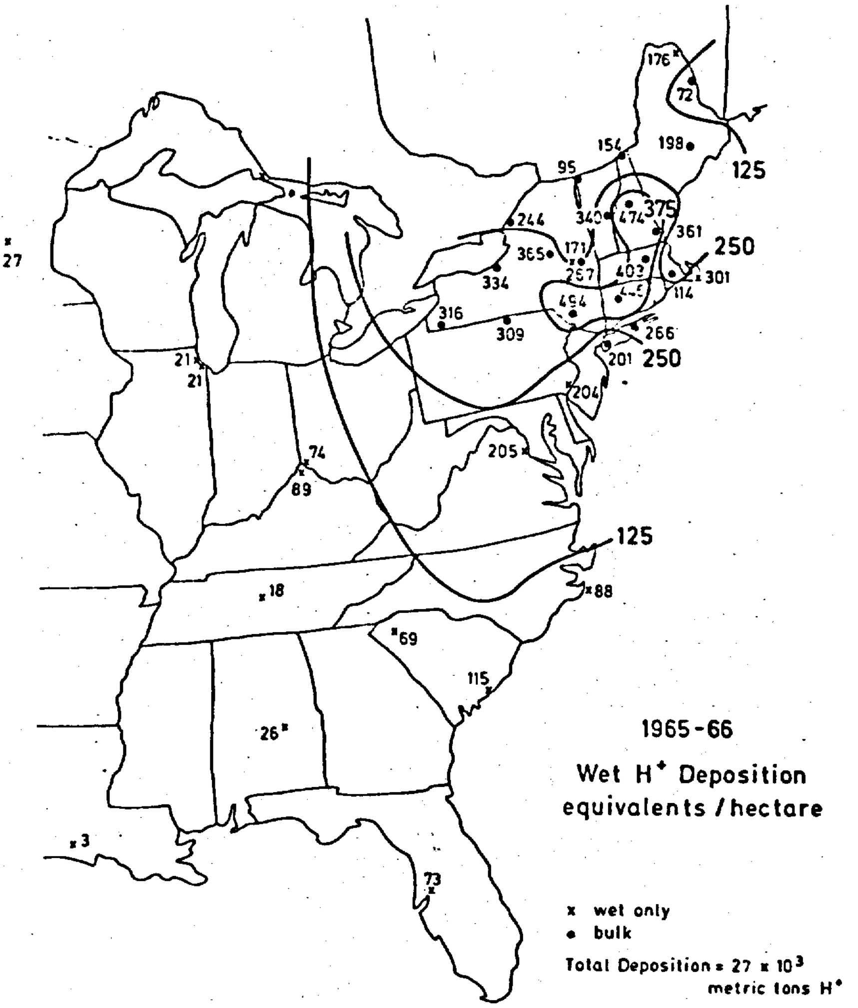


Figure 4. Wet Hydrogen Ion Deposition (equivalents/hectare) for 1965-1966.

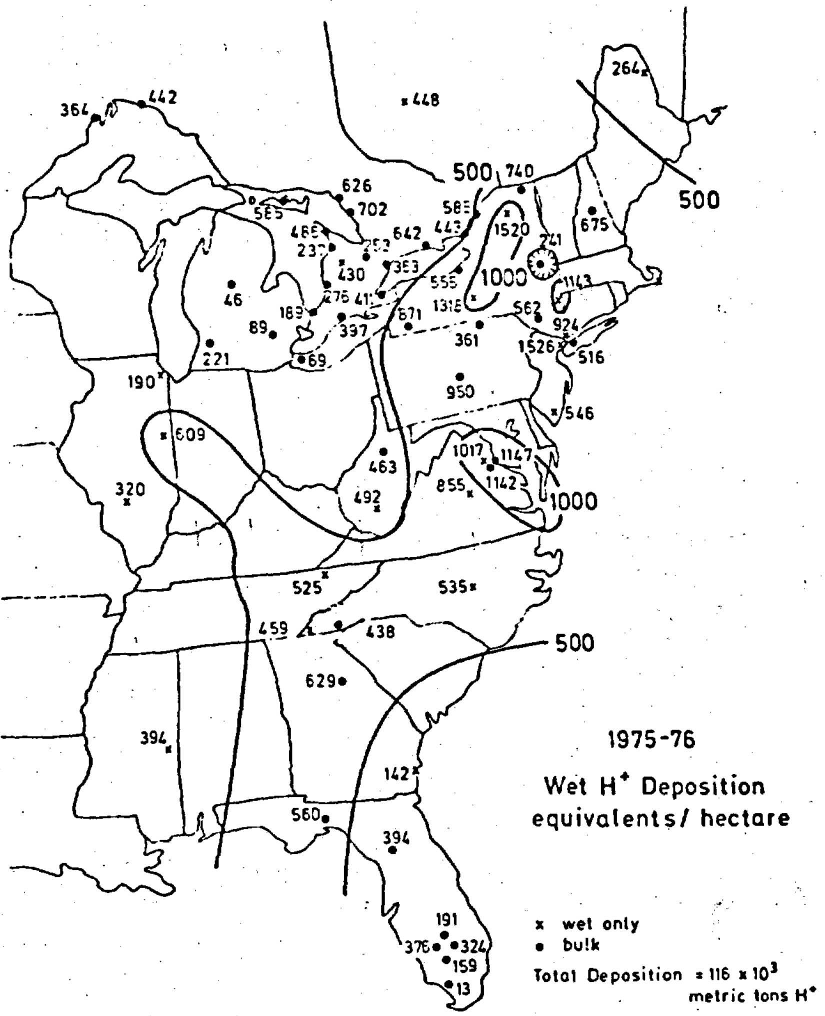
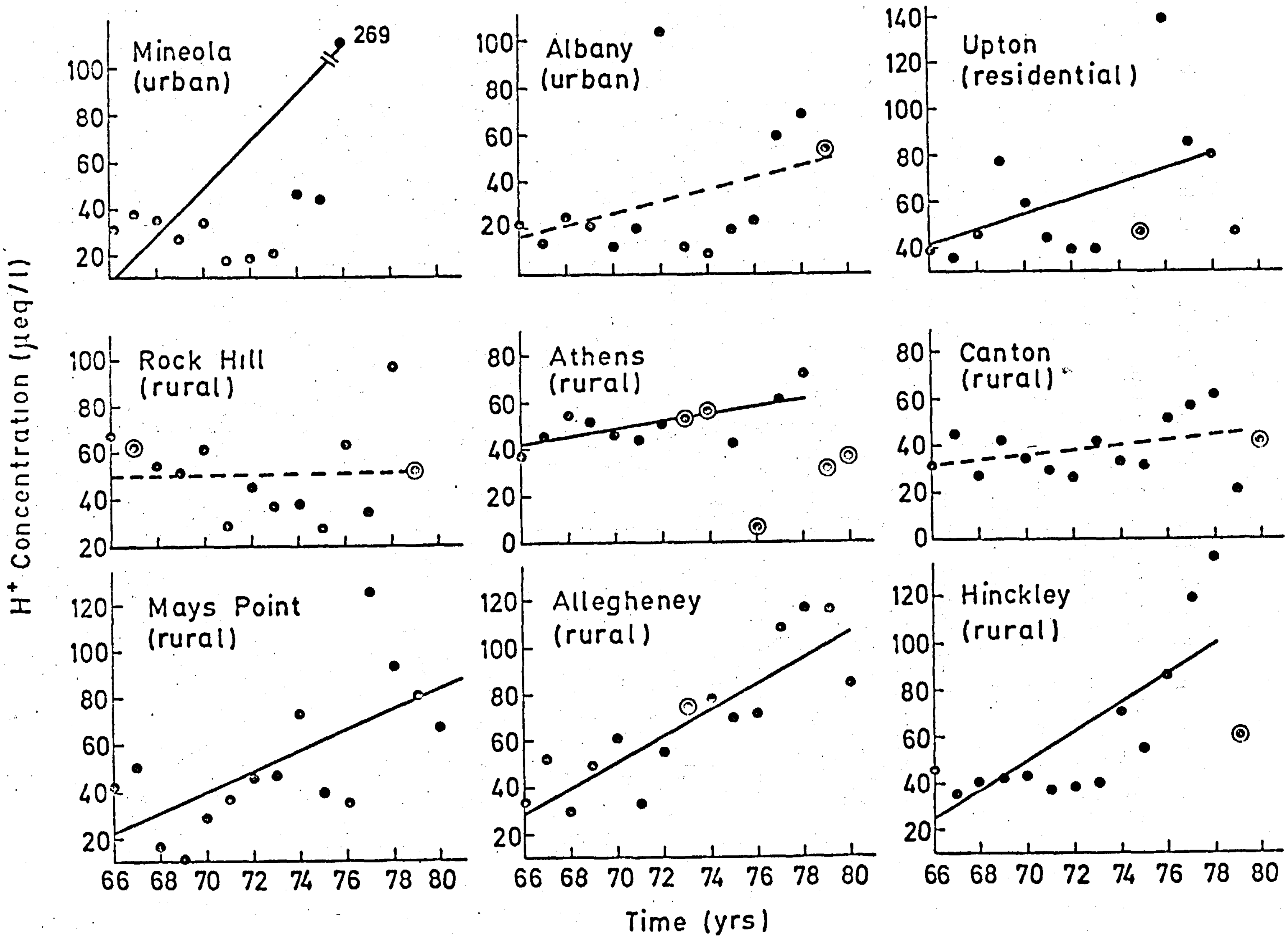


Figure 5. Wet Hydrogen Ion Deposition (equivalents/hectare) for 1975-1976.

Figure 6. Hydrogen Ion Concentrations at the Nine USGS Network Sites in New York and Pennsylvania for the Period 1966 to 1980



- The areal spread of acidity west and south seems to be fairly well substantiated from the existing data.
- Because of the uncertainty of the data set, direct reliability between emissions and precipitation chemistry data would not be fruitful.
- The only reliable trend data over North America are those collected from the late seventies.

5. Conclusions

From the data available at single stations or short-term networks over the last twenty-five years, it is difficult to establish trends in acidity over the northeastern United States. However, there is evidence of areal spreading to the west and south from data from different sites and networks in the same general area.

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SECTION III

THE SEASONAL DEPENDENCE OF ATMOSPHERIC DEPOSITION AND CHEMICAL TRANSFORMATION RATES FOR SULFUR AND NITROGEN COMPOUNDS

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1. Introduction

The objective of this report is to compare wintertime deposition and chemical transformation rates for sulfur and nitrogen compounds with the corresponding summertime values, in order to determine if, on the basis of current theoretical and experimentally determined information, there are significant differences between the summer and wintertime parameters commonly used in mathematical long-range transport models - differences which should be taken into account by the modelers. The objective was not to recommend values of deposition/transformation rate parameters to be used in current models: indeed, in some of the relevant areas (e.g. dry deposition of particulate sulfur and nitrogen, or incloud processes) our lack of understanding seems to preclude any such recommendations at present. Due to time limitations, an exhaustive and critical review of the literature was not possible. However, it is hoped that the most relevant scientific investigations have been included in this report.

Chapter 2 deals with wet and dry deposition of sulfur dioxide and sulfates, both from the viewpoint of general theoretical consideration and the results of relevant field and laboratory studies. Chapter 3 takes the same approach with regard to chemical transformation rates. Since information on nitrates is so scarce, all the relevant data on these compounds are summarized in Chapter 4.

The conclusions of this investigation are given in Chapter 5, where some brief recommendations are made for modellers concerning the seasonal dependence of deposition/transformation rates, and areas needing further study are also given.

2. Atmospheric Deposition

2.1 Wet Deposition

The atmospheric wet deposition of particulate matter and gases has usually been parameterized either in terms of a scavenging coefficient Λ or a washout ratio W (e.g. Dana, 1979). The former results from the assumption that wet deposition is an exponential decay process (since particles or gases are repeatedly exposed to cloud or precipitation elements, with some chance of collection for each exposure) obeying the equation:

$$C_t = C_o \exp(-\Lambda t) \qquad (1)$$

where

C_t = atmospheric concentration at time t

C_o = atmospheric concentration at time zero

Λ = scavenging coefficient (in units of time $^{-1}$).

The washout ratio is defined as the concentration of contaminant in precipitation divided by its concentration in air (usually at the suface level), i.e.,

$$W = \frac{X}{C} \qquad (2)$$

where

X = concentration of contaminant in precipitation

C = concentration of contaminant in unscavenged air

W = washout ratio (dimensionless)

Most of the discussion to follow will be in terms of the scavenging coefficient, but the same considerations apply to the washout ratio, since Λ and W can be related. For example, for the simple case of pollutant washout from a column of air having a uniform concentration over height h, one obtains:

$$\Lambda = \frac{WJ}{h} \tag{3}$$

where

J = the precipitation intensity.

2.1.1 General Considerations

When comparing wet deposition rates by rain and snow, it is convenient to express the scavenging coefficient as follows (Engelmann, 1968; Slinn, 1977):

$$\Lambda = \int_0^\infty FEAdD \tag{4}$$

where

A = the cross-sectional area of drops of diameter D

F = the flux density of drops with diameter between D and D+dD (drops/area x time x diameter interval)

E = the collection efficiency (i.e. the fraction of particles or gas molecules in the path of the drop which are washed out by it). For particulates the the collection efficiency depends not only on the size of the droplet/snowflake, but also on that of the particle under consideration.

The following approximations to Equation (4) have been suggested for rain and snow scavenging (Slinn, 1981):

For rain,

$$\Lambda \approx \frac{\alpha\, JE(D_m)}{D_m} \qquad (5)$$

where

α = a constant

D_m = mean raindrop size

$E(D_m)$ = collection efficiency of drops with diameter D_m

For snow,

$$\Lambda \approx \beta \frac{JE(\lambda)}{D_s} \qquad (6)$$

where

β = a constant

λ, D_s = characteristic snowflake dimensions which depend on crystal type (see Slinn, 1981)

$E(\lambda)$= collection efficiency of snowflakes having characteristic dimension λ.

A consideration of Equations (5) and (6) suggests a number of factors which could lead to differences between summer and wintertime scavenging coefficients.

(i) The scavenging coefficient depends on the precipitation intensity, which can have seasonal variations at any given location.

