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An Investigation of Factors Affecting Total Sulfate Supply and Sulfate Concentrations in Individual Rainfalls at Windsor, Ontario.

by

Robert Wilfred Osborne

A Thesis submitted to the Faculty of Graduate Studies through the Department of Geography in Partial Fulfillment of the requirements for the Degree of Master of Arts at The University of Windsor

Windsor, Ontario, Canada

1976
Abstract

The principal objective of this study was to determine the significance of six variables in the explanation of variations in total sulfate supply and sulfate concentrations observed in individual rainfalls. Total sulfate supply (mg) is defined as the weight of sulfate falling on a unit area. Sulfate concentration (mg/l) is defined as the weight of sulfate per unit volume of precipitation. Hypotheses were formulated relating total sulfate supply and sulfate concentration to atmospheric sulfur dioxide concentration, total precipitation, precipitation duration, drop area, drop temperature and submaximum sulfur dioxide concentration fall time.

Precipitation samples were collected at the University of Windsor Weather Station, Windsor, Ontario, during the period from April 28, 1975 through September 26, 1975. Atmospheric sulfur dioxide concentrations were calculated by plume diffusion equations using wind direction and wind speed data obtained from the Windsor Airport. Precipitation data were obtained from the University of Windsor Weather Station.

Total precipitation, precipitation duration, and drop area explained a significant proportion of the variation in total sulfate supply. Sulfate concentration was determined to be a function of atmospheric sulfur dioxide concentration. It was found that synoptic conditions effect
the applicability of plume diffusion equations for the prediction of atmospheric sulfur dioxide concentrations.

Even though a significant explanation of the total sulfate supply and sulfate concentration is provided, there is a need to extend this research to locations where continuous point source emissions of sulfur dioxide are not present.
Acknowledgements

The author wishes to express his gratitude to all people who helped to make this research possible.

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CHAPTER I

Introduction

Investigations attempting to determine the chemical composition of atmospheric precipitation have been undertaken for the past 200 years. Until the 1950's, most studies were concerned with making estimates of nutrients and minerals supplied to the soil by rainfall for agricultural purposes. During that decade interest grew in the mechanisms whereby radioactive material from atmospheric nuclear weapons tests was returned to the ground and in the early 1960's the Fallout Studies Branch, Division of Biology and Medicine, United States Atomic Energy Commission sponsored conferences on the topic.

With the moratorium on atmospheric weapons testing, the effort devoted to the study of "precipitation scavenging", as the removal process came to be known, was channeled towards the investigation of the removal of non-radioactive atmospheric pollution. At present, there is worldwide interest in the environmental and economic impact of air, land and water pollution. Because precipitation affects these three constituents of the biosphere, precipitation scavenging is of particular significance.
Sulfur dioxide (SO₂), as released into the atmosphere, is a relatively harmless pollutant. However, in the presence of water it is oxidized to form sulfuric acid; H₂SO₄. Cogbill and Likens (1974) concluded that the acidity of precipitation is predominantly the result of the in-drop oxidation of SO₂ to sulfate (SO₄). Scandinavian interest in the environmental impact of "acid precipitation" led to the development of a network of precipitation chemistry sampling stations in 1952. In Canada, no co-ordinated precipitation sampling had been carried out on a national basis prior to the establishment of the World Meteorological Organization regional stations in 1974. At present, the Atmospheric Environment Service is involved in a number of projects designed to evaluate the ability of the atmosphere to cleanse itself, and to determine the amount of material, such as strong acids or nutrients, that is deposited on a specified portion of the earth's surface.

The present study is concerned with both the total SO₄ supply (mg of SO₄ supplied to a surface area) and SO₄ concentration (mg of SO₄ per litre of precipitation) associated with individual precipitation events. The environmental impact of increasing SO₄ concentrations in atmospheric precipitation has been studied by Likens and Bormann (1974), among others. They conclude that an increase in the SO₄ concentration in precipitation can be associated with increased leaching of nutrients from foliage, and
disruption of leaf physiology and growth.

Tikkanen and Yläsrä (1973) found that high SO₄ concentrations in precipitation contribute to the corrosion of metals commonly used by the manufacturing and construction industries.

There is little doubt that constant deposition by precipitation will result in a buildup of SO₄ in soils and water ecosystems. The long-term effect of such deposition is dependent upon the total supply of SO₄ received at the earth's surface. The continuous buildup is a major factor resulting in the increased leaching of soil nutrients and the acidification of inland water systems. Shaw and Whelpdale (1973) found that the annual SO₄ deposition by precipitation over Lake Ontario is about 1% of the total mass of SO₄ in the lake.

It is the purpose of this thesis to rationalize a set of factors from the literature which affect the removal of SO₂ from the atmosphere by precipitation and to test their significance in the control of the total SO₄ supply and SO₄ concentration observed at the earth's surface.
CHAPTER II

Literature Review

The review of literature presented here is based upon one compiled by Eriksson (1952). The initial investigation of chemical compounds found in precipitation began with the study of nitrogenous compounds in 1749 by the German chemist Margraf, who made the first discovery of nitrate in rainwater. Interest in the field was stimulated by revolutionary discoveries in agricultural chemistry which linked plant nutrition and growth to elements known to exist in the atmosphere. In 1799 a Dutchman, John Ingenhauss, published studies concerning the assimilation of CO$_2$ by plants from the atmosphere and in 1804 De Saussure in France, showed that inorganic constituents of plants were taken up from the soil by plant roots.

By the middle of the 19th century another French researcher, Bousignault and a German, Liebig, had made estimates (of the order of 2.7 grams m$^2$/year) of the annual contribution of combined nitrogen from rainwater to the soil. Research of this nature continued so that most of the organic and inorganic compounds present in
rainwater were known by 1850.

Unlike with nitrogen, most early determinations of sulfurous compounds in rainwater were carried out comparatively recently and for the most part, in the United States. In 1911 Hunt and Peterson studied the sulfur requirements of farm crops in Wisconsin in relation to the soil and atmospheric supply sources. A number of papers of descriptive nature have since appeared to provide an extensive survey of the contribution of atmospheric sulfur to the soil.

Herman and Gorham (1956) found the mean total \( \text{SO}_4 \) supply received at Kentville, Nova Scotia to be 0.2 grams/m\(^2\)/month at an average concentration of 0.1 mg/l. In this study concentrations were found to be less in snow than in rain. It was concluded that a raindrop is a more efficient collector of gaseous atmospheric constituents because the solution of such elements is more rapid in the liquid rather than in the solid phase.