(ii) It is also a function of the raindrop/snowflakes size distribution and effective scavenging area. In this connection it should especially be noted that compared to rain, snow has a larger surface area-to mass ratio, and thus is potentially a much more effective scavenger of aerosol particles than is rain (Knutson and Stockham, 1977). However, there is also a strong dependence on the type of snow. Plane dendrites, for example, are predicted to be much more effective as scavengers than graupel (Slinn, 1977).

(iii) For aerosol scavenging, the value of E depends on the size and chemical compositon of the particles, because several processes which depend upon these factors are involved during within and beneath cloud scavenging (rainout and washout respectively), including Brownian motion, phoretic attachment, inertial impaction and nucleation (see, for example, Slinn, 1977; Scott, 1978). Actually, for an atmospheric aerosol consisting of a mixture of different sizes, the right-hand side of Equations (4) to (6) should be integrated over all aerosol sizes, and even relatively simple theoretical considerations indicate a resulting strong dependence of Λ on aerosol size distribution (Hales, 1978). Hence, the scavenging coefficient for particles could have a strong seasonal variation if the particle size distribution and chemical properities vary due to seasonal changes in emission characteristics, meteorological factors such as temperature and relative humidity, or atmospheric chemical reaction mechanisms, for example.

(iv) The collection efficiency of gases in Equation (4) depends on the solubility and chemical reactivity of the gas in water, and a number of other factors related to interfacial transfer between raindrop/snowflake and the ambient air - see, for example, Hales (1978) and Barrie (1978) for more detailed discussions for the case of sulfur dioxide scavenging. With reference to seasonal variations in the gas scavenging rate, snow scavenging is usually negligible compared to rain scavenging because of low gas absorption rates on ice crystals (Engelman, 1968; Slinn, 1981). However, the type of snow should again be considered, since wet snow can have a much higher gas scavenging efficiency than dry snow (Summers, 1977; Hales et al., 1971). Also, it should be noted that for sulfur dioxide, due to the nature of its solubility characteristics in water, the scavenging coefficient is expected to depend strongly on seasonal variations in the ambient temperature and precipitation pH (Barrie, 1981).

(v) There is one more factor, which is implicit in the above discussion, but perhaps deserves elaboration - viz., the importance of seasonal variations in storm type at a given geographical location. This is especially important with regard to incloud (rainout) processes, because the mechanisms whereby particles and gases are removed by such processes can depend strongly on the storm type. For example, Scott (1978) has discussed the dependence of sulfate rainout upon the mechanism of precipitation formation (- it should be noted that rainout is thought to be the dominant process responsible for particulate sulfur removal on a regional scale - see, for example, Scott (1978) and Garland (1978)), and has predicted scavenging rates to differ by a factor of 10 or more depending upon whether or not the precipitation originated as snow. Similarly, Summers (1977) has shown striking differences in removal rates of sulfur dioxide by summertime convective storms and snowstorms. These results will be discussed in more detail in the following section.

2.1.2 Experimental Results

For comparing wet deposition rates for sulfur dioxide under winter and summer like conditions, one of the more relevant data sets is that of Summers (1977). For the rainout and snowout of sulfur dioxide, he obtained the following equations:

$$\Lambda \text{ rainout} = 3 \times 10^{-5} \, J \text{ sec}^{-1} \tag{7}$$

$$\Lambda \text{ (dry) snowout} = 10^{-6} \, J \text{ sec}^{-1} \tag{8}$$

Taking into account representative rainfall rate data for various types of precipitation, and using Equations (7) and (8), Summers estimated the following range of values for Λ :

light, moderate and heavy snow $-J = 10^7$, so $\Lambda = 1$, 5 and 25 respectively; moderate rain or showers, heavy rain or thunderstorms $-J = 10^4$, so $\Lambda = 3$ and 7.5 respectively. Clearly, for regions where the wintertime precipitation largely consists of dry snow (- as for much of Central Canada), the above results indicate a seasonal change in the wet scavenging rate of two or three orders of magnitude, which cannot be ignored in air quality modeling work. It is interesting to note - see Figure 1 - that the snowfall drops sharply south of the states of Pennsylvania, Ohio, Indiana and Illinois.

Other areas, such as the east and west coasts of Canada and much of the United States, receive appreciable amounts of wet snow and cold rain during the winter months. Fortunately, our understanding of the physical and chemical processes involved in sulfur dioxide wet deposition is sufficiently complete to allow estimates of the resulting seasonal deposition changes. Summers (1977) has argued that, because of the large sweepout area associated with wet snow (which should have a collection efficiency E similar to that of rain), its scavenging coefficient should be somewhat greater than for rain at an equivalent rainfall rate (- he recommends a value approximately twice as great). On the other hand, for sulfur dioxide removal by rain droplets, several relevant theoretical investigations are available, which are based on the acceptable assumption that, for purposes of regional transport modeling, the sulfur dioxide in the air is in equilibrium with that in the rain (- see, for examples, Hales and Dana, 1979a; Barrie, 1981). Figure 2, for example, taken from Barrie (1980), shows the predicted functional dependence of the washout ratio W, for sulfur dioxide, on rainwater pH and temperature. In going form 25 to 0°C, for example, W increases roughly by a factor of four. It should be noted that in much of North Eastern America precipitation tends to be somewhat more acidic in summer than winter (e.g., Pack and Pack, 1979), so from Figure 2 the expected difference between the winter and summertime values of W for rain would be even greater than predicted on the basis of temperature alone. For example, for a unit increase in pH and a change in temperature from 25 to 0°C, which might be representative of the seasonal variation at some of the stations in the northeastern U.S. (Pack and Pack, 1979), the predicted increase in W is roughly one order of magnitude. Limited experimental measurements of sulfur dioxide in precipitation support the above arguments (Hales and Dana, 1979). As a matter of interest, Figure 3 gives the N. American percentage frequency of hourly temperatures below 0° C in January and 10°C in July, and above 10°C in January and 21°C in July, from which the importance of the above temperature effect can be estimated.

For the case of particulate sulfur, very few data are available on which to base conclusions about winter-summertime differences in wet deposition, and our understanding of the details of rain and snow interactions with particles is not nearly as complete as for the case of sulfur dioxide. The existing theories are of little help if one wants to go beyond order-of-magnitude washout rate estimates. The only work where a direct experimental comparison of rain and snow scavenging coefficients has been made, for particles comparable in size to sulfates, is that of Graedel and Franey (1975). They found below-cloud Λ values for snow to be twenty times or more than those for rain. However, Graedel and Franey's interpretation of their data has been questioned by Slinn (1976).

Knutson and Stockham (1977) have developed equations for the scavenging coefficient of snow from laboratory study results with single snowflakes, which usually agreed with available field data to within a factor of three. For particles of about 0.5 microns in diameter, and a precipitation intensity of 1 mm h^{-1}, their model predicts scavenging coefficients in the range of $0.5 - 1.0 \times 10^{-5}$ sec $^{-1}$, depending on the type of snow. These values may be compared to some data on rain scavenging coefficients for particles of similar size compiled by McMahon and Denison (1979). Table 1 is abstracted from their Table 9. No attempt was made at a critical evaluation of the methods used to arrive at the scavenging coefficients in this Table. However, the last value shown (for 0.3 - 0.5 micron particles) was obtained by Graedel and Franey (1977) (- McMahon and Denison, in their Table 9, have incorrectly labelled Graedel and Franey's data as being obtained from snowfalls), and if we accept Slinn's criticism of their methodology (see above) and reject their data point, all we can say is that, for a particle size which might be representative of sulfates, most of the available data suggest that below-cloud rain and snow scavenging coefficients should be about the same order-of-magnitude for comparable rainfall rates. The scanty relevant data on washout ratios support the above conclusion (see McMahon and Denison, 1979) although in this case both within and below cloud processes are involved. Scott (1981) has recently presented data on washout ratios of sulfates in snowstorms, which fall within about the same range of values as has been observed for a number of other substances in rain. However, he found that the washout ratio is strongly dependent on the microphysical processes of precipitation growth, W values being 10 to 50 times higher when abundant cloud water was available (and snowflake growth was primarily through collection of supercooled droplets) than when negligible liquid water was detected in the clouds (and growth was primarily by vapour deposition on snowflakes).

2.1.3 Summary

To summarize the above discussion on wet deposition of sulfur compounds: it would seem that for sulfur dioxide, the washout coefficient for both within and below cloud processes can show a strong seasonal dependence (order-of-magnitude or more), even after seasonal variations in precipitation rate are taken into account, because of temperature and pH effects on the solubility, and the low uptake of the gas by ice crystals.

The available data on particulate sulfur wet scavenging are too meager to allow any definite conclusions about seasonal difference. All one can say is that below cloud scavenging coefficients for rain and snow seem to be of the same order-of-magnitude. However, rates of incloud processes depend strongly on the specific mechanisms involved (Scott, 1978; 1981), and seasonal variations in storm type could result in corresponding changes in scavenging rates of an order-of-magnitude or more, but more data are needed to substantiate or disprove this speculation.

Table 1. Field Measurements of Rain Scavenging Coefficients of Particles Expected to be Mainly in the Submicron Size Range.

Source of Data	$10^5 \Lambda (s^{-1})$	Comments
Kalkstein et al. (1959)	2	SO_4 washout
Makhonko (1964)	1	Fission products washout
Bakulin et al. (1970)	3	Pb washout from thunderstorm
Burtsev et al. (1970)	$15 J^{0.5}$	0.2 um particle washout
Greadel and Franey (1977)	18	0.3-0.5 um particle washout

Figure 1. Average Annual Distribution of Snowfall in North America (cm) from Findlay (1980).

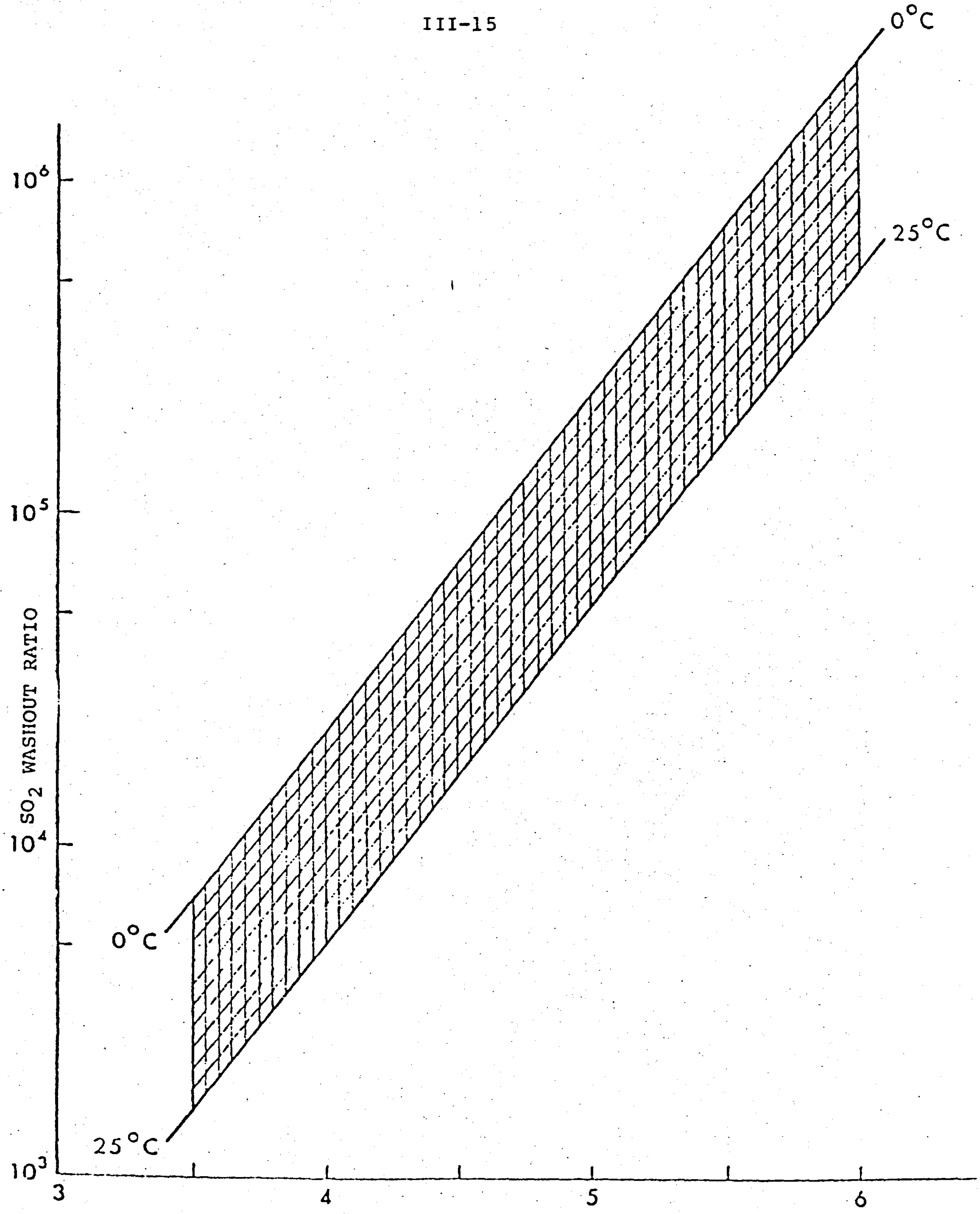

Figure 2. Dependence of the Washout Ratio of SO_2 on pH and Temperature for Equilibrium Scavenging Conditions from Barrie (1981).

Figure 3. The Percentage Frequency of Hourly Temperature for North America (A-January, less than 0°C; B-January, greater than 10°C; C-July, less than 10°C; D-July, greater than 21°C) After Rayner (1961).

2.2 Dry Deposition

The dry deposition rate of gases and particles to the earth's surface has usually been parametrized using a deposition velocity v, defined by the equation

$$v = Mc^{-1} \tag{9}$$

where M = the flux of material
C = the ambient concentration at a particular height

and v (which is a function of height) refers to the same level as the concentration measurement.

2.2.1 General Consideration

To better understand the role of different factors which affect the deposition velocity, it is convenient to work in terms of resistances to transport. The total resistance r_t, defined as the reciprocal of v,

$$r_t = v^{-1} \tag{10}$$

can be broken down into an aerodynamic resistance r_a and a surface resistance r_s:

$$r_t = r_a + r_s \tag{11}$$

The surface resistance can be further split into a resistance due to a (usually thin) stagnant air film adjacent to the absorbing surface, r_b, and an actually resistance to transport within the surface (for plants, this is largely the canopy stomatal resistance), r_c (Wesely and Hicks, 1977; Chamberlain, 1979):

$$r_s = r_b + r_c \tag{12}$$

The magnitude of the aerodynamic resistance r_a is largely governed by atmospheric turbulence in the boundary layer, which in turn depends on factors such as wind speed, atmospheric stability, and characteristics of the surface (i.e. the surface roughness). There are well-known micrometeorological formulate relating r_a to meteorological and surface parameters (see e.g., Garland, 1978; Wesely and Hicks, 1977). The value of r_a decreases as the wind speed and surface roughness increase, and also depends to a certain extent on the atmospheric stability, although the latter dependence only seems to become marked when the atmosphere is very stable - e.g., for Pasquill stability category F (Sheih et al., 1979). Because of the dominant influence of turbulent diffusion, r_a should be the same for both particles and gases, except where the particles are so large that gravitational settling plays an important role in the deposition process (e.g., Sehmel, 1980). In view of the above considerations, seasonal variations in meteorology and surface characteristics will obviously change the aerodynamic resistance to transport of both particles and gases.

The stagnant film resistance, r_b, also depends to a certain extent on the same factors as r_a, since surface drag forces and the intensity of atmospheric turbulence will determine the average thickness of the film and also the intrusion of turbulent eddies into the film. However, because of the importance within the film of molecular diffusion for gases, and Brownian diffusion and impaction for aerosols, r_b is also strongly dependent on the characteristics of the material under consideration - in particular, the diffusivity of gases and the particle size distrubtion of aerosols (see, for example, Wesely and Hicks, 1977: Sehmel, 1980). As with r_a, it can be seen that seasonal variations in meteorological and surface factors can lead to corresponding variations in r_b. In addition, if for particles there are appreciable seasonal changes in the size distribution, potentially large changes in r_b could result (e.g. Sehmel, 1980; Ibrahim et al., 1980).

As implied by its definition, for a given substance r_c depends only on the characteristics of the surface. For particles, probably for lack of reliable information to the contrary, it has sometimes been assumed that r_c is equal to zero (e.g. Ibrahim et al., 1980; Sievering, 1979 a). For gases, r_c depends on the properties of the gas (- mainly the solubility in water (Hill, 1971) and molecular diffusivity (Wesely and Hicks, 1977)) and the absorbing surface. For surfaces covered by vegetation, r_c depends on the nature, and state of growth and condition, of the plant in question, the latter being influenced by the water availability, solar radiation level, and air temperature, among other things. Obviously, seasonal changes in the surface coverage will lead to corresponding changes in r_c.

For a more detailed discussion of the resistances which determine the overall magnitude of the deposition velocity, and the factors affecting them, see Wesley and Hicks (1977), Shieh et al. (1979), Chamberlain (1979) and Sehmel (1980).

2.2.2 Experimental Results

Several authors have recently presented compilations of experimental data on the deposition velocities of gases and particulates, which are of value in assessing the effects of seasonal variation on v (see Garland, 1978; McMahon and Denison, 1979; Chamberlain, 1979; Sehmel, 1980).

For the case of sulfur dioxide, a reasonably consistent picture emerges. For a wide range of surfaces, including vegetation, water, and soils, the deposition velocity has been found to be typically in the range 0.4 to 0.8 cm s^{-1}. Garland (1978) rationalizes the above result by pointing out that in general, there is a counter-balance between the aerodynamic and surface resistance terms (r_a and r_s in Equation (11)). For relatively smooth surfaces, r_s has been found to be rather small, and uptake is largely determined by r_a. On the other hand, surfaces with taller vegetation, such as wheat and forest, exhibit a higher r_s, which counteracts the reduced r_a. Of course, there are exceptions to the above generalizations: for example, much higher v values than indicated above may apply to wet or snow covered forests (Chamberlain, 1979). However, it would seem that such exceptions have only marginal relevance when seasonal variations are being considered (unless, for example, the percentage of the time that a forest is wet changes significantly, due to seasonal changes in precipitation).

It is interesting to compare measured deposition velocities to snow with the 0.4 to 0.8 cm s^{-1} range in v noted above, which is assumed to be representative of surfaces for most of the year other than winter. Table 2 lists the available data for sulfur dioxide deposition to snow surfaces. The values measured generally tend to be lower than 0.4, although a "representative" v of 0.1 cm s^{-1} for snow, as suggested by Husar et al. (1978b), would seem to be too low, except for very stable atmospheric conditions.

The above results suggest that seasonal variations in sulfur doxide dry deposition velocities should be relatively modest - certainly less than the order-of-magnitude changes expected for wet deposition. It seems that for the wintertime, at least in Canada and the northern United States, dry deposition velocities of sulfur dioxide should be somewhat lower than in the summer, due to the larger proportion of the surface covered by snow and dead vegetation. In this connection, it is interesting to compare some estimates of v for the summer (June - August) and winter (December - February) months in Ontario, made using the methods of Shieh et al. (1979). Surfaces characterized according to their classification, and values of surface roughnesses and resistances of Pasquill stability classes at 22 stations in Ontario was provided by the Atmospheric Environment Service. Calculated seasonal average deposition velocities are shown in Figure 4 and 5. A comparison of these figures supports the expectation that, for sulfur dioxide, seasonal changes in v should not be large.

The picture for sulfate particulates is much more confusing, because of the current controversy regarding depostion velocities of particles in the 0.1 - 1.0 micron size range (where most of the sulfate mass is expected to occur). Theoretical predictions (see, for example, Sehmel and Hodgson, 1978; Ibrahim et al., 1980) indicate that, for this size range, $(r_a + r_b)$ should be generally larger than 10 s cm^{-1} (i.e., v should be no greater than 0.1 cm s^{-1}). Available experimental data on deposition velocities of sulfates, or other substances such as lead (which are expected to be in a similar size range) are shown in Table 3. It would seen that for relatively smooth surfaces, such as snow, water, or filter paper, the deposition velocity is about 0.1 - 0.2 cm s^{-1}, or in some cases so small that the removal of particles is countered by surface emissions (i.e., the effective deposition velocity is negative). For rougher surfaces and vegetation there is little data, but values ranging from less than 0.1 to about 1.0 cm s^{-1} have been reported, including a number of negative values. For such surfaces, Sheih et al. (1979) have proposed sulfate deposition velocities comparable to those for sulfur dioxide. However, at present, because of the large uncertainty in v for particulate sulfate, little can be said about seasonal variations in this parameter.

2.2.3 Summary

To summarize: there are several theoretical reasons why dry deposition velocities for both gaseous and particulate sulfur could have a significant seasonal variation. However, for sulfur dioxide, this variation is probably rather small, as far as long-range transport modeling is concerned. Summertime values have been typically observed to be in the range 0.4 to 0.8 cm s^{-1}. Wintertime observations (Table 2) indicate a "representative" range of 0.1 to 0.4 cm s^{-1}. The few available data suggest that this latter range is also representative of the deposition of particulate sulfates to smooth surfaces. However, for rougher surfaces and vegetation, the picture is so confusing at present that little can be said concerning seasonal variations in the particulate dry deposition velocity.

Table 2. Deposition Velocities of Sulfur Dioxide to Snow

Reference	v cm s^{-1}	Comments
Whelpdale and Shaw (1974)	1.6 0.52 0.05	Lapse Neutral Stable
Garland (1976)	0.10 - 0.17	Ice-laboratory experiments; r_s 5 s cm^{-1}
Dovland and Eliasen (1976)	~0.1	Low wind speed, stable atmosphere; r_s 5 s cm^{-1} (Garland, 1976)
Barrie and Walmsley (1978)	0.25 ± 0.20	Determined from simulaneous deposition and concentration measurements during a pollution episode
	0.3 - 0.4	Determined from sulfur accumulation by snow and ambient concentrations calculated with a dispersion model.

Table 3. Deposition Velocities for Submicron Particles

Reference	v cm s^{-1}	Comments
Cawse (1976)	0.2 - <0.7	Vanadium on filter paper at 1.5m.
	<0.1 - <0.6	Arsenic on filter paper
Dovland and Eliasen (1976)	0.16	Lead on snow, stable atmosphere
Garland (1978)	<0.1	Atmospheric sulfate over grass
Droppo (1979)	0.1, 0.27	Sulfates over arid vegetation
	Negative (surface source)	Sulfates, daytime, non-arid vegetation
Sievering (1979)	<0.5	Estimated annual average over Lake Michigan, submicron atmospheric aerosols
Sievering et al. (1979)	0.2 ± 0.16	Atmospheric sulfate over Lake Michigan, stable atmosphere
Wesley and Hicks (1979)	~ 1	Submicron particles to grass
	Negative (surface source)	Night-time, pine plantation, senescent maize
	Negative	Snow, and cold, wet, bare soil
Everett et al. (1979)	1.4	Atmospheric particulate sulfur over slightly rolling grassland
Ibrahim et al. (1980)	0.1 - 0.2	Bimodal ammonium sulfate aerosol over snow. (These results are complicated by the fact that, although over 90% of the total mass was in the 0.7 micron mode, most of the material actually deposited came from the 10 micron mode).

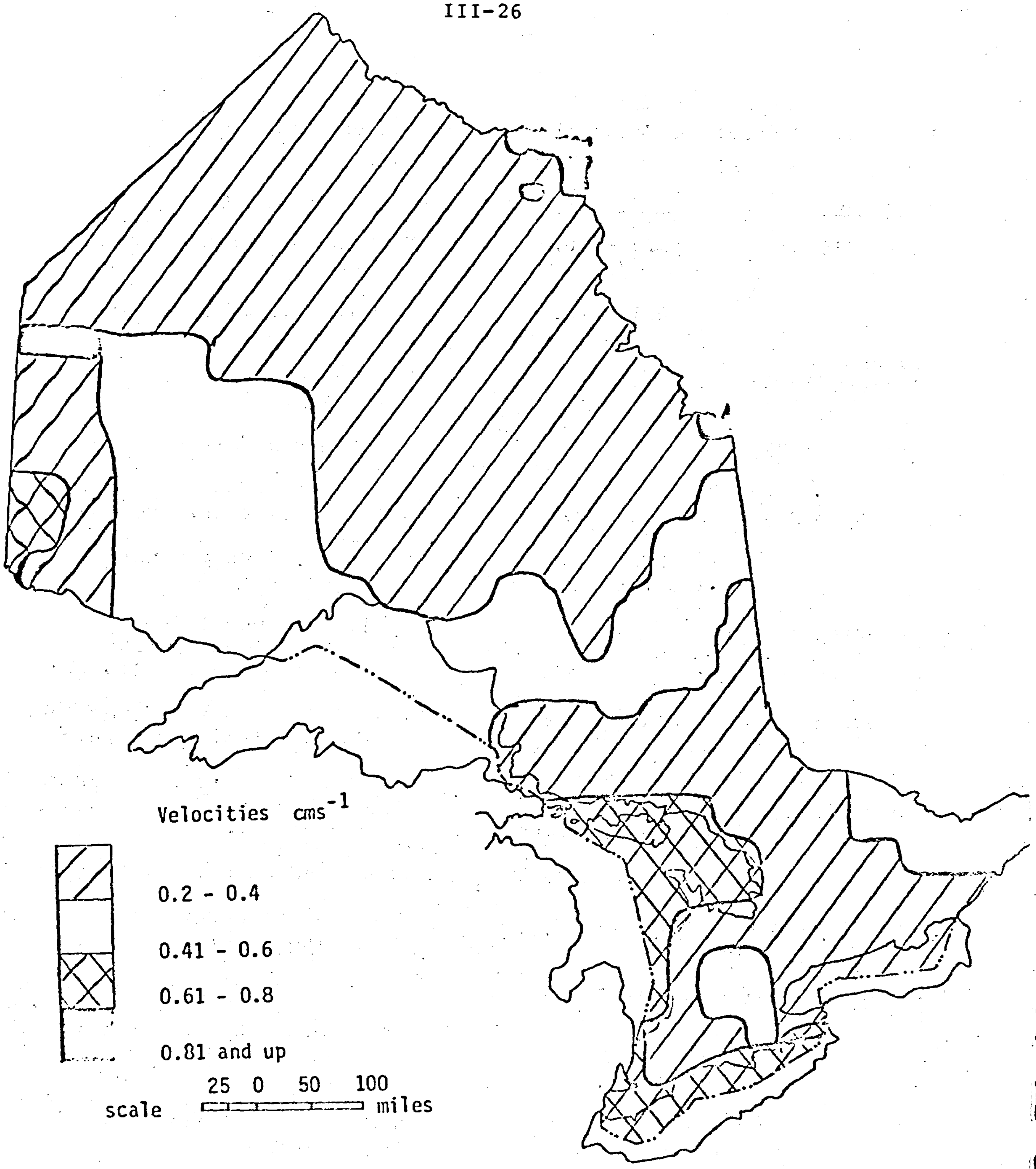

Figure 4. Deposition Velocities of SO_2 for June-August.