Junge and Werby (1958) mapped the \( \text{SO}_4 \) concentrations found in monthly precipitation samples from 58 collection sites in the United States. They concluded that industry is an important but not the predominant source of excess \( \text{SO}_4 \) concentration. High values of \( \text{SO}_4 \) concentration (up to 10.68 mg/l) in the southwest and other areas with little or no industry led to the conclusion that the soil
surface must be an efficient source of sulfur. However, it must be noted that no consideration was given to the amount of precipitation or the total supply of $SO_4$ received at each location.

Wagner and Holloway (1975) found relationships to exist between total supply and concentration of $SO_4$ and monthly amounts of precipitation in Arkansas. They determined that peak supply periods of $SO_4$ were associated with spring and fall maxima of rainfall. The concentration of $SO_4$ was inversely related to amounts of precipitation.

The effect of dry fallout (contamination reaching the surface without the aid of precipitation) a factor to be considered in all monthly sampling designs was investigated by Whitehead and Feth (1964) in northern California. It was concluded that such "bulk precipitation" samples contained 40% or more mineralization than rainwater. With the utilization of samples obtained from individual rainfalls, we can examine the precipitation removal process free from the influence of dry fallout.

Georgii and Weber (1960) studied the chemical composition of individual rainfalls in Frankfurt, West Germany. This investigation revealed a decrease in the concentration of $SO_4$ with increasing quantity of rainwater per rainfall. It was also determined that the $SO_4$ concentration in rainfalls which occurred after a dry period of at least three days was about twice the concentration
compared with rainfalls taking place after 12 hours without rain.

Gambell and Fisher (1964) in North Carolina, analyzed samples taken at intervals during precipitation events and observed the SO$_4$ concentration to decrease during the initial period of rainfall, then level off for the remainder of the storm. The explanation offered proposed the existence of different rates of drop evaporation at successive intervals during the precipitation event. It was concluded that the first drops fall into dry air and partially evaporate. This results in high SO$_4$ concentrations. Throughout the duration of the rainfall the air is increasingly saturated to a point where drop evaporation is no longer significant and the SO$_4$ concentration remains at a constant level.

SO$_2$ Production, Transport, Removal and Oxidation Processes

Sulfur oxides are produced by the combustion of fuels, particularly those used in fossil fueled power plants. The compounds of major interest are SO$_2$, sulfur dioxide; SO$_3$, sulfur trioxide; H$_2$SO$_3$, sulfuric acid; and H$_2$SO$_4$, sulfuric acid. The sulfur salts CuSO$_4$, copper sulfate; CaSO$_4$, calcium sulfate and MgSO$_4$, magnesium sulfate; can be released by power plant and industrial processes, most notably smelters.

Sulfur dioxide is a non-flammable, colourless gas.
The concentration for taste detection ranges from 0.79 mg/m$^3$ to 2.62 mg/m$^3$ in air and the odor threshold is about 1.31 mg/m$^3$ (Perkins, 1974). Estimates for 1965 production of sulfur oxides in the U.S. indicate that 50% of the national total was emitted by power plants (Bach, 1972). Perkins (1974) states that in power plant combustion processes, SO$_2$ forms in the ratio of 40 to 80 parts per part of SO$_3$. Therefore, the emission of major concern is SO$_2$.

Sulfur occurs in coal as iron pyrites, FeS$_2$, organic compounds and SO$_4$. The sulfur content of coal varies from 2% to 12% depending upon the quality. Residual fuel oil, commonly burned in power plants, has a sulfur content ranging from 0.75% to 2.5% (Perkins, 1974). The SO$_3$ emitted during the combustion of coal or oil is the result of the reaction of SO$_2$ with atomic oxygen in the flame, or by a secondary catalytic oxidation of SO$_2$, with molecular oxygen on hot surfaces with ferric oxide and vanadium pentoxide acting as catalysts.

Precipitation scavenging is only one of four possible mechanisms presented by Junge (1958) by which trace gases may be removed from the atmosphere.

Removal can result from:

a) escape into space.

b) absorption and/or decomposition at the earth's surface.
c) decomposition in the atmosphere by reactions which result in the formation of aerosols or other gases.

d) removal by precipitation.

Although all of these processes are active in the removal of trace gases from the atmosphere, it is generally concluded that removal by precipitation is of greatest importance.

Engelmann (1956) subdivides the precipitation removal process into three stages involving:

a) transport of the gas to the scavenging site.

b) rainout or the incloud scavenging of gases by cloud elements.

c) washout or the below cloud scavenging of gases by precipitation elements.

A number of investigations (Rossby, 1955; Cartrell, et al., 1959; Jacobs, 1959; Munn and Katz, 1959; Newall and Ebene, 1962; Schmidt and Velds, 1969; Peterson, 1970; Scott, 1971) which appear in the literature, have studied concentrations of atmospheric SO$_2$ with respect to meteorological conditions (i.e. the effect of meteorological conditions on the transport of SO$_2$ from source locations.)

Munn and Katz (1959) studied ground level concentrations of sulfur dioxide in the Windsor-Detroit area. It was concluded that SO$_2$ concentrations were greatly affected
by the position of the sampling station with respect to the location of point source emissions.

Schmidt and Velds (1969) in Rotterdam, found that 92% of the total variance of ground level SO₂ concentrations could be attributed to windspeed, circulation type and precipitation. The general decline of SO₂ concentrations was associated with a reduction in the frequency of unfavourable circulation types (persistent high pressure systems), increased windspeed and precipitation.

Peterson (1970) determined the significant variables explaining SO₂ concentrations at various levels in the lower atmosphere to be air temperature, surface wind direction, mean wind speed and atmospheric stability.

The mathematical models used to predict pollutant concentrations from an emission source are based upon the Gaussian approach, which makes the assumption that concentrations of pollutants from continuous sources follow a binomial probability distribution in the vertical and crosswind directions downwind from the source.

The variables used in formulae presented by Pasquill (1962), Bach (1972) and Perkins (1974) include the variables found to be significant to the explanation of atmospheric SO₂ concentrations presented in the previously discussed studies. In addition, source strength and emission release elevation parameters are included in order to facilitate calculation of downwind pollutant con-
centrations.

The relative importance of rainout versus washout merits consideration. Experiments by Beilke and Georgii (1969) have shown in cloud scavenging to be the more efficient means of SO$_2$ removal, because the total surface area of tiny cloud droplets at equal liquid water content is considerably greater than the total surface area of raindrops. The relative importance of these processes in an uncontrolled environment is dependent upon the atmospheric distribution of the pollutant in question. With a uniform distribution rainout will predominate. However, in an area where trace gases are largely of anthropogenic origin, the low elevation of contaminant release will result in maximum concentrations occurring below cloud level. In this situation the less efficient process, washout, will predominate.