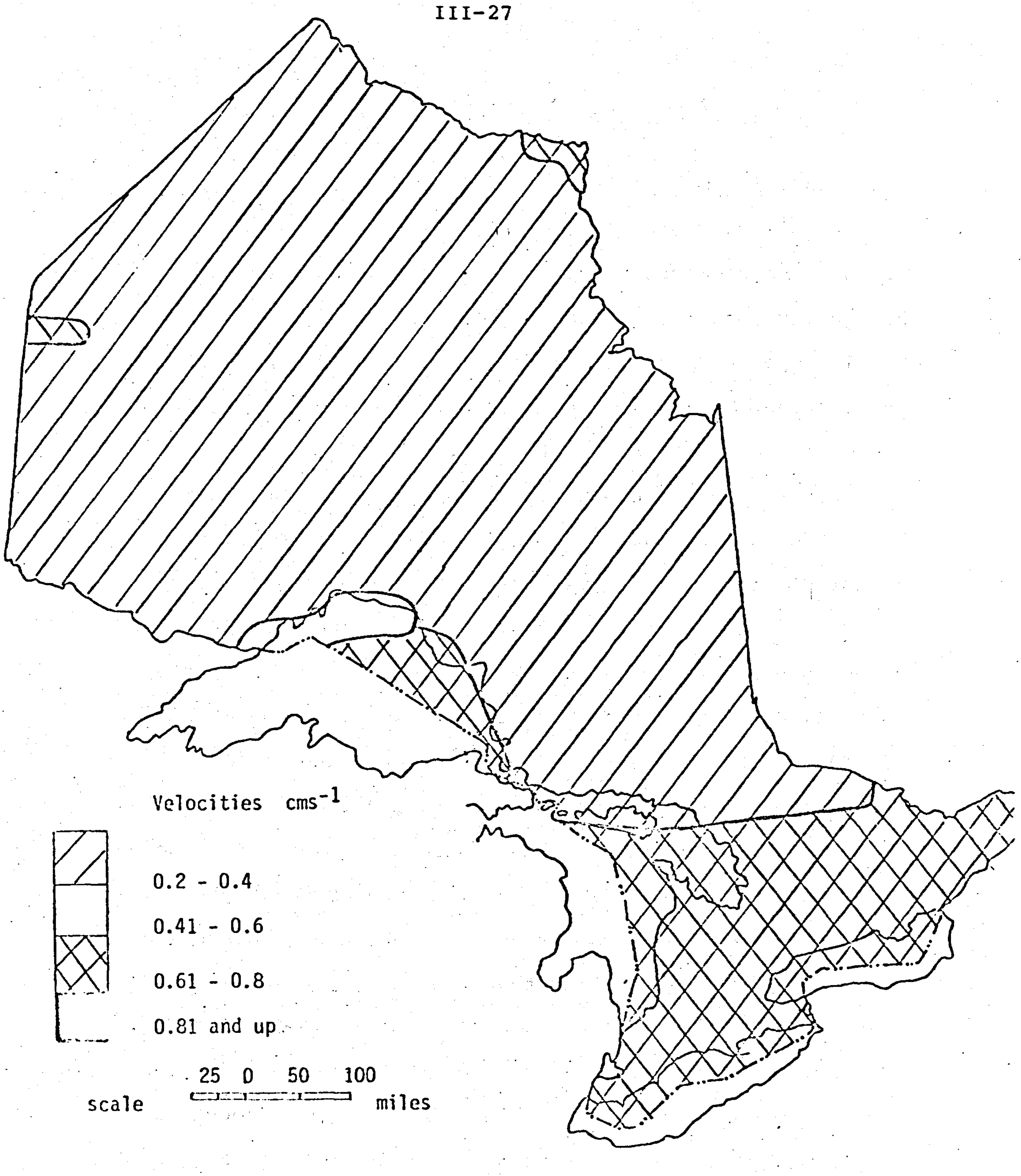

Figure 5. Deposition Velocities of SO_2 for December-February.

3. Atmospheric Chemical Transformations

3.1 General Considerations

Both laboratory studies and computer simulation of atmospheric chemical reactions have shown that gas-phase homogeneous, as well as heterogeneous, reactions are potentially important for oxidation of sulfur dioxide to sulfates in polluted air - see, for example, Calvert et al. (1978) and Beilke and Gravenhurst (1978).

Homogeneous reactions can lead to conversion rates as high as 4% h^{-1} in the summertime, largely due to attack of sulfur dioxide by hydroxyl, hydroperoxyl and alkylperoxyl radicals (Calvert et al., 1978). The seasonal dependance of homogeneous reactions has been discussed by a number of authors, and is reasonably well understood. Thus Altshuller (1979), on the basis of computer modeling studies, found that while seasonal effects are small at lower latitudes, at middle and higher latitudes the ratio of summer-winter noontime and average diurnal photochemical rates can be large: for example, at 35°N, summer noontime and averge diurnal rates are 4-5 times greater than the corresponding winter values. At 55°N, the summertime values are 16-20 times greater. In fact, Altshuller finds that during the winter months, homogeneous oxidation reactions cannot account for any significant conversion of SO_2 to sulfate at latitudes greater than 45°N. Bottenheim et al. (1977), in their study of seasonal effects on photochemical air pollution at 60°N, have come to similar conclusions. These results are largely due to changes in available ultraviolet solar intensity (Nieboer et al., 1976; Bottenheim et al., 1977; Altshuller, 1979), although temperature effects may also play a role (Carter et al., 1979). Table 1, taken from Altshuller (1979), illustrates the expected effects of season and latitude on noontime sulfur dioxide homogeneous oxidation rates in clean air. In polluted air, the corresponding rates could be a factor-of-two or so higher (Calvert et al., 1978; Altshuller, 1979).

Heterogeneous sulfur dioxide oxidation processes are less well understood than their homogeneous counterparts. Oxidation can take place in droplets, liquid films surrounding particles at high relative humidity, or on dry particle surfaces. At present, the most important heterogeneous reactions which take place in the aqueous phase are thought to be (Beilke and Gravenhurst, 1978): (1) SO_2 oxidation by O_2 in the presence of catalysts (e.g., dissolved transition metals); and (2) SO_2 oxidation by strongly oxidizing agents (e.g., ozone and hydrogen peroxide). The reaction with hydrogen peroxide in particular has recently excited the interest of the scientific community, due to its potential atmospheric importance (- see, for example, Penkett et al., 1979; Dasgupta, 1980). To date, there has been no clear demonstration that SO_2 - dry particle reactions are of atmospheric significance, except possibly in smokestack plumes close to the chimney (where concentrations are relatively high). For example, Britton and Clark (1980) have recently reviewed past work on heterogeneous SO_2 reactions on dry particles, and have presented the results of some of their own studies with soot and SO_2/NO_2 mixtures. In their conclusions, they state: "From the point of view of the overall SO_2 oxidation process in the atmosphere the heterogeneous reactions on soot or other particles play a negligible part compared to either photochemical or droplet phase mechanisms...". Therefore, such processes will not be considered further here.

It was noted above that, for homogeneous processes, large seasonal changes may be theoretically expected in the oxidation rate, depending on the latitude. The picture is not as clear for heterogeneous reactions. It has been theorized (e.g., Foster, 1969; Freiberg, 1974) that the oxidation rate involving trace metal catalysts should be increased at high ambient ammonia concentrations and relative humidities, both of these factors leading to lower solution acidity and hence higher sulfite ion concentrations (- sulfite ions are thought to be the species actually oxidized to sulfate by dissolved O_2). Lower temperatures may also promote oxidation by hydrogen peroxide or trace metal catalysts (Penkett et al., 1979; Freiberg, 1974). Thus, seasonal variations in all these factors - e.g., lower wintertime temperatures and ambient ammonia concentrations - could potentially have an effect on the conversion rate. These effects are difficult to predict. For example, Middleton et al. (1980) have carried out a modeling study into the relative importance of various urban sulfate aerosol production mechanisms, including photochemical reactions followed by sulfuric acid vapor condensation, and catalytic as well as non-catalytic heterogeneous oxidation. They conclude that the dominant mechanism for sulfate production can depend on the season and time of day. During the daytime in summer, photochemical reactions/sulfuric acid vapor condensation are the most important, followed by liquid phase oxidation by hydrogen peroxide. At night, however, catalytic and non-catalytic oxidation mechanisms on the wetted aerosol surface become important. In the winter, most of the daytime SO_2 oxidation is predicted to take place by reactions with hydrogen peroxide in droplets, at overall rates comparable to those in the summer. However, the above conclusions are based on a large number of assumptions about reaction mechanisms and model input conditions, and should not be regarded as final. For a better assessment of winter/summertime difference in atmospheric chemical transformation rates, the results of actual field studies were consulted (see below).

3.2 Experimental Results

A large number of field investigations have been carried out into the oxidation of sulfur dioxide in urban, industrial and power plant plumes. Since, on the basis of our present understanding of atmospheric chemistry, there is a fundamental difference between urban plumes and those from strong point sources (- at least, before the latter have been well-mixed into the "background" air), the two will be considered separately. Also, in view of the suggested importance of latitude when considering winter and summertime difference in photochemical processes (see above), the geographic location of each experiment will be noted whenever possible in the following discussion.

Newman (1980) has recently summarized the available results on atmospheric oxidation of SO_2 from power plant and smelter plume studies. Table 5 is largely based on the most relevant references taken from his paper. In preparing this table, we have concurred with Newman in that some of the early, and often-cited, studies of plume oxidation, such as that by Gartrell et al. (1963) and Stephens and McCaldin (1971), are probably flawed, and the results are unreliable. Rather we have emphasized those particular more recent studies which have a direct bearing on seasonal effects on the plume oxidation rate.

An inspection of Table 5, and the references cited therein, leads to the following general conclusions about the sulfur dioxide oxidation rate in power plant and smelter plumes:

1. The "dry" oxidation rate is usually no more than a few percent per hour.
2. Although there is still a debate about the relative importance of homogeneous gas-phase reactions, and heterogeneous processes involving catalytic plume aerosols, most of the evidence suggests the former are important, and can lead to SO_2 transformation rates of up to about 4% h^{-1}. Heterogeneous reactions may dominate near the point of emission where the particle concentration is high, or under high humidity conditions.
3. Under conditions where homogeneous photochemical reactions are not expected to be significant (e.g., during the night or early morning, or during the winter at far northern locations), conversion rates have been observed to be small - generally, well below 1% h^{-1}.
4. Temperature or relative humidity may or may not have an effect on the conversion rate (compare Lusis et al., Forrest et al., Chan et al., Garber et al., with Eatough et al., Dittenhoefer and DePena in Table 5). However, the degree of plume dilution due to atmospheric mixing is certainly important (Wilson and Gillani, 1980).

It must be emphasized that the above summary represents a considerable simplification of what happens during atmospheric SO_2 oxidation in chimney plumes, and a more rigorous treatment would require separate consideration of each point source, including the composition of the emissions as well as that of the background air into which the plume is mixing.

Before drawing any conclusions on the seasonal dependence of the SO_2 transformation rate from the above data, consider the corresponding data obtained from studies of urban plumes. Although urban plume data are more relevant to long-range transport modeling than chimney plume data, which generally have represented conditions within the first hour or two of emission, they are also more difficult to interpret. To extract the oxidation rate from the data, assumptions have to be made about other atmospheric processes such as air parcel dilution and dry deposition (see, for example, Alkezweeny and Powell, 1977). This should be kept in mind when evaluating the urban plume results.

Alkezweeny (1980) has summarized the available data on SO_2 oxidation in urban plumes, and the results in Table 6 are largely taken from his paper. An inspection of this table suggests that:

1. "Dry" oxidation rates in urban plumes are somewhat higher than those in chimney plumes (- at least, before the latter have been mixed into the background air), possibly by a factor-of-two or more.

2. Although homogeneous photochemical processes are important (Alkezweeny, 1980), heterogeneous mechanisms may play a greater role in urban than in power plant and smelter plumes (close to the source). Thus, whereas power plant and smelter plume data suggested very low oxidation rates under conditions where homogeneous processes are not expected to be significant, the urban plume data in Table 6 indicate that quite high oxidation rates have been observed in the wintertime at latitudes greater than 45°N (- see, for example, the results of Benarie et al., Elshout et al., Prahm et al., and Smith and Jeffrey). Alkezweeny (1980) also has noted in his own data that high oxidation rates seem to be associated with high aerosol loadings.
3. There is some indication that temperature may have an effect on the conversion rate, although, as with chimney plume studies, the information is conflicting (compare Benaire et al. with Meszaros et al.). There is also confusion on the correlation of conversion rate and relative humidity (compare Benaire et al. with Smith and Jeffrey).

3.3 Summary

The above experimental results make it difficult to draw any firm conclusions on the seasonal variation of SO_2 oxidation rate. Perhaps this much can be said: during the summer months, photochemical processes are important, and both point source and urban plume data indicate daytime "dry" rates of several percent per hour (a summertime diurnal average of 1-2% h^{-1} might be suitable for long-range transport modeling, although some of the urban plume data suggest rates several times greater than this). In the winter, it is not clear what one should expect. The chimney plume data, most of which may be of questionable relevance to long-range transport modeling because estimates were determined at short distances from the chimneys, indicate oxidation rates generally considerably less than 0.5% h^{-1} at latitudes where photochemical reactions should not be contributing appreciably. On the other hand, the limited urban plume data suggest a greater role of heterogeneous processes, and therefore appreciable oxidation rates, but at the same time they have been derived with more assumptions about the history of the air parcel, and are therefore more open to criticism (- see, for example, Forrest et al., 1979b). It must be concluded that at present the available data is too conflicting to draw any firm conclusions about the seasonal dependence of the SO_2 oxidation rate.

There is one more factor which makes any conclusions difficult at the present time - viz., the possibly important role of clouds (both precipitating and fair weather) in converting SO_2 to sulfates. Recently, there has been a considerable amount of speculation that in-cloud processes contribute significantly to SO_2 oxidation (see, for example, Hegg and Hobbs, 1978; Hales and Dana, 1979b; Newman, 1979; McNaughton and Scott, 1980; Scott, 1980). If this can be proven experimentally (work is currently in progress by several groups of researchers), then expected seasonal variations in SO_2 transformation could increase considerably, especially in areas where clouds consist largely of dry ice crystals in the winter (and hence have very low chemical transformation potential, as compared to summertime conditions).