General circulation conditions in the atmosphere will affect the vertical distribution of trace gases and the relative importance of rainout versus washout. Petrenchuck and Drozdova (1971) in the Soviet Union found that with clearly marked transfer of air masses, unstable atmospheric conditions and moderate wind speeds, the distribution of SO$_2$ decreased with height. Under anticyclonic conditions, peak concentrations of SO$_2$ were found at higher elevations.

In the atmosphere, there are a number of possible
mechanisms responsible for the conversion of SO\textsubscript{2} to H\textsubscript{2}SO\textsubscript{4} and sulfate salts. The photochemical oxidation of SO\textsubscript{2} in the air was studied by Cox and Fenkett (1970). In the presence of normal sunlight the rate of photochemical oxidation is low (.65%/hr) and cannot account for SO\textsubscript{4} concentrations found in rainwater. Certain metal compounds are known to promote the oxidation of SO\textsubscript{2}. Wright, et.al. (1974) investigated the effect of increasing the manganese concentration in the atmosphere on the oxidation rate of SO\textsubscript{2}. It was concluded that although manganese does act as a catalyst, an increase in atmospheric concentrations beyond their present level would not accelerate the rate of oxidation of SO\textsubscript{2}.

Junge and Ryan (1958) concluded that oxidation of SO\textsubscript{2} occurs primarily in cloud and precipitation elements. This liquid phase mechanism involves the absorption of atmospheric SO\textsubscript{2} and in droplet oxidation to form SO\textsubscript{4}. Tarraglio and Manganelli (1967) through laboratory experiments found that the absorption of atmospheric SO\textsubscript{2} increased with time at a steadily decreasing rate for all atmospheric concentrations and the approach to the saturation point was more rapid at higher atmospheric concentrations.

Junge and Ryan (1958) found that the oxidation of SO\textsubscript{2} to SO\textsubscript{4} in water can only take place in the presence of a catalyst and that minute traces of metal ions will serve in this capacity. A more efficient conversion
of SO₂ to SO₄ results if traces of ammonia (NH₃) are present. Scott and Hobbs (1968) studied the formation of SO₄ in water droplets using the SO₂-NH₃-liquid H₂O system. They present the following equations as a description of the oxidation process:

\[
\frac{d(\text{SO}_4)}{dt} = k(\text{SO}_3) \quad (1)
\]

the rate equation where \( k \) is the reaction rate constant.

\[
(\text{SO}_3) = 9.84 \times 10^{-10} \frac{P_{\text{SO}_2}}{(H^+)^2} \quad (2)
\]

where \( P_{\text{SO}_2} \) is the partial pressure of SO₂.

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4 \quad (3)
\]

From equation (3) it follows that as the production of SO₄ continues the concentration of hydrogen ion increases, which in turn causes the production of SO₃ to decrease according to equation (2). This implies that the rate of production of SO₄ given in equation (1) is a negative self catalytic reaction. In the presence of NH₃ which maintains electroneutrality throughout the reaction, it was found the production of SO₄, after 24 hours, to be about two orders of magnitude greater than the concentration produced in the absence of NH₃.

From the literature cited it may be concluded that under conditions of high humidity, fog or rain, physical absorption and reaction with water apparently determines
the conversion rate of $\text{SO}_2$ to $\text{SO}_4$.

Factors Affecting Total $\text{SO}_4$ Supply and Concentrations

The supply and concentration of $\text{SO}_4$ received during a storm will no doubt be a function of:

1) the transport of $\text{SO}_2$ to the removal location.
2) physical and chemical characteristics of the precipitation elements which control the interception.
3) absorption and oxidation of $\text{SO}_2$.
4) storm characteristics controlling the extent of the removal process.

An extensive review of the literature was used to derive a number of factors which may have a possible effect on the removal of $\text{SO}_2$ from the atmosphere by precipitation and the supply and concentration of $\text{SO}_4$ received at the earth's surface.

Atmospheric $\text{SO}_2$ Concentration

In the previously discussed studies (Junge and Ryan, 1958; Scott and Hobbs, 1966; Terraglio and Manganelli, 1967) and others appearing in the literature (van den Heuvel and Mason, 1963; McKay, 1970) which investigated the absorption and oxidation of $\text{SO}_2$, drop saturation was achieved after periods ranging from 1 to 24 hours, the differences being due to experimental design. Since the exposure time of a falling drop in the polluted layer of the atmosphere would not approach these values, the limit of drop saturation
FIGURE 1: SO\textsubscript{4} CONCENTRATION vs. SO\textsubscript{2} CONCENTRATION

Source: Junge and Ryan, 1958
would not be reached.

Figure 1 and equation (2) illustrate the general conclusion that the rate of absorption and oxidation is dependent upon the partial pressure or concentration of SO$_2$ in the atmosphere. It is more likely that the final mass of SO$_4$ produced in a falling raindrop would be a function of the SO$_2$ concentration through which it falls and not the exposure time of the drop.

In the context of the present study it is hypothesized that the concentration and total supply of SO$_4$ from individual rainstorms should increase with increasing concentrations of atmospheric SO$_2$.

**Total Precipitation and Storm Duration**

A number of investigations (Greenfield, 1957; Bleichrodt, et al. 1959; Georgii and Weber, 1960; Gambell and Fisher, 1964; Dingle and Gatz, 1966) have shown that the concentration of contaminants in precipitation samples decreases with increasing amounts of precipitation and storm duration. Makhon'ko (1967) theorized that this observation was the result of gradual exhaustion of contaminated matter due to continuous capture by raindrops. Gambell and Fisher (1964) found that after precipitation begins the contaminant concentration in water decreases, but with a lapse of time, levels off at a constant value. The achievement of a constant value indicates the establishment of a state of dynamic equilibrium where the rate of
contaminant removal from the polluted layer is equal to the contaminant flow into the scavenging area.

Extrapolation of curves presented by Beilke (1970) indicates that total washout of \( \text{SO}_2 \), at a concentration of \( 0.08 \text{ mg/m}^3 \) would occur after 20 minutes for a rainfall of intensity equal to 50 mm/hr and after 40 minutes for a rainfall of intensity equal to 20 mm/hr. The possibility of total washout occurring in an area with continuous source emissions is unrealistic. Wiebe and Whelpdale (1975) estimated that less than 1% of the sulfur emitted during a precipitation event is removed during that event. Considering these observations it is probable that dilution of the contaminated layer of the atmosphere in an area with continuous source emissions will be insignificant with respect to the total supply and concentration of \( \text{SO}_4 \) received during a storm.

The Wiebe and Whelpdale (1975) observation leads to the hypothesis that the total supply of \( \text{SO}_4 \) will increase with increasing amounts of precipitation received. It is also hypothesized that the total amount of precipitation will have no effect on the \( \text{SO}_4 \) concentration.

Studies which have measured contaminant concentrations in the atmosphere during a precipitation event (Georgii, 1963; Katzborn and Abraham, 1970) have noted that the concentration of \( \text{SO}_2 \) in the lower layers of the atmosphere often increases throughout the duration of the
storm. This observation leads to the "reversible" theory of gas washout proposed by Hales (1972) and described as follows.

The initial step in the capture of trace gas molecules is their migration from the atmosphere to the surface of the drop. After passage through the liquid-vapour interface they may take part in chemical reaction or exist as dissolved gas molecules, the existence of which will result in a gas concentration (characterized by a vapour pressure) within the drop. When the concentration within the drop exceeds the concentration outside the drop, there will be a tendency for the gas to leave the liquid. Dana et al. (1975) found that the process of gas desorption led to a redistribution of $SO_2$ plumes to sub-plume layers over the duration of a storm. The result of this process would be to lower the maximum atmospheric $SO_2$ concentration to which the falling drop is exposed.

If gas desorption is of sufficient magnitude in the uncontrolled atmosphere the hypothesis can be made that the concentration of $SO_4$ should decrease as storm duration increases. If total washout does not occur during a storm, the production of $SO_4$ will continue and the total $SO_4$ supply will increase with increasing storm duration.
Sub-Maximum SO$_2$ Concentration Drop Fall Time

Plume diffusion theory predicts that contaminant concentrations will be found in a binomial distribution about the plume centerline (i.e., concentrations will decrease with distance from the maximum centerline value). A drop will therefore be falling through steadily increasing concentrations of SO$_2$ until it reaches the plume centerline after which it falls through decreasing concentrations. Hales, (1972, pg. 649) concludes that "If a drop falls through a plume and emerges into cleaner air before reaching the ground, it may release a majority of the gas that is removed from more concentrated regions."

The amount of gas desorbed by the falling drop will be dependent upon the distribution of gas and the fall time of the drop below the plume centerline (as mass transfer coefficients are expressed in units of time.) Using the Gaussian approach, the minimum concentration of SO$_2$ below the plume will occur at ground level. The ratio of that concentration to the maximum concentration at the plume centerline will be a function of the elevation of the plume centerline. The elevation of the plume will also be a factor along with drop size in the determination of the fall time of the drop through the sub-plume layer.

Based upon Hales' (1972) theory it can be hypothesized that both the total supply and the concentration of SO$_4$ will decrease as the fall time of the drop through the sub-maximum SO$_2$ concentration layer increases.
Drop Area

Drop size parameters will affect the ability of a falling drop to contact, absorb and provide a chemical reaction medium for gaseous contaminants in the atmosphere. Engelmann (1966) stated that the washout of trace gases is a function of drop diameter which determines the volume of air swept out by the drop. Assuming the drop is not at a level of contaminant saturation, it follows that as the drop diameter increases the amount of SO$_2$ contacted and absorbed will increase.

Van den Heuvel and Mason (1963) found that the mass of ammonium sulfate, (NH$_4$)$_2$SO$_4$, produced in the NH$_3$-SO$_2$-liquid H$_2$O system is proportional to the surface area of the drop and to the time of exposure. Curves presented by these authors indicate that for exposure times less than 7.5 minutes the rate of change of drop diameter exceeds the rate of change of SO$_4$ produced. From these observations we can hypothesize that as the drop area increases the total amount of SO$_4$ produced and supplied to the surface will increase. However, an increase in the drop area will result in a decrease of the SO$_4$ concentration.

Application of the results of the experiments by van den Heuvel and Mason (1963) to the uncontrolled atmosphere imply that the total surface area of the drop acts as a collecting surface. Berg (1970) discusses investigations into the possibility of collection on the backside of
falling drops but fails to conclude as to the existence of such a process with respect to gases. Fuchs (1964) states that definite hydrodynamic conditions are essential before backside collection of aerosols will occur. The flow velocity in the vortices must be great enough to insure inertial deposition but the vortices must not be carried away from the object to quickly. The possibility of backside collection of gases is not mentioned.

In this study it will be assumed that collection occurs on the front side of the falling drop only. Thus one half the drop area will be used as the drop size parameter.

Drop Temperature

The solubility of a gas will determine the amount of gas dissolved by a drop over a given period of time. McKay (1971) studied the effect of temperature on the absorption and oxidation of SO₂ in water droplets. It was found that the in-drop concentrations of SO₄, after 45 minutes, at 15°C was double that observed at 25°C for ambient SO₂ concentrations ranging from .02 mg/m³ to .2 mg/m³. Although a reduction in drop temperature will lower the oxidation reaction rate within the drop, McKay (1970) concluded that the increased solubility of SO₂ more than counter balances the fall in the rate of production of SO₄. Figure 2 illustrates the solubility of SO₂ in water as a function of temperature.
FIGURE 2: SOLUBILITY of SO₂ vs. TEMPERATURE

"Absorption Coefficient - the volume of gas absorbed per unit volume of water at temperature, t and under 1 atm. of pressure."

Source: Forsythe, 1956
The actual measurement of drop temperature was impossible in this study. The dew point temperature, the temperature to which the air must be cooled to bring it to saturation by condensation, will be used to estimate the drop temperature.

The hypothesis can be made that both the total SO₄ supply and SO₄ concentration will increase with decreasing drop temperature.

**Summary of Hypotheses**

The following hypotheses will be evaluated in the analysis section of this thesis.

1) Hypotheses related to total SO₄ supply.

   1. Total SO₄ supply will increase with increasing levels of atmospheric SO₂ concentrations.

   2. Total SO₄ supply will increase with increasing amounts of precipitation received during a rainfall.

   3. Total SO₄ supply will increase with increasing duration of the precipitation event.

   4. Total SO₄ supply will decrease as the drop fall time below the sub-maximum concentration level increases.

   5. Total SO₄ supply will increase as the drop area increases.

   6. Total SO₄ supply will increase with decreasing drop temperature.

11) Hypotheses related to SO₄ concentration.