Table 4. Effects of Month and Latitude on Photochemical Homogeneous Oxidation of Sulfur Dioxide in Clean Air (Noontime rates in % h^{-1} from Altshuller, 1979)

	Latitude (°N)						
Month	5	15	25	35	45	55	65
January	1.81	1.10	0.61	0.26	0.08	0.01	0.01
February	1.81	1.21	0.74	0.32	0.13	0.04	0.01
March	2.06	1.55	1.01	0.48	0.21	0.09	0.03
April	2.01	0.79	1.36	0.73	0.35	0.17	0.07
May	1.82	1.68	1.48	1.01	0.58	0.30	0.16
June	1.81	1.72	1.56	1.22	0.74	0.42	0.25
July	1.78	1.80	1.58	1.30	0.88	0.52	0.31
August	1.86	1.78	1.61	1.31	0.82	0.45	0.26
September	1.91	1.68	1.50	1.15	0.76	0.34	0.17
October	1.79	1.54	1.29	0.84	0.39	0.17	0.06
November	1.56	1.33	0.98	0.48	0.19	0.06	0.02
December	1.58	1.16	0.74	0.33	0.11	0.02	0.01

Table 5. Conversion of SO_2 in Power Plant and Smelter Plumes

Source	SO_2 Oxidation Rate ($\% \ h^{-1}$)	Comments
Forrest and Newman (1977)	<1.5	-four coal-fired power plants (30° - 40°N) -no correlation could be found between conversion and temperature (10 - 25°C), humidity or time of day.
Husar et al. (1978a)	1 - 4 (noontime) <0.5 (night)	-St. Louis (38°N) -power plant -photochemistry may be the dominate mechanism.
Lusis et al. (1978)	1 - 3 (June, noon and p.m.) <0.5(winter, or summer early a.m.)	-Fort McMurray (57°N) -power plant -evidence of photochemical activity during relative high conversion rates -temperature varied from -13 to 23°C.
Dittenhoefer and de Pena (1979)	0 (<65% RH) 1 (65 - 90% RH) 2-6 (90% RH)	-Pennsylvania (41°N) -power plant -evidence that both gas phase and aqueous phase oxidation are important.
Forrest et al. (1979a)	<2	-Tarpon Springs, Florida (28°N) -oil-fired power plant -no correlation was found between individual meteorological parameters and extent of oxidation, although higher conversions were observed in August than in February.
Forrest et al. (1980)	0.1 - 0.8 (night, early a.m.) 1 - 4 (late a.m. and afternoon)	-Cumberland coal-fired power plant (35°N) -reactions were correlated with solar radiation.

Table 5 (continued)

Source	SO_2 Oxidation Rate (% h^{-1})	Comments
Garber et al. (1980)	<1	-Northport oil-fired power plant (41°N) -a wide range of meteorological conditions were examined. The data suggest a weak positive correlation of conversion rate with temperature, water partial pressure and insolation.
Hegg and Hobbs (1980)	0. - 5.7	-five coal-fired power plants, W. and Midwest U.S.A. -various times of year -evidence of photochemical reactions. Conversion depended on u.v. light intensity.
Gillani et al. (1980)	rate = 0.03 R.H.O_3 R = solar radition H = mixing height O_3 = background ozone	-plumes from Labadie, Cumberland and Johnsonville power plants -for dry conditions only.
Chan et al. (1980)	<0.5	-Sudbury smelter plume (47°N) -no correlation of rate with temperature, relative humidity.
Eatough et al. (1980)	<0.5 to 6	-Western U.S. smelter and power plant plumes -positive temperature dependence of oxidation rate; data are consistent with a homogeneous mechanism.

Table 6: Conversion Rates of SO_2 in Urban Plumes

Source	SO_2 Oxidation Rate (% h^{-1})	Comments
Benarie et al. (1972)	6 to 25	-Rouen (49°N) -wintertime results -aerosol catalysis important; acid formation increases as temperature decreases.
Robert and Friedlander (1975)	1.2 to 13	-Los Angeles (34°N) -July, October.
Mezaros et al. (1977)	30	-Budapest (48°N) -mainly June to September.
Alkezweeny and Powell (1977)	10 to 14	-St. Louis (38°N) -August.
Alkezweeny (1978)	8 to 12	-St. Louis (38°N) -summertime
Breeding et al. (1976)	5 to 32	-St. Louis (38°N) -October, April
Alkezweeny (1980)	1 to 5	-Chicago, Gary (42°N) -summertime -conversion dominated by photochemical reactions.
Forrest et al. (1979b) Chang (1979)	4	-St. Louis (38°N) -Flight Da Vinci II, June.
Alkezweeny (1980)	0, 6.8	-Milwaukee (44°N) -measurements on two days in August.
Elshout et al. (1978)	0.6 to 4.4	-Arnheim, Amsterdam (52°N) -January to March.
Prahm et al. (1976)	1.1	-Faroe Island and British Isles (50 to 60°N) -February/
Smith and Jeffrey (1975)	0 to 3	-British Isles (52 to 56°N) -mainly September to November -relative humidity is important.
Lavery et al. (1979)	0.7	-Ohio Valley (40°N) -August.

4. Nitrogen Oxides Deposition and Chemistry

The atmospheric chemistry and deposition of sulfur oxides has in the past received considerably more attention than that of nitrogen oxides. However, the recognition that the latter are important precursors of acid deposition, and that emissions of nitrogen oxides will grow considerably more than those of sulfur oxides in the coming two decades (U.S.-Canada Research Consultation Group on LRTAP, 1979), has recently led to a substantial increase in the level of research devoted to the atmospheric nitrogen compounds. Nevertheless, at present relatively little has been published on deposition and chemical transformation rates of nitrogen oxides. Most of the information we are aware of is summarized in the present chapter.

Since many of the general physical and chemical considerations regarding deposition and transformation (outlined in Sections 2.1.1, 2.2.1 and 3.1) also apply to nitrogen oxides, some speculation is possible in the absence of field data regarding their transformation and deposition rates and the seasonal dependence of these rates, but this has been kept to a minimum in the discussion below. The situation is somewhat more complicated than for the sulfur oxides, because the behavior of more species must be considered. Thus, although anthropogenic emissions are primarily in the form of nitric oxide (NO), this compound is converted relatively rapidly to nitrogen dioxide (NO_2), nitric acid (HNO_3) and particulate nitrates, and peroxyacetyl nitrate (PAN) (- see, e.g. Spicer, et al., 1980). The chemical reactions and atmospheric deposition of each of these species will be considered separately below.

Nitric oxide has a very low solubility in water (Sherwood and Pigford, 1952). Since the rate of wet deposition, especially unde the "equilibrium scavenging" conditions of relevance to long-range transport (Hales, 1978), is directly dependent on the solubility of the gas under consideration, the wet scavenging coefficient of NO is also expected to be low. As far as dry deposition is concerned, a number of investigators, working with different types of surfaces (see Table 7), have found the deposition velocity of NO to be very small - about one-tenth that for SO_2 over the same surface. Moreover, NO is oxidized to products fairly rapidly (in the order of a few hours) in the summertime, so the short lifetime and low wet and dry scavenging rates of this gas suggest that its contribution to deposition is small. Under wintertime conditions, at latitudes where photochemical reactions are of relatively little importance (see Section 3.1), the atmospheric lifetime of NO could be increased considerably, and the amount deposited by wet and dry removal processes could become important. However, no information is available on scavenging coefficients and deposition velocities of NO under these conditions, especially to snow surfaces.

Nitrogen dioxide is formed in the atmosphere mainly from the oxidation of NO by ozone and various free radicals (see, for example, Bottenheim et al., 1977; Calvert et al., 1978; Altshuller, 1979). It dissolves in water according to a fairly complex chemical mechanism (Sherwood and Pigford, 1952), the overall reaction be

$$2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2.$$

As can be seen from the above reaction, the solubility of NO_2 will, like that for SO_2, depend on the acidity of the rain or cloud droplet, and laboratory experiments (Beilke, 1970) have shown the scavenging coefficient of NO_2 to be roughly one-quarter that for SO_2. Experiments on dry deposition rates of NO_2 to a number of surfaces have shown the deposition velocity of NO_2 to be roughly one-half that for SO_2 under comparable conditions (see Table 7). No wet and dry deposition data for NO_2 under wintertime conditions are available, especially to snow, but it seems reasonable that qualitatively the same differences in winter and summertime deposition behavior will obtain as for SO_2.

As far as atmospheric chemistry is concerned, NO_2 is formed so quickly from NO under summertime conditions that, in mathematical modeling of long-range transport (where time steps of the order of several hours are involved in the calculations), as a first approximation emissions can probably be assumed to consist of NO_2 (i.e., the role of NO as an independent precursor species of nitrates and PAN can be neglected). This may not be true under nighttime conditions, or in the winter at northerly latitudes, but the scope of this report does not allow for more detailed speculation on this point.

Nitric acid is now thought to be one of the major products of NO emissions (e.g., see Spicer, 1979; Spicer et al., 1980). Under typical atmospheric conditions, it exists mainly in the vapor form. However, it is a highly soluble vapor (e.g., see Okita and Ohta, 1979), and potentially has a higher scavenging coefficient than that of SO_2 (no experimental data are available to verify this). There are also reports of unpublished experimental results which suggest that, unlike SO_2, HNO_3 is scavenged very efficiently by snow. Thus, even though no experimental data are available on wet removal rates of HNO_3, one can speculate that the seasonal dependence of Λ for this substance is probably smaller than that for SO_2 (and its overall magnitude is larger). Similarly, because of the apparently high reactivity of HNO_3 with all types of surfaces, it would seem reasonable to assume that the total resistance to mass transport is approximately equal to the aerodynamic resistance (i.e. $r_s << r_a$ in Equation (11)), and to use values calulated from micro-meteorological theories (see, for example, Table 1 in Garland, 1978). This leads us to expect fairly small seasonal variations of the deposition velocity for HNO_3, probably smaller than those for SO_2.

Nitric acid can be formed by homogeneous reaction pathways, mainly by reaction with hydroxyl radicals, or in the droplet phase (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). Homogeneous processes are relatively well understood compared to the heterogeneious ones, and are probably more important during the daytime in summer, and display a similar seasonal dependence to those for SO_2 oxidation (see Section 3.1 and also Bottenheim and Strausz, 1980). Nitrogen oxides transformation rates of over 20% h^{-1} have been observed in urban plumes, most likely due to homogeneous reactions (Spicer, 1979), and power plant plume studies have also yielded nitrate formation rates several-fold those of sulfates (e.g., Forrest et al., 1980) which are consistent with a homogeneous reaction mechanism. Heterogeneous processes may be an important source of nitrates at night and in the winter (Middleton and Kiang, 1979), but too little reliable information is available on the chemistry involved to speculate on seasonal trends in the HNO_3 formation rate.

<u>Particulate nitrates</u> are probably formed by heterogeneous processes, and consist of a number of salts, with ammonium nitrate being one of the most important (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). During the summertime,

particulate nitrate concentrations are apparently relatively small compared to those of vapor phase nitric acid (e.g., see Spicer, 1979; Spicer et al., 1980; see also, Tang, 1980). During the winter, especially at northern latitudes, the reverse could be true, but due to difficulties involved in sampling HNO_3 and particulate nitrates separately, insufficient data are available to answer this question. Little can be said about the wet and dry deposition of nitrates, and its seasonal dependence. In the absence of experimental data, one might postulate a behavior similar to that of sulfates. As far as chemical formation rates are concerned, some theoretical estimates suggest that wintertime rates for particulate nitrate may be considerably greater than those in the summer (Middleton and Kiang, 1979), but again, this result requires experimental verification.

The other major nitrate product to be considered is peroxyacetyl nitrate. This substance is stated by Hill (1971) as being "relatively insoluble", and Garland and Penkett (1976) found negligible PAN uptake rates by water in a wind tunnel. This suggests a relatively low value of the scavenging coefficient. The dependence of PAN solubility on the temperature, and the nature of its interactions with snow, are unknown; therefore, we will not speculate on the seasonal dependence of its wet scavenging rate. Some data are available on the dry deposition rate of PAN over a number of surfaces

(Table 7), and, with the exception of water, the PAN deposition velocity seems to be about one-third that for SO_2. Again due to lack of supporting data, speculation on the seasonal dependence of the PAN dry deposition rate is not possible.

As for as chemical formation rates are concerned, PAN is the product of photochemical reactions involving peroxyacetyl radicals and NO_2:

$$CH_3CO(O_2) + NO_2 \rightleftarrows PAN.$$

The proportion of PAN and HNO_3 appearing in the irradiated, polluted air mixture depends on the level of hydrocarbons present in the mixture (Spicer et al., 1980), but limited field measurements suggest that the two products can exist in comparable amounts (e.g., Spicer, 1979). Thus, PAN formation rates are expected to be several percent per hour under conditions where photochemical reactions are important. As far as the seasonal dependence of the PAN formation rate is concerned, one would expect it to be qualitatively similar to that resulting from the photochemical components of the sulfuric and nitric acid formation rates (see also Bottenheim et al., 1977), but it must be noted that the PAN formation reaction (see above) is reversible. The stability of PAN is a strong function of the temperature, and its atmospheric half-life at 275°K is about two orders of magnitude greater than that at 305°K (Hendry and Kenley, 1979). This will offset some of the seasonal dependence in net PAN formation rate due to photochemical reactions alone, but quantitative conclusions are not possible at present.

Table 7 summarizes the published data on wet and dry deposition rates that we are aware of. Also shown are some of the chemical transformation rates that have been measured in field experiments.

Table 7: Deposition and Chemical Transformation Rates for Nitrogen Compounds

Compound	Parameter	Rate	Reference	Comments
NO_2	Λ	$\Lambda_{NO_2} \sim 1/4 \Lambda_{SO_2}$	Beilke (1970)	
	v	0.3-0.8 cms^{-1}	Judeikis & Wren (1978)	Soil, cement surfaces. For the same surfaces, deposition velocities for SO_2 were in the range 0. 3-2.5 cms with most values around 1 cms.
		1.9 cms^{-1}	Sehmel (1980)	Alfalfa canopy, calculated from experiments of Hill (1971). For the same canopy, deposition velocity for SO_2 was 2.7 cms^{-1}.
NO	v	0.1-0.2 cms^{-1}	Judeikis & Wren (1978)	Soil, cement surfaces. See comments for NO_2 above.
		0.1 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
PAN	v	0.8 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
		0.25 cms^{-1}	Garland & Penkett (1976)	Water. Grass and soil surfaces.
HNO_3	Conversion rate from NO_x	3 to 10 times SO_2 conversion rate	Richards et al. (1980)	Daytime measurements, Navajo generating station plume (Arizona); June-July and December.
HNO_3 and particulates nitrates	Conversion from NO_x	0.1 to 3% h^{-1} (night-time) 3 to 12% h^{-1} (daytime)	Forrest et. al. (1980)	Cumberland coal-fired generating station, August. NO_x conversion rate was 2 to 4 times SO_2 rate.
NO_x	Removal rate	14 to 24% h^{-1}	Spicer (1979)	Boston urban plume, August.
NO_x	Removal rate	4% h^{-1}	Chang et. al. (1979)	Annual average, Los Angeles.