   1. SO₄ concentrations will increase with increasing levels of atmospheric SO₂ concentrations.
2. $\text{SO}_4$ concentrations will not vary significantly with the total amount of precipitation received during a storm.

3. $\text{SO}_4$ concentrations will decrease with increasing duration of the precipitation event.

4. $\text{SO}_4$ concentrations will decrease as the drop fall time below the sub-maximum concentration level increases.

5. $\text{SO}_4$ concentrations will decrease as the drop area increases.

6. $\text{SO}_4$ concentrations will increase with decreasing drop temperature.
Chapter III

Methodology

Study Area

The Windsor-Detroit area is situated at 42°N, 83°W and at an elevation of approximately 180 metres above sea-level. The terrain in the vicinity of the Detroit River is nearly flat, rising from 175 metres at the river to 190 metres southeast of Windsor. In Michigan the elevation rises to 182 metres a short distance from the river bank and increases to 240 metres 32 km from the river. There are no major terrain elevation differences which would affect the dispersion of SO$_2$ in the study area.

The thirty year (1941-1970) average amount of precipitation received at the Windsor Airport for the period April through September is 457 mm. The average number of days with precipitation during this time period is 64 days (I.J.C., 1971).

The International Joint Commission (1971) determined that the combined contributions of United States point and area sources to the observed SO$_2$ concentrations in the Windsor area reached values as high as .1048 mg/m$^3$ compared to the acceptable annual average value of .0524 mg/m$^3$ set by Ontario standards. It was concluded that far more...
SO\(_{2}\), SO\(_{3}\), and SO\(_{4}\) pollution is being transported from the U.S. into Canada then from Canada into the U.S.

Figure 3 shows the location of SO\(_x\) point source emissions of at least 28,766 mg/sec (1000 tons/yr). These 28 locations emitted 10,908,055 mg/sec of SO\(_x\) during 1968 (I.J.C., 1971) with a projected increase of 25\% by 1971.

Sample Collection and Analysis

Sampling was carried out at the University of Windsor Weather Station located at the corner of California and College Avenues in Windsor during the late spring, summer and early fall period from April 30 through September 28, 1975.

A bulk precipitation sampler, similar to that described by Shiomi and Kuntz (1973), was used (Figure 4). Rainfall was collected in a plastic funnel approximately 2.1 m above the ground surface with a collection area of 410.25 cm\(^2\). The sampling unit was rinsed twice daily with distilled water (as suggested by Georgii and Weber, 1960) to minimize the collection of dry fallout. After each rainfall the samples were removed and stored in polyethylene bottles at 4°C until time of analysis.

SO\(_4\) concentration (mg/l) was determined by the turbidimetric method (Appendix A) described in Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971; published jointly by the American Public Health Association, American Water Works Association and The Water Poll-
FIGURE 3: SOx POINT SOURCES (at least 28,766 mg/sec)

- O.M.E. Air Sampler
- University of Windsor Weather Station
- Windsor Weather Office, Windsor Airport

LEGEND
- • location of SOx point sources
- ▲ data collection sites

Source: I.J.C., 1971
FIGURE 4: PRECIPITATION SAMPLER

Source: Shiomi and Kuntz, 1973
ution Control Federation. Analysis of all samples took place within ten days of the time of collection. It was determined by examination of samples of known concentration (Appendix B), that no variation of concentration took place during the storage period beyond the known standard deviation of the method. Total SO$_4$ supply (mg/collection area) was obtained by taking the product of SO$_4$ concentration (mg/l) and the total precipitation collected (l).

It was also determined (Appendix C) that at least 50 ml. of sample was necessary to provide accurate analysis. This sample volume limits the study to occurrences of precipitation of 1.25 mm or greater. A total of 28 samples exceeded this requirement.

Data Collection

The time of precipitation, total precipitation (mm) and duration of precipitation (min) data was taken from a Belfort continuous recording gauge located 8 metres from the sampling location at the University of Windsor Weather Station.

Precipitation intensity, calculated from the above data, was used to determine drop diameter from relationships presented by Best (1950). Figure 5 shows the relationship between drop diameter and precipitation intensity from which the half drop surface area parameter was calculated.

Munn and Katz (1959) concluded that SO$_2$ concentrations are extremely sensitive to point source locations. For this
FIGURE 5: DROP DIAMETER vs. PRECIPITATION INTENSITY

Source: Best, 1950
reason it was necessary to calculate the concentration of 
$SO_2$ above the sampling location. The maximum concentra-
tion, the concentration at the same elevation as the effec-
tive stack height, above the sampling location was calcu-
lated using the equation given by Perkins (1974):

$$C(x,y,z,H) = \frac{Q}{\sigma_y \sigma_z \mu} \exp \left( \frac{-y^2}{2\sigma_y^2} + \frac{H^2}{2\sigma_z^2} \right) \tag{1}$$

where:

- $C$ - concentration of $SO_2$, mg/m$^3$.
- $Q$ - source strength, mg/sec.
- $x$ - distance downwind from source, km.
- $y$ - horizontal displacement from plume centre, m.
- $z$ - vertical displacement from plume centre, m.
- $\sigma_y$ - horizontal plume dispersion coefficient, m.
- $\sigma_z$ - vertical plume dispersion coefficient, m.
- $\mu$ - mean wind speed, m/sec.
- $H$ - effective stack height, m.

The effective stack height ($H$) is the actual stack
height ($h$) in metres plus plume rise ($\Delta h$) which is cal-
culated using the formula for stable and neutral conditions
given by Smith (1968) in the form:

$$\Delta h = 150 \left( \frac{F}{u^3} \right) \tag{2}$$

where:

- $\Delta h$ - plume rise, m.
- $u$ - mean wind speed at stack height, m/sec.

and

$$F = g V_s \left( \frac{D}{2} \right)^2 \frac{T_s - T_a}{T_a} \tag{3}$$

where:

- $D$ - stack diameter, m.
- $V_s$ - emission velocity, m/sec.
- $g$ - acceleration of gravity $= 9.806$ m/sec$^2$.
- $T_s$ - stack gas temperature, K.
- $T_a$ - air temperature, K.

The plume dispersion coefficients used in equation
(1) are dependent upon distance from the source, solar
heating and wind speed and are given by Perkins (1974). The source strength data used represent the average rates of emission during 1967 and updated to 1970 where possible (I.J.C., 1971).

Because the sources of \( \text{SO}_2 \) in the Windsor-Detroit area are continuous, the mean windspeed and mean wind direction during the period of precipitation were used in the calculations. These data along with air and dew-point temperatures were obtained from the hourly observations made at the Windsor Weather Office located at the Windsor Airport 9.1 km to the southeast of the sampling location.

The stack parameters necessary for the calculation of (2) were considered uniform for all emission sources. Representative figures provided by Mr. D. Smith, Department of Chemical Engineering, University of Windsor are as follows:

- Stack diameter \( (D) = 1.5 \text{ m.} \)
- Emission velocity \( (V_e) = 15.5 \text{ m/sec.} \)
- Stack gas temperature \( (T_e) = 480 \text{ K.} \)
- Stack height \( (h) = 50 \text{ m.} \)

The \( \text{SO}_2 \) concentrations above the sampling location resulting from each point source location were calculated and summed to provide the maximum \( \text{SO}_2 \) concentration through which the precipitation elements fell.

Samples collected at times when the wind direction was between \( 80^\circ \) and \( 175^\circ \) were not affected by plumes from the point source locations shown on Figure 3. For these days atmospheric \( \text{SO}_2 \) concentrations were taken from the Ontario
Ministry of the Environment air sampler located on University Avenue, Windsor, 2.25 km to the northeast of the sampling location. The air sampler is also not affected by plumes from the point source locations at times when the wind direction is between 80° and 175°.

The drop fall time below the sub-maximum SO₂ concentration will be a function of the fall velocity of the drop and the elevation of the maximum SO₂ concentration. Because of the nature of plume dispersion theory and the data used, the maximum SO₂ concentration will occur at an elevation equal to the effective stack height calculated for each occurrence of precipitation. The terminal velocity of water drops used to calculate drop fall time below the sub-maximum SO₂ concentration level was taken from Figure 6.

The data collected utilizing the methodology outlined in this section was analyzed as presented in the following chapter in order to test the hypotheses formulated in Chapter II. A summary of the data collected and observed sample characteristics is provided in Table 1.
FIGURE 6: TERMINAL DROP VELOCITY vs. DROP DIAMETER

Source: Mason, 1957
### Table 1: Sample and Storm Characteristics

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>$SO_4$ Sup. $(mg/410.25 cm^2)$</th>
<th>$SO_4$ Conc. $(mg/l)$</th>
<th>$SO_2$ Conc. $(mg/m^3)$</th>
<th>Tot. Pre. $(mm)$</th>
<th>Storm Durat. $(min)$</th>
<th>Sub-max. $SO_2$ Fal. $(sec)$</th>
<th>Drop Area $(mm^2)$</th>
<th>Dew Pt. Temp. $(\degree C)$</th>
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* - denotes poor ventilation case
CHAPTER IV

Analysis of Results

The primary aim of this study is to determine which variables are significant in explaining variation in the total SO$_4$ supply and SO$_4$ concentration in precipitation. A stepwise multiple regression procedure (BMD02R) was employed with the aid of the University of Windsor I.B.M. 360 model 65 computer to determine the significance of the six variables assumed to be independent in this study: atmospheric SO$_2$ concentration, total precipitation, precipitation duration, half drop area, sub-maximum SO$_2$ concentration fall time and drop temperature.

Prior to analysis all variables were tested for normality using procedures outlined by Hammond and McCullagh (1974). It was determined that the total SO$_4$ supply, total precipitation, precipitation duration and half drop area were log-normally distributed and the data were transformed accordingly.

The correlation matrix of the variables incorporated in the study is shown in Table 2. According to Hauser (1974) there is no auto-correlation of sufficient magnitude between the independent variables that would affect the results of the stepwise regression procedure.
Table 2: Correlation Matrix

<table>
<thead>
<tr>
<th></th>
<th>Total $\text{SO}_4$ Supply</th>
<th>$\text{SO}_4$ Conc.</th>
<th>Atmos. $\text{SO}_2$ Conc.</th>
<th>Total Precip.</th>
<th>Storm Duration</th>
<th>Dew Point Temp.</th>
<th>Drop Area</th>
<th>Sub-max. $\text{SO}_2$ Fall time</th>
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<tr>
<td>Total $\text{SO}_4$ Supply</td>
<td>1.000</td>
<td>0.071</td>
<td>-0.108</td>
<td>0.893</td>
<td>0.479</td>
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<td>-0.261</td>
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<td>Storm Duration</td>
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<td>Dew Point Temperature</td>
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<td>Drop Area</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Sub-max. $\text{SO}_2$ Fall time</td>
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<td>1.000</td>
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Figure 7 shows the wind direction associated with each of the 28 samples included in this analysis. One rainfall, August 25, occurred during calm wind conditions.

Table 3 provides a summary of the stepwise regression with total $\text{SO}_4$ supply as the dependent variable. The significant variables, total precipitation, sub-maximum $\text{SO}_2$ concentration fall time, half drop area and precipitation duration explain 85.41% of the variation in the total $\text{SO}_4$ supply received at the sampling location. Total precipitation alone accounts for 79.8% of the observed variation. It was determined that the atmospheric $\text{SO}_2$ concentration and drop temperature are not significant.

The summary of the stepwise regression with $\text{SO}_4$ concentration as the dependent variable is provided by Table 4. Atmospheric $\text{SO}_2$ concentration and sub-maximum $\text{SO}_2$ concentration fall time are significant variables and explain 61.1% of the variation of the $\text{SO}_4$ concentration with the atmospheric $\text{SO}_2$ concentration accounting for 53.23%.

On the basis of this analysis we can accept the hypotheses that total $\text{SO}_4$ supply will increase as the total precipitation, half drop area and precipitation duration increase and that $\text{SO}_4$ concentration will increase with higher atmospheric $\text{SO}_2$ concentrations. Theoretically both the total $\text{SO}_4$ supply and $\text{SO}_4$ concentration should decrease as the sub-maximum $\text{SO}_2$ concentration fall time increases. However, the total $\text{SO}_4$ supply and concentration are posi-
FIGURE 7: WIND DIRECTION at TIME of PRECIPITATION

LEGEND

- location of SOx point sources
- University of Windsor Weather Station
- wind direction vectors

Source: I.J.C., 1971
### Table 3: Summary of Stepwise Regression, Total SO\textsubscript{4} Supply