5. CONCLUSIONS

A literature survey has been carried out into the seasonal variations of the wet and dry deposition rate, as well as the chemical transformation rate, of sulfur and nitrogen oxides, with particular reference to deposition and transformation parameters of relevance to long-range transport mathematical models. Both relevant theoretical and experimental results have been considered although a critical evaluation of the references has not been attempted.

As indicated in Chapters 2, 3 and 4, from a theoretical viewpoint the deposition and transformation rates of sulfur and nitrogen compounds could potentially have a substantial seasonal variation. However, it is difficult to draw conclusions about the magnitude of this variation with any degree of confidence from the current theories, with the possible exception of the wet and dry deposition of sulfur dioxide and the photochemical component of its chemical transformation rate. Therefore, the available field data were also considered, although these were often too scanty to be of much assistance.

An attempt is made in Table 8 to summarize the available information on the seasonal variation of transformation/deposition rates for the sulfur compounds. It is not intended to recommend the values shown in this Table for use by the long-range transport modeler - much more experimental and theoretical work is needed before this will be possible - but rather, to indicate whether seasonal changes in the parameter of interest are expected to be greater or less than an order of magnitude (at present, little more than this can be done). The following conclusions can be made on the basis of Table 8 and the discussions in Chapters 2 to 4:

1. The scanty available data suggest that the washout rates of sulfates (and probably nitrates) should be comparable in summer and winter. The rainout rates could be strongly dependent on storm type, and hence the time of year, because of the different mechanisms whereby particles can be incorporated into precipitation (- some data suggest variations of an order-of-magnitude or more).
2. Experimental results and theoretical considerations suggest a seasonal variation of the wet scavenging coefficient for sulfur dioxide which can be up to several orders of magnitude, depending on the latitude, being most pronounced in the northern parts of America which receive appreciable amounts of snow in the winter. Probably the same conclusions also apply to nitrogen dioxide. Nitric acid vapor, being highly reactive with all kinds of surfaces, is expected to show a smaller seasonal dependence of the scavenging coefficient.

3. The situation is too confusing at present to draw any conclusions about the seasonal dependence of the dry deposition rate for sulfates (or nitrates). In the winter, deposition velocities would seem to be 0.2 cms^{-1} or less, but values reported for summertime conditions range over an order of magnitude, including negative numbers.

4. The dry deposition velocity of sulfur dioxide is expected, from available experimental and theoretical results, to show only a modest seasonal variation - generally, less than a factor-of-two or so in any given area. The same is probably true of nitrogen dioxide and nitric acid vapor.

5. The gas-phase homogeneous component of sulfuric and nitric acid formation rates is relatively well understood, and has a strong seasonal variability, especially at the northern latitudes. However, our knowledge of the heterogeneous component, including in-cloud processes, is too poor at present to allow any conclusions regarding the seasonal dependence of the overall chemical transformation rate of sulfur and nitrogen oxides.

6. For many of the parameters under consideration, during the winter months, rates are strongly dependent on latitude - e.g., photochemical conversion rates of sulfur and nitrogen oxides above 45°N become negligible,

as do also wet deposition rates of gases such as sulfur dioxide (because precipitation is largely in the form of dry snow). This indicates that not only the seasonal, but also the spatial variability of deposition and transformation rates should be taken into account in long-range transport models. Although it may be too early to speculate, the following approach does not seem unreasonable: during the summer months, one might assume, as a first approximation, the same values for deposition/transformation parameters irregardless of location, for each species of interest. During the winter months, while rates at the southerly latitudes might stay roughly the same as those in the summer, the models would include a dependence of deposition/transformation on latitude, which could be quite pronounced for some of the parameters (such as wet deposition of sulfur dioxide).

7. For the sulfur compounds, more experimental data are badly needed, both under summer and winter-time conditions, particularly on wet and dry deposition rates of particulates and chemical transformation rates in regional scale air masses (as opposed to chimney plumes). Very little is also known about in-cloud transformation and deposition processes. For the nitrogen compounds, data are required in almost every area of interest, and

immediate support for laboratory and field investigations into deposition and transformation rates of the major species (NO, NO_2, HNO_3, nitrates and PAN) is strongly recommended.

Table 8: Summary of Deposition and Chemical Transformation Rates for Sulfur Compounds

	Representative Range (Observed)			
Parameter	Summer Conditions	Winter Conditions	Suggested (Winter/Summer) Ratio	Comments
$\Lambda (s^{-1})$ Sulfates	$\sim 10^{-5}$	$\sim 10^{-5}$	~ 1	-washout: based on very few data.
			10^{-1} (?)	-rainout: order-of-magnitude seasonal variation could be possible, depending on storm types (e.g., Scott, 1981).
$\Lambda (s^{-1}) SO_2$	$(3-8) \times 10^{-4}$	$(1-25) \times 10^{-7}$	$\sim 10^{-3}$	-rainout: based on data of Summers (1977); applies to areas where wintertime precipitation is largely in the form of dry snow.
			~ 10 (?)	-theoretically predicted possibility for areas which largely receive cold rain or wet snow during the winter.
$v (cm s^{-1})$ Sulfates	(?)	<0.2	(?)	-very large uncertainty about deposition velocity for sulfates
$v (cm s^{-1})$ SO_2	0.4 - 0.8	0.1 - 0.4	1/2	-seasonal changes expected to be modest (i.e., not order-of-magnitude).
$SO_2 \rightarrow SO_4$ transformation rate h^{-1}	1-4 (chimney plumes) 1-30 (urban plumes)	<1 (chimney plumes) 1-25 (urban plumes)	(?)	-gas-phase homogeneous processes should be smaller at latitudes greater than 45°N in the winter. However, there is too much uncertainty about the magnitude of heterogeneous processes, including in-cloud SO_2 conversion, to allow conclusions about seasonal variations.

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SECTION IV

THE GLOBAL DISTRIBUTION OF ACIDIC PRECIPITATION AND THE IMPLICATIONS FOR EASTERN NORTH AMERICA

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1. INTRODUCTION

The question is occasionally asked "how do we know that the low pH measured in precipitation in the eastern part of North America is due to regional anthropogenic sources when measurements in remote locations (in the sense of being well moved from population centres and industrial areas) also indicate comparably low pH values at times?" Alternatively the question could be rephrased as follows" how much of the acidity measured in precipitation at a given location is due to anthropogenic sources and how much to natural sources and for either case, can we distinguish between regional sources and world-wide background?"

Clearly, if one is to fully understand the patterns of pH over eastern North America, and especially if one is to use these as a basis for developing an emissions control strategy and international agreements, one must consider these patterns in the total North American and global context.

In this paper, the available data* on precipitation pH around the world will be reviewed and discussed in terms of the large-scale processes taking place that could explain the observed pH values. At the start it must be cautioned that the data-base is very sparse and generally for a short time period, and that the explanations, are therefore, preliminary and somewhat speculative. The purpose of this chapter is to stimulate discussion and indicate the further observations and research that will be required to improve our understanding of the issue.

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* Much of this is only now becoming available through draft reports and has not yet appeared in the scientific literature.

2. GLOBAL DISTRIBUTION OF EMISSIONS

2.1 Sulfur Emissions

The most recent estimates of sulphur emissions (Cullis and Hirschler, 1980) have been summarized in Table 1 by hemisphere for man-made and natural sources.

TABLE 1 - Man-made and Natural Emissions of Sulfur (Tg S per year)* in 1976

	Northern Hemisphere	Southern Hemisphere	Global Total
Man-made	98	6	104
Natural	76	71	147
TOTAL	174	77	251

On a global basis, natural emissions exceed man-made at the present time by about 40%. This gap is slowly narrowing and, depending on the general rate of worldwide industrial growth, the rate of increase of coal use for electric power and effectiveness of SO_2 emission controls, then man-made emissions could become equal to natural emissions early in the next century.

The situation in each of the hemispheres is quite different. In the sparsely populated and generally less industralized southern hemisphere, natural far outweight man-made emissions by a factor 12:1. In the northern hemisphere man-made emissions already exceed natural by about 30%.

An important feature of the northern hemisphere distribution is the concentration of most of these emissions into a few heavily industralized regions (Barnes, 1979) as summarized in Table 2.

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* 1 Tg = 10^{12} g = 10^9 kg = 10^6 metric tons

TABLE 2 - Emissions of SO_2 from Stationary Sources in the ECE Region (1973)

Region	Emissions Tg S / Year
Western Europe(ECE)	11.2
Eastern Europe	6.0
U.S.S.R.	12.0
U.S.A.	15.0
Canada	3.5
Total	47.7

Note that the total in Table 2 is considerably less than the northern hemisphere total in Table 1. The discrepancy is due to the increases in emissions that have taken place since 1973, and the fact that emissions from other regions, especially Japan and China, are not included in Table 2 and the different methods of estimates. However, Table 2 does show that the man-made emissions in the northern hemisphere are concentrated into a few regions in each of which the man-made emission strength far exceeds the natural.

The natural emissions in both hemispheres are widely distributed with the oceans being the major source as shown in Table 3. (Cullis and Hirschler, 1980).

TABLE 3 - Distribution of Estimated Natural Emissions of S among Land and Ocean by Hemispheres (Tg S per year)

	Northern Hemisphere	Southern Hemisphere	Global Total
Land (biogenic & volcanoes)	35	18	53
Oceans (sea-spray & biogenic	41	53	94
TOTAL	76	71	147

2.2 Nitrogen Emissions

The other major contribution to the acidity of precipitation is nitrate originating from emissions of oxides of nitrogen (NO_x). Unfortunately data on these emissions is less complete than for SO_2, but in very general terms the current estimates are given in Table 4.

TABLE 4 - Estimated Emissions of NO_x Expressed as NO_2 (Tg/year)

	Man-made (Tg NO_2/year)	Natural
Global Total (1978)	75	53
USA	30	
ECE	11	

In summary, Table 4 shows that natural emissions of NO_x are about one-sixth those of SO_2 (294 Tg/year) and man-made emissions about one-third of those for SO_2. This is reflected in the rainfall chemistry since significant amounts of nitrate are found only in precipitation in areas within, and downwind of, industrialized regions. The most concentrated emissions of NO_x are in the eastern United States and the European Economic Community (EEC). Little data is available from elsewhere around the world.

2.3 Emissions of Alkaline Material

As will be discussed in more detail later, the pH of precipitation is determined by the balance (or more correctly the H^+ ion imbalance) between the acidic and aklaline materials. Sulfates and nitrates are the major acidic components and calcium and ammonium are the major alkaline or neutralizing components. Unfortunately, onlv very crude estimates are available for natural (or man-made emissions) of either of the latter two. In general, natural far outweigh the man-made emissions. The main sources of calcium are fly-ash (now largely removed from stack emissions) and windblown soil materials. The former, where they still exist, occur in polluted regions in association with generally larger amounts of acid forming pollutants.

The windblown materials tend to be in highest concentration in the arid and semi-arid areas of the world. These are regions of low population and industrial activity and, therefore, are not associated with high acidic loadings. Also, relatively dry agricultural areas (such as the Canadian Prairies and the U.S. high plains) with low industrial activity tend to have high calcuim loadings. These loadings are heavily dependent on frequency of precipitation and are highest in drought years. There is a seasonal variation with maxima in spring and fall when seeding and plowing are going on. In the summer the crops themselves and irrigation reduce the atmospheric loadings and in the winter frost and snow cover inhibit the release of material from the surface.

3. INFLUENCES ON PRECIPITATION CHEMISTRY AND pH

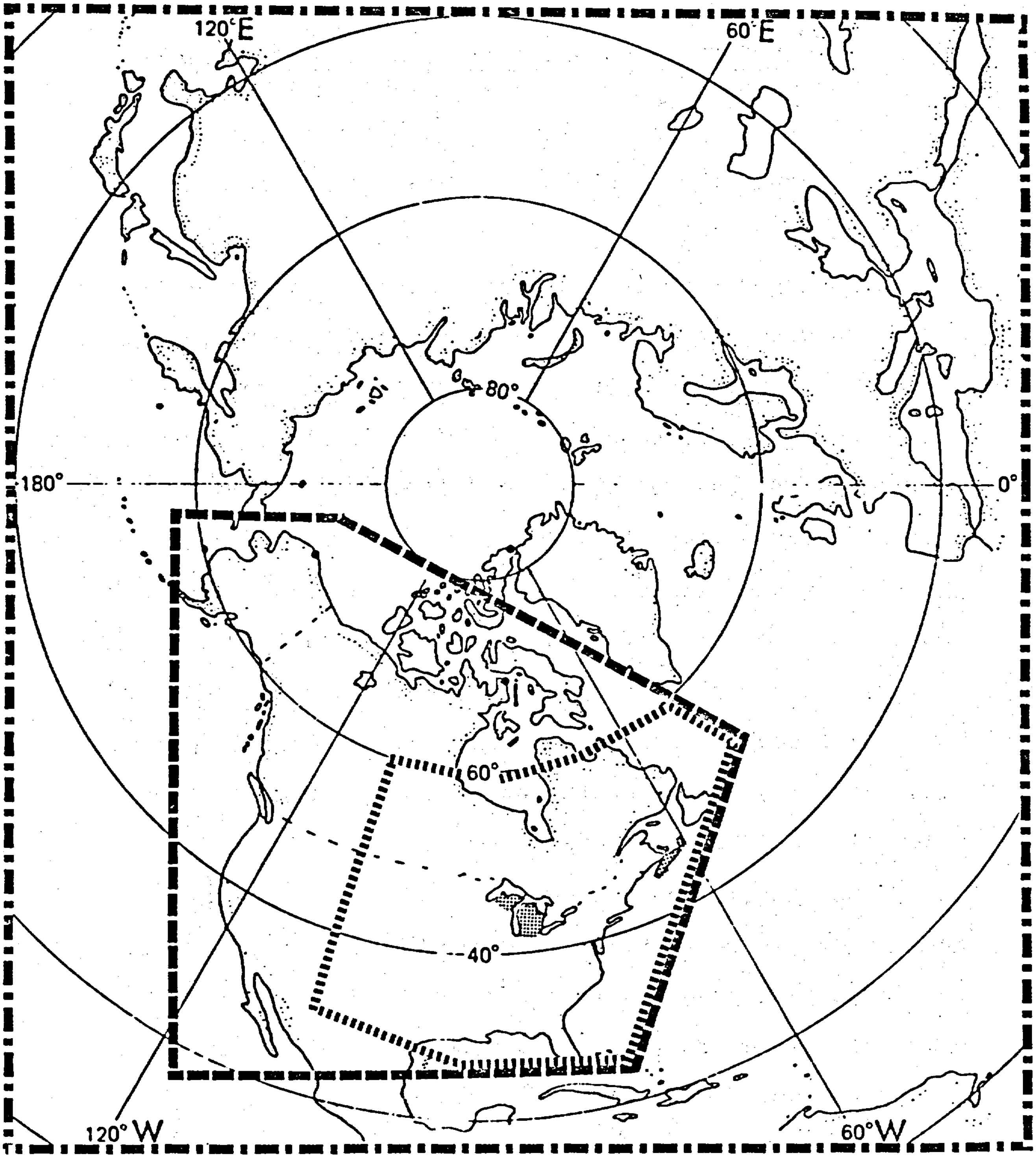
The chemical composition of precipitation and its pH when it reaches the ground is the end product of a complex series of processes.