<table>
<thead>
<tr>
<th>Step Entered</th>
<th>Variable</th>
<th>Multiple R</th>
<th>Standard Error</th>
<th>Multiple R\textsuperscript{2}</th>
<th>Increase in R\textsuperscript{2}</th>
<th>Regression Coefficient</th>
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<td>2</td>
<td>Sub-max. SO\textsubscript{2} Fall Time</td>
<td>0.9068</td>
<td>0.1784</td>
<td>0.8255</td>
<td>0.0275*</td>
<td>b\textsubscript{1} = 0.7941*</td>
<td>0.0735</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{2} = 0.0051</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Drop Area</td>
<td>0.9120</td>
<td>0.1789</td>
<td>0.8317</td>
<td>0.0061</td>
<td>b\textsubscript{1} = 0.7808*</td>
<td>0.0751</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{2} = 0.0052</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{3} = 0.1617</td>
<td>0.1729</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Storm Duration</td>
<td>0.9242</td>
<td>0.1701</td>
<td>0.8541</td>
<td>0.0224*</td>
<td>b\textsubscript{1} = 0.6062*</td>
<td>0.1171</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{2} = 0.0060</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{3} = 0.5918</td>
<td>0.2817</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{4} = 0.2494</td>
<td>0.1126</td>
<td></td>
</tr>
</tbody>
</table>

Further steps do not result in significant improvement of R\textsuperscript{2}.

* - significant at the 0.05 level.
Table 4: Summary of Stepwise Regression, SO\textsubscript{4} Concentration

<table>
<thead>
<tr>
<th>Step</th>
<th>Variable Entered</th>
<th>Multiple R</th>
<th>Standard Error</th>
<th>Multiple R\textsuperscript{2}</th>
<th>Increase in R\textsuperscript{2}</th>
<th>Regression Coefficient</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atmospheric SO\textsubscript{2} Concentration</td>
<td>0.7296</td>
<td>1.9305</td>
<td>0.5323</td>
<td>0.5323*</td>
<td>b\textsubscript{1} = 60.491*</td>
<td>11.119</td>
</tr>
<tr>
<td>2</td>
<td>Sub-maximum SO\textsubscript{2} Concentration</td>
<td>0.7816</td>
<td>1.7956</td>
<td>0.6110</td>
<td>0.0787*</td>
<td>b\textsubscript{1} = 54.771*</td>
<td>10.651</td>
</tr>
<tr>
<td></td>
<td>Fall Time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b\textsubscript{2} = 0.060*</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Further steps do not result in significant improvement of R\textsuperscript{2}.

* - significant at the 0.05 level.
tively related to the fall time. Possible explanations will be discussed later.

The generation of SO\textsubscript{2} concentrations using plume dispersion theory cannot account for the possible buildup of SO\textsubscript{2} in the lower layers of the atmosphere during extended periods of poor ventilation. Schmidt and Velds (1969) found that maximum atmospheric concentrations of SO\textsubscript{2} were associated with persistent high pressure systems and accompanying low wind speeds.

The introduction of synoptic conditions to the present study began with a review of hourly wind speed observations made at the Windsor Weather Office. The number of consecutive hours with wind speeds less than 5 m/sec preceding each occurrence of precipitation was recorded. These data were combined with the examination of daily synoptic weather maps to determine which samples were associated with conditions favourable for the buildup of SO\textsubscript{2} in the atmosphere.

It was found that 10 of the 28 samples collected were the result of precipitation events which occurred following periods of poor ventilation and stagnating circulation types. Figure 8 illustrates the synoptic conditions leading up to sample collection at 2:30 a.m. August 3, 1975. The persistent high pressure system associated with light predominately southerly flow is characteristic of 4 of the 10 cases considered.
FIGURE 8: SYNOPTIC CONDITIONS ASSOCIATED with AUGUST 3, 1975

Source: Weatherwise, 1975
Figure 9 illustrates the synoptic conditions leading up to sample collection at 9:15 a.m. July 19, 1975. This air mass configuration results in a more moderate and consistent southwesterly flow than that illustrated in Figure 8. However, as was concluded by Munn and Katz (1959) highest SO₂ concentrations near the sample collection site are associated with southwesterly winds.

The data were then subdivided into strong and weak ventilation groups for further analysis. Table 5 shows the results of tests for significant differences in total SO₄ supply and SO₄ concentration between the two groups. There is no significant difference in the total SO₄ supply between the two synoptic subdivisions. There is a significant difference in the SO₄ concentration observed for the two groups. It should be noted that a substantial difference in total SO₄ supply exists between the two synoptic classes although not a significant one at the .05% confidence level. Even though the difference is not statistically evident, the mean values for the total SO₄ supply vary between synoptic classes in the same sense as do the values for SO₄ concentration.

The results of the stepwise regression for the strong ventilation group with SO₄ concentration as the dependent variable are given in Table 6. Under these synoptic conditions atmospheric SO₂ concentration is the only significant variable and accounts for 75.36% of the observed variation in SO₄ concentration.
FIGURE 9: SYNOPTIC CONDITIONS ASSOCIATED with JULY 19, 1975

July 17

July 18

July 19

Source: Weatherwise, 1975
Table 5: Tests for Significant Difference between Synoptic Classes

Total SO$_4$ Supply:
Mean total SO$_4$ supply, strong ventilation cases; $X_1 = 0.1922$
Mean total SO$_4$ supply, poor ventilation cases; $X_2 = 0.3800$
$X_1 - X_2 = 0.1877$
t-observed = 1.1581
t-critical = 2.0600

There is no significant difference in the SO$_4$ supply observed for the two synoptic classes at the 0.05 level of significance.

SO$_4$ Concentration:
Mean SO$_4$ concentration, strong ventilation cases; $X_1 = 5.75$
Mean SO$_4$ concentration, poor ventilation cases; $X_2 = 8.45$
$X_1 - X_2 = 2.8790$
t-observed = 2.8201
t-critical = 2.0600

There is a significant difference in the SO$_4$ concentration observed for the two synoptic classes at the 0.05 level of significance.
Table 6: Summary of Stepwise Regression, SO$_4$ Concentration
(strong ventilation cases)

<table>
<thead>
<tr>
<th>Step Entered</th>
<th>Variable</th>
<th>Multiple $R$</th>
<th>Standard Error</th>
<th>Multiple $R^2$</th>
<th>Increase in $R^2$</th>
<th>Regression Coefficient $b_1$</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atmospheric SO$_2$ Concentration</td>
<td>0.8681</td>
<td>1.3067</td>
<td>0.7536</td>
<td>0.7536*</td>
<td>69.350*</td>
<td>9.915</td>
</tr>
</tbody>
</table>

Further steps do not result in significant improvement of $R^2$.

* - significant at the 0.05 level.
Analysis of the SO₄ concentration under strong ventilation conditions resulted in the elimination of sub-maximum SO₂ concentration fall time as a significant variable. In the original analysis 10 of the 28 samples were collected following periods of poor ventilation. Examination of the data reveals that the mean sub-maximum SO₂ fall time for these storms was 17.4 seconds as opposed to 7.7 seconds for rainfalls occurring during periods of strong ventilation. This agrees with the observation made by Petrenchuck and Drozdova (1971) that during periods of light winds the maximum SO₂ concentration is found at higher elevations in the atmosphere. This higher elevation in addition to the apparent build-up of SO₂ in the atmosphere results in a positive relationship between SO₄ concentration and sub-maximum SO₂ concentration fall time.

The mean total precipitation received during storms following periods of poor ventilation was 12.06 mm compared to the 5.74 mm received during rainfalls associated with strong ventilation. The inclusion of the poor ventilation cases would result in a positive relationship between total SO₄ supply and sub-maximum SO₂ concentration fall time.

It is probable that some bias, introduced into the analysis, was responsible for sub-maximum SO₂ concentration being significantly related to SO₄ concentration and total SO₄ supply in the analysis of all cases.
Rank correlation coefficients between $SO_4$ concentration and the independent variables for the weak ventilation cases are provided in Table 7. Under these synoptic conditions, drop area and atmospheric $SO_2$ concentration are significantly correlated with $SO_4$ concentration.
Table 7: Rank Correlation Coefficients, $SO_4$ Concentration
(poor ventilation cases)

<table>
<thead>
<tr>
<th>Total Precipitation</th>
<th>Storm Duration</th>
<th>Dew Point Temperature</th>
<th>Drop Area</th>
<th>Sub-max. $SO_2$ Conc.</th>
<th>Fall Time</th>
<th>Atmos. $SO_2$ Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_4$ Concentration</td>
<td>-0.410</td>
<td>-0.100</td>
<td>0.010</td>
<td>-0.840*</td>
<td>0.070</td>
<td>0.800*</td>
</tr>
</tbody>
</table>

* - significant at the 0.05 level.
CHAPTER V

Discussion and Conclusions

Atmospheric $SO_2$ Concentration

It was hypothesized in Chapter II that total $SO_4$ supply should increase as the atmospheric $SO_2$ concentration increased. Observations made by authors of previous studies indicated that the rate of $SO_2$ absorption and the eventual production of $SO_4$ was a function of the atmospheric $SO_2$ concentration. The analysis of the Windsor data showed that the atmospheric $SO_2$ concentration does not have a significant part in the explanation of the variations observed in total $SO_4$ supply. This implies that for the majority, if not all of the storms sampled, the maximum limit of the in drop $SO_4$ production for a given atmospheric $SO_2$ concentration was not achieved. This observation leads to the conclusion that the rate of absorption and oxidation of $SO_2$ by a falling drop is not rapid enough to result in drop saturation during the fall time of the drop.

The hypothesis that the $SO_4$ concentration should increase as the atmospheric $SO_2$ concentration increased was accepted for all synoptic cases studied. In the analysis of all cases and strong ventilation cases (Figures 10 and 11 respectively) a significant relationship was determined.
FIGURE 10: $SO_4$ CONCENTRATION vs. $SO_2$ CONCENTRATION (all cases)
FIGURE 11: $\text{SO}_4$ CONCENTRATION vs. $\text{SO}_2$ CONCENTRATION

(strong ventilation)
to exist through regression techniques. A significant rank correlation was found between the SO₄ concentration and atmospheric SO₂ concentration under conditions of poor ventilation (Figure 12). The conclusion can be made that although total drop saturation is not achieved, the atmospheric concentration does determine the rate of SO₂ absorption, oxidation and the final drop concentration of SO₄.

The relationship improved with the elimination of the weak ventilation cases from the data. This indicates that the application of plume dispersion theory to the prediction of atmospheric SO₂ concentrations is more rational when used at times where synoptic conditions favour strong ventilation.

**Total Precipitation and Storm Duration**

Total precipitation and storm duration were hypothesized and found to be positively related to the total amount of SO₄ supplied by a single storm. These hypotheses were based upon the observations made by Wiebe and Whelpdale (1975) who found that in an area with continuous emissions of SO₂, total washout of the contaminated layer of the atmosphere would not occur.

Figures 13 and 14 illustrate that, over the range of total precipitation received (1.27 mm to 49.99 mm) and the duration of storms experienced (5 min to 330 min), the total SO₄ supply constantly increased. It appears that regardless of the total amount of precipitation or the
FIGURE 12: $SO_4$ CONCENTRATION vs. $SO_2$ CONCENTRATION

(poor ventilation)
FIGURE 13: TOTAL SO₂ SUPPLY vs. TOTAL PRECIPITATION
duration of the storm, total washout of atmospheric SO$_2$ does not occur.

The hypothesis was made that the SO$_4$ concentration would not vary with the total amount of precipitation received during a storm. The acceptance of this hypothesis indicates that not only is total washout not achieved, but also dilution of the contaminated layer of the atmosphere is not of sufficient magnitude to affect the observed concentration of SO$_4$.

Hales' (1972) theory predicts that SO$_2$ plumes would be redistributed to lower levels of the atmosphere through the duration of a storm. In an area without continuous source emissions this process would result in a reduction of the maximum SO$_2$ concentration to which the drop is exposed lowering the concentration of SO$_4$ produced. The results of the present investigation cannot be used to speculate on the existence or magnitude of such a process. However, it is clear that in an area of continuous source emissions, gas desorption does not alter the maximum SO$_2$ concentration through which the drop falls.

**Sub-maximum SO$_2$ Concentration Drop Fall Time**

It was hypothesized that as the drop fall time below the maximum SO$_2$ concentration increases the total SO$_4$ supply and SO$_4$ concentration should decrease. The opposite was found to be true for the analysis of all cases. This observation was attributed to the introduction of bias, the
result of the inclusion of the poor ventilation cases where the maximum SO₂ concentration was assumed to be at a higher level.

The analysis of the strong ventilation cases resulted in the sub-maximum SO₂ concentration drop fall time having no significant effect on the total SO₄ supply and SO₄ concentration observed at ground level. The insufficiency of sub-maximum SO₂ concentration drop fall time leads to two alternative conclusions with respect to Hales' (1972) theory of reversible washout:

1. The desorption of undissoved gas from a raindrop may take place but is of insufficient magnitude to significantly alter the total amount of SO₄ produced within the drop.

2. The concentration of undissoved gas in the drop below the maximum SO₂ concentration level does not exceed the concentration of SO