The composition is made up of material incorporated into the cloud water through the initial nucleation processes, material incorporated into the growing cloud droplets ("rain-out") and material scavenged out by the falling precipitation between cloud-base and the ground ("washout"). These processes obviously take place at different heights in the atmosphere, and since nucleation efficiency and scavenging efficiency depends on the composition and size distribution of the particles, the source of the incorporated materials could be quite different in each case. The final chemical composition will, in turn, depend on the proportion of incorporated material from each of these sources.

Conceptually one can separate the source of the materials into three general categories - global background, regional, and local - although the exact cut-off in terms of time and space scales separating one from the other is somewhat arbitrary (see Figure 1).

3.1 Global Background

In the past, the global background level of atmospheric particles has been of great interest to cloud physicists searching for the origins of the cloud condensation nuclei



SCALE	NATURAL & ANTHROPOGENIC SOURCES
GLOBAL	LUMPED, BUT NOT USED
CONTINENT	SEPARATED, BUT NOT USED
MODELING DOMAIN	SEPARATED AND USED
STATE/PROVINCE	SEPARATED AND USED, BUT SMOOTHED

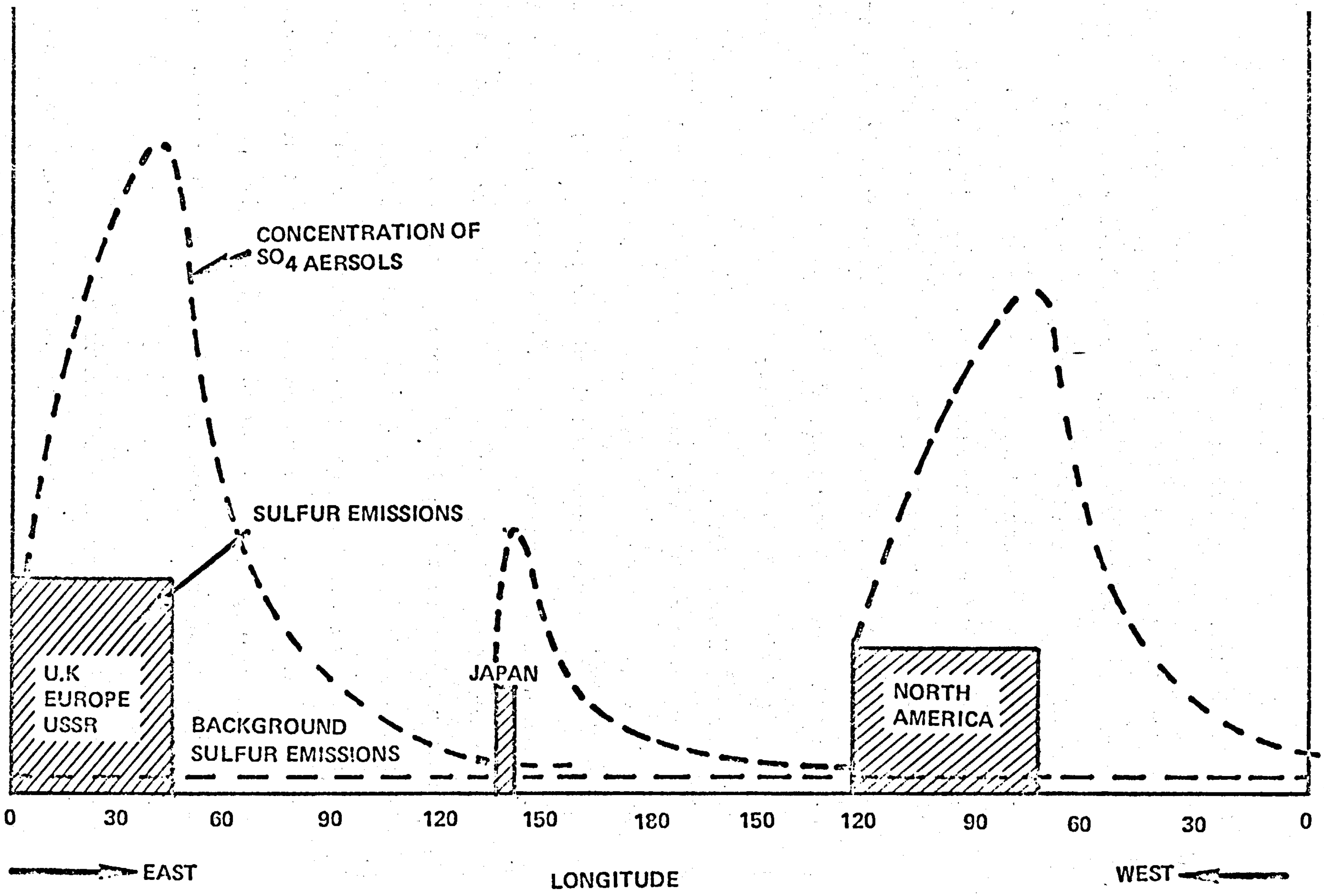
Figure 1: Natural and Anthropogenic Sources of Background Concentrations/Depositions for State/Province to Global Scales As Defined and Used by the Modelers

and freezing nuclei so essential to the processes of precipitation formation. Now we are also concerned about the impacts such particles have on the chemical composition of precipitation. One of the most ubiquitions of the substances in the global background is sulphur in the form of ammonium sulfate or sulphuric acid aerosols. Both of these, being highly hygroscopic, act as efficient condensation nuclei and are therefore readily removed from the atmosphere by precipitating clouds. The size of these particles is <0.2u and they, therefore, have very large residence times in the atmosphere and can be transported over long distances and be mixed to considerable heights in the troposphere.

Some measurements of background levels of such particles have been made in remote areas and these indicate levels of $SO_4^=$ between 0.1 and 0.5 μg S m^{-3} (Granat et al., 1976). Over the North Atlantic (which may be considered as in the "plume" from North American) levels of 0.3 to 1.0 μg S m^{-3} have been observed (Meszarios, 1978).

The concept of the residence time of particles in the atmosphere can be used in a schematic sense, as shown in Figure 2, to describe subjectively the background levels. Considering the northern hemisphere, most of the man-made pollutants are emitted in the mid-latitude belt 30° to 60°N where the westerly winds transport the material, on average, around the globe from west to east. Around the belt there will be an almost uniform background emission of sulphur and a background concentration of $SO_4^=$ attributable to this. The three major man-made emissions areas are the U.K.-Europe-U.S.S.R., Japan and North America. In these regions, $SO_4^=$ levels will be elevated to values at least one order of magnitude above background and reaching two orders in severe pollution episodes. Since the removal processes are in general linearly related to concentration, the concentration will fall off exponentially with time (or downwind distance) as shown in Figure 2. It is clear that nowhere will the concentrations of SO_4 reach zero, and on the west coast of North America or Europe one would expect small quantities of residual man-made emissions to be present. The size of this residual cannot be estimated at the present time since it requires an in-depth review of existing data and an attempt to quantify this qualitative concept. The latter could be done by a simple box model approach to ultra LRTAP on a hemispheric scale using large emission blocks, mean transport time across the oceans etc.

Figure 2: Schematic Representation of Behavior of Emissions and $SO_4^=$ Aerosol Concentrations around the Northern Hemisphere in the Mid-Latitude (30°-60°) Westerlies Belt.



3.2 Regional SO_2 and $SO_4^=$ Levels

The regional levels of $SO_4^=$ have been studied in detail in Western Europe and North America and appear to be the main source of acidic materials leading to regional acid precipitation problems. The concentrations are elevated by one to two orders of magnitude above background and are well mixed in the lowest levels of the atmosphere up to and and sometimes above the typical cloud base. These materials are therefore present in updrafts or general ascent feeding cloud systems, as well as in the subcloud layer through which precipitation would be falling.

3.3 Local SO_2 and $SO_4^=$ Levels

These are highly variable in space and time but are obviously highest in point source plumes and over and downwind of urban areas (the so-called "urban plume"). Whether such material is incorporated into precipitation is clearly dependent on the local spatial distribution of the precipitation pattern (especially for convective showers) in relation to the plume geometry. This tends to be an "on-off" situation - either the precipitation falls through the plume or it doesn't. This in turn leads to very variable precipitation chemistry, in terms of both substances and concentrations, at samplers located near to (<50 km) from large sources (c.f. Metromex).

3.4 Alkaline or Neutralizing Substances

The previous three sections have indicated the general sources of acidic material found in precipitation. However, the final pH will be determined by the amount of alkaline material also present. The main alkaline component in the atmosphere is calcium which originates from fly ash (now largely removed from plumes by precipitators) and wind blown dust. Alkaline particles tend to be much larger (>10u) than acidic particles and, therefore, have much shorter residence times and are not mixed as high through the atmosphere. Thus, such particles remain much closer to the source and exhibit very marked regional patterns over land - high concentrations are found over arid areas, agricultural areas and as component of the pollution in the near downwind of major sources. Over the oceans, well removed from sources, concentrations of calcium are near zero and there is no global background in the same sense as there is for $SO_4^=$. Because of their larger size and shorter residence time, calcium particles are not found in significant quantities much above the surface boundary layer.

4. THE FACTORS CONTROLLING pH

4.1 General Considerations

The discussion in the previous four sections suggests the following general sequence of events in determining the pH of the precipitation, as illustrated schematically in Figure 3.

(a) Formation of cloud droplets will tend to take place around an acidic nucleus and thus the pH will be less than 5.6 (the value for clean liquid water in equilibrium with atmospheric CO_2).

(b) Rain formation in the cloud will collect other small particles which could be both acid or alkaline, but with a tendency toward the former. Thus, in cloud rain-drops will tend to remain acidic.

(c) Falling rain will scavenge material in the sub-cloud layers which will be in larger concentrations than in the cloud. The final pH at ground impact will thus be strongly controlled by the character of the sub-cloud atmospheric loading. There are four possible general cases for the modulation imposed by the sub-cloud layer as follows:

i) in remote marine areas the sub-cloud layer will be dominated by the marine aerosol produced by breaking waves i.e. sodium chloride which is a neutral salt. Thus the pH is mainly determined by the background acid aerosol and values will be less than 5.6.

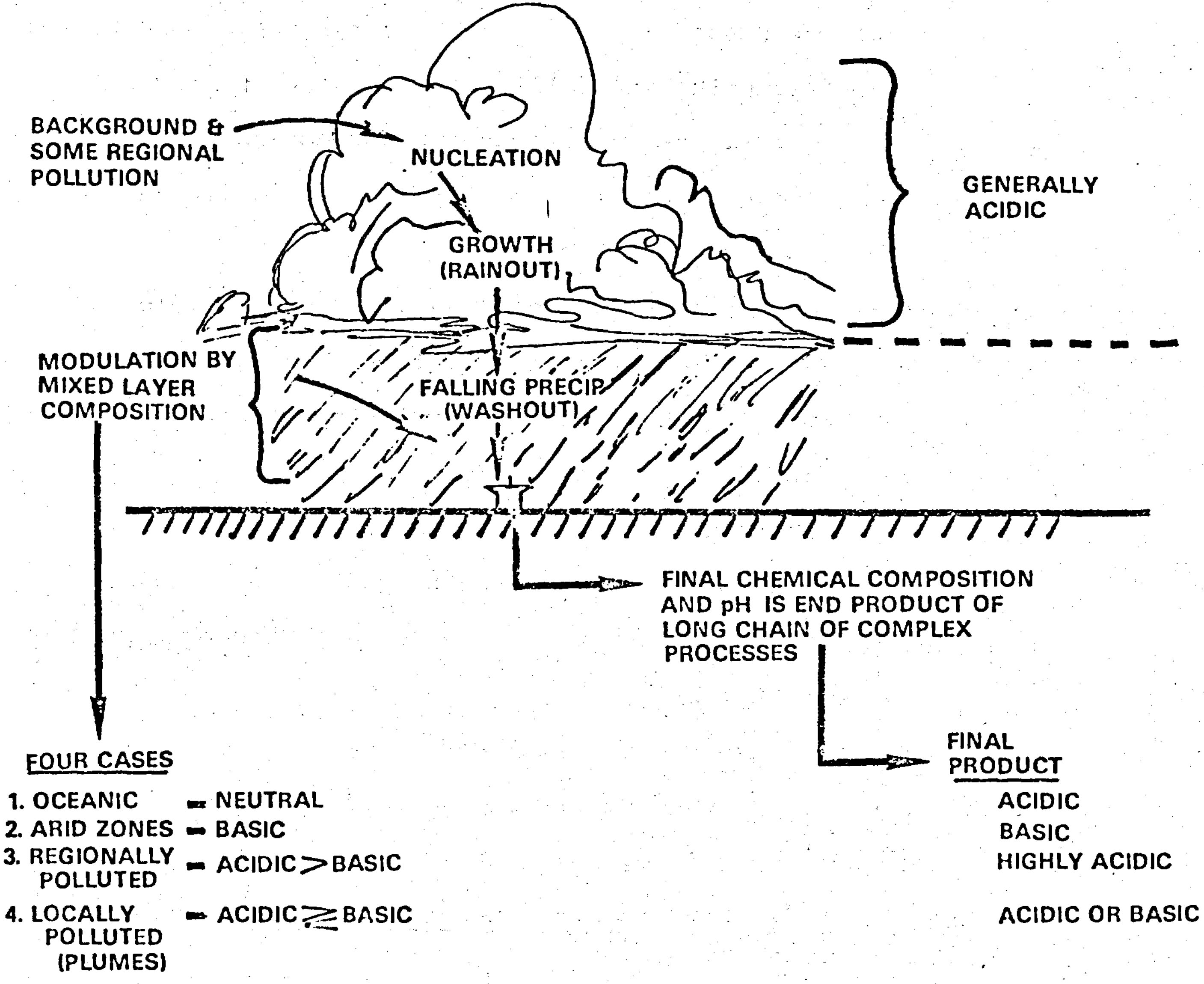


Figure 3: Factors Controlling the pH of Precipitation

ii) over arid land, or agricultural areas (especially in spring and fall) the wind blown dust will usually neutralize the acidic components and produce rain with a pH greater than 5.6 and as high as 6.0 or 7.0.

iii) over regionally polluted areas both acidic and alkaline materials will be scavenged, but with the former usually being dominant and resulting in acidic precipitation.

iv) in falling through a plume the precipitation will again scavenge both acidic and alkaline materials producing a wide variation of resultant final pH.

In the later two cases c(iii) and c(iv) the background aerosol is clearly a very small component of the final chemical composition and, therefore, has little impact of the final pH.

4.2 Examples Using Data from the Canadian Network for Sampling Precipitation (CANSAP)

The CANSAP data show a very wide variation in annual average pH ranging from 4.0 to 7.0 during the three years 1977-1979. In order to show the role of $SO_4=$ and Ca^{++} (the major anions and cations found in Canadian precipitation) on the average pH, the data from four regions are shown in Table 5. The groupings have been arranged to minimize the within-class variation of the two chemical constituents and to maximize the between-class differences.

Table 5: Example from the Canadian Network for Sampling Precipitation (CANSAP) Illustrating the Role of $SO_4^{=}$ and Ca^{++} in Determining Precipitation pH. (Averages are for the three year period 1977 to 1979.)

Region Symbol	Regional Characteristics	Station	Concentration in Precipitation		pH
			$SO_4^{=}$ (mg l^{-1})	Ca^{++} (mg l^{-1})	
A	Dry, prairie agricultural area with no regional pollution.	Lethbridge, AB	2.6	3.7	6.6
		Kindersley, SK	2.1	3.2	6.8
		Wynyard, SK	2.6	3.1	6.4
Fp	Moderately wet, native mixed forest on perphery of regionally polluted region	Gander, NF	2.3	0.2	4.6
		Truro, NS	2.6	0.3	4.5
		Seven Isles, PQ	2.5	0.1	4.4
Ap	Moderately wet, agricultural area with high regional pollution levels	Mt. Forest, ON	6.1	1.3	4.4
		Peterborough, ON	6.7	1.4	4.1
		Simcoe, ON	6.3	0.8	4.1
		St. Hubert, PQ	7.7	2.2	4.2
		Quebec City, PQ	6.8	1.2	4.2
F	Relatively dry northern forested area with no regional pollution	Fort Chimo, PQ	1.2	0.2	5.1
		Cree Lake, SK	1.2	0.4	5.1
		Fort Reliance, NT	0.9	0.2	5.3

Note: Only stations sufficiently far from the coast to neglect the oceanic influence and with more than 15 months of record are included in the table.

The lowest concentrations of both $SO_4^{=}$ and Ca^{++} occur in the northern forest region (F), but there is sufficient excess of acidic over alkaline material to give an average pH of 5.1 to 5.3.

In the prairie agricultural region (A), $SO_4^{=}$ is somewhat higher but large amounts of Ca^{++} originating from wind-blown soil more than neutralize the acids and the result is a pH far in excess of 5.6. These pH values of between 6.0 and 7.0 are the highest in Canada.

In the wetter forest regions on the periphery of the regionally polluted region (Fp) in eastern Canada, $SO_4^{=}$ concentrations are about the same as in region A, but Ca^{++} amounts are very low and the pH is about 4.5 representing an acidity value about 10 times that in clean rain.

Finally, the agricultural region in southern Ontario and the St. Lawrence lowlands with high regional pollution values (Ap) has by far the highest $SO_4^{=}$ concentrations. Even though there are moderate concentrations of Ca^{++} originating from the calcareous soils in the region, the resultant precipitation pH is still the lowest in Canada with average annual values between 4.1 and 4.4.

The role of $SO_4^{=}$ and Ca^{++} concentrations in determining the pH of precipitation in Canada is clearly evident from the above analysis. $SO_4^{=}$ plays the dominant role in regionally polluted regions and Ca^{++} plays the dominant role elsewhere in determining pH.

Note that nowhere does the $SO_4^=$ concentration fall much below 1.0 mg l^{-1} even in remote arctic areas and this could thus be interpreted as the typical "background" contribution. With no other alkaline components, such a concentration would result in a pH of about 5.0 which could, therefore, be considered the background value of pH. Departures from this value, rather than from pH 5.6, should be considered in discussing regional and local influences.

4.3 Observed Variation of pH with Height

The ideal way to verify the sequence suggested in section 4.1 would be detailed airborne observations collecting cloud droplets, in-cloud precipitation and falling precipitation from the same cloud system. This has not been done in any systematic way, although there are isolated airborne measurements that are not inconsistent with the hypothesis.

Two sets of ground level measurements on mountains are available from Mauna Loa, Hawaii in an essentially remote, largely unpolluted oceanic environment and from Whiteface Mountain, N.Y. immediately downwind of a heavily polluted area.

Mauna Loa, Hawaii

Data collected from June 1975 to June 1980 at several sites ranging from sea-level to the Mauna Loa observatory at 3400 m MSL have been reported by Miller and Toshinaga (1981)

There is wide variability at all elevations with the rainfall pH of daily and bi-weekly samples ranging between extreme values of 3.5 and 6.2. However, both the median and mean values showed a steady decline with increasing altitude. The mean value at sea-level was 5.2 decreasing to 4.3 at elevations above 2500 m MSL. The corresponding concentrations of sulfate ranged from 0.3 to 8.0 mg l^{-1}, but most of the values were <1.0 mg l^{-1} and this is down by a factor 5 from the annual average in the region of maximum concentration in eastern North America (see Region Ap in Table 5).

Whiteface Mountain, N.Y.

Observations at the observatory atop Whiteface Mountain (elevation 1483m) have been compared with data from the nearest low-elevation MAP3S station at Ithaca. These show the pH of rain to be generally lower atop the Mountain. In addition, the Whiteface data shows the mean pH to be lower in non-precipitating clouds (i.e., small droplets) by about 0.4 to 0.5 units than in precipitating clouds (larger drops).

4.4 Observations at Remote Locations

In recent years sampling stations have been set up at remote locatons by several agencies. The World Meteorological Organization (WMO) have instituted a global monitoring network to establish global trends in CO_2 and other atmospheric chemistry parameters. NOAA have also set up a less widespread network. The stations can be separated into two broad categories - oceanic and continental (but in regions of low population usually coinciding with arid areas). A third category of locations which is useful for studying background precipitation chemistry consists of stations on the west coast of the major continents in the westerlies belt where most of the precipitation occurs with on-shore air-mass trajectories. Finally, data from the polar regions represents the most remote locations. Data on precipitation pH in each of these categories are summarized on Table 6.

Remote oceanic stations

These locations indicate considerable varability with monthly average pH values of precipitation ranging over at least 1.5 units. In all cases, the median value is less than pH 5.6 with lowest values about 4.6 to 4.7. This represents an increase in acidity by a factor of 10 above that expected in "clean" rain.

West-coast stations

Except for the heavily populated areas around Los Angeles, San Francisco and Seattle-Vancover, pH values on the west-coast of North America average about 5.0.

On the west-coast of Norway (well removed from the polluted region in the south) the pH of the rain is averaging over 6-month periods between 4.6 and 4.9. The sulfate content

TABLE 6. The pH of Precipitation in Some Remote Areas

	Monthly Average Precipitation pH			Length of Record or Number of Events
	Median	Minimum	Maximum	
OCEANIC				
SAMOA (1)	5.3	4.5	6.0	36
MAUNA LOA (1)	5.0	3.3	6.7	47
HILO, HAWAII (2)	4.6	3.7	5.4	100's
AMSTERDAM Island (2)	4.7	3.8	5.4	17
BERMUDA (2)	5.1	4.0	5.6	33
WEST COAST				
CAPE GRIM, TASMANIA (1)	6.3	5.8	7.2	12
INDIA (4 STNS) (1)	6.3	5.8	6.6	13
IRELAND (3)	4.8 → 5.6			1968 - 1974
NORWAY (3)	4.8 → 5.2			Oct. 1977 - Sept. 1979
NORTH AMERICA (3)	~ 5.0			Variable
CONTINENTIAL				
INDIA (9 STNS) (1)	7.5	5.8	8.9	51
GRAND JCT (COLO) (1)	6.5	5.4	8.0	40
ALAMOSA (COLO) (1)	6.8	5.0	8.2	73
SAN ANGELO (TEXAS) (1)	6.6	5.2	7.3	43
POLAR				
CANADIAN ARCTIC*	~5.0			Few
INLAND ANTARCTIC*	4.6 → 5.6			Few

STIMATEDD FROM ION BALANCE (see text)

URCES: (1) Acid Rain - An Assessment based on Acid-Base Considerations of Factual Data, R. Sequira, 1981 (In Press).

(2) Progress Report - Global Precipitation Chemistry Network, Jan. 1981, J. Galloway, W.C. Keene, G. E. Likens (Draft Report to NOAA).

(3) See Text.

is low at between 0.1 and 0.4 ug S m^{-3} with the lowest values with winds in the sector W through NE (Jorranges et al., 1980).

A study of rain chemistry over Ireland (Fisher, 1980) shows pH on the exposed west-coast stations between 5.1 and 5.6. It is estimated that about 50% of the measured sulfate in the rain is attributable to natural background.

Continental remote

Except for a few individual months, the pH is greater than 5.6 and occasionally alkaline (pH >7). The main cause of this is the wind blown dust in arid and semi-arid areas which is calcium rich. There is more than required to neutralize any background acidic components and thus the remainder produces rain more basic than pH 5.6.

Remote Polar regions

A joint study by Canada, the U.S. and Denmark has been monitoring air chemistry on sites in the Arctic. These show that the winter months sufficient acid particulate material reaches high latitudes to reduce visibility producing arctic haze. Concentrations of sulfates measured at Mould Bay and Igloolik range between 1 and 3 ug/m^3 in the winter months (Barrie, 1980) and in the absence of any significant alkaline content would be sufficient to produce snow with a pH of about 5.0.

In Antarctica the chemistry of snow has been investigated by Delmas et al., (1979), by sampling freshly fallen snow on transects from the coast inland for 800 km. The concentrations of sodium and chloride fell off rapidly and the main influence had disappeared 200 km inland. The sulfate concentrations remained essentially constant at between 60 and 100 x 10^{-9} g g^{-1} (0.1 ppm). Although the pH was not measured directly, the authors estimated that the excess of acid over basic components would be sufficient to reduce the pH by up to 1.0 unit below the CO_2 equilibrium value of 5.6.

5.0 CONCLUSIONS

A review of the world-wide data on precipitation pH in remote and exposed mid-latitude west-coast areas indicates that all precipitation contains at least small quantities of acid materials. In the absence of any neutralizing basic components this is sufficient to reduce the pH to a value of about 5.0 and in some cases less. Nowhere, though, are pH values in remote aras as low as those found in the most acidic precipitation areas of the northeastern U.S. and western Europe. The minimum median value is pH 4.6 at a few isolated locations. In contrast to this, there is a large contiguous area in eastern North America containing about 90 monitoring stations reporting annual average pH less than 4.6 and as low as 4.1. The latter value represents an increase in acidity by a factor 30 above that in "clean" rain, and clearly shows the regional influence of the concentrated man-made emission sources.

Several authors are now suggesting that the reference level of 5.6 (the pH of rainwater in equilibrium with atmospheric CO_2) is not appropriate and that departures from a value of near 5.0 would indicate the regional and local modulations to the influence of "global background".

While pH is a useful single number that characterizes the precipitation, it is the total deposition of acidity (H^+ ions) that is important in assessing the effects on ecosystems. The deposition is the product of the concentration and the rainfall amount. Thus in considering the relevance of the low pH values in remote areas, this must be considered. Sensitivity, in the form of the buffering capacity of the receptor surfaces is also important in defining the seriousness of impact. Most remote areas, especially arid regions, are well buffered and so the impact of any acidic deposition is minimized. In contrast, the regions with lowest pH and highest depositions of H^+ ion in the northeastern U.S., eastern Canada and southern Scandinavia cover large areas of poorly buffered lakes and soils and thus have a major impact on the receptors there.

While there is considerable varability in the background pH values, they are in general consistent with the concepts proposed in sections 3 and 4. The limited vertical profiles available are also supportive of the hypothesis that most precipitation starts off as acidic cloud droplets. The higher the elevation the more important is the global background of chemical components relative to those generated locally.

It must also be pointed out that some of the observations cannot be readily explained and clearly, more analysis of existing data bases (for example trajectory analyses to identify whether observed background levels are due to natural sources or far downwind residuals from man-made sources) are required to refine the ideas presented here.

6.0 RECOMMENDATIONS FOR FURTHER MONITORING AND RESEARCH

The number of remote stations that have been established in recent years is now beginning to generate substantial data relevant to the issue of establishing and understanding the background levels of air and precipitation chemistry. Rather, than establishing many more such stations the priority should be to analyse and interpret the existing data base.

Some specific recommendations are as follows:

-- wherever possible at precipitation chemistry stations sampling should be done on an event or at least on a weekly basis.

-- the precipitation chemistry data are much more valuable and can be interpreted more readily if concurrent basic air chemistry measurements are made such as filter-pack sampling.

-- more observations of the vertical distribution of precipitation chemistry (and where possible air chemistry) are needed. This can be done in two ways

a) at mountain sites
b) with instrumented aircraft

-- continuing efforts are required to refine the estimates of natural emissions of acid components into the atmosphere (they are presently less accurate than estimates of man-made emissions yet are equally important on the global scale).

-- estimates (however approximate) are required for emissions of the most important alkaline materials into the atmosphere; at present none exist.

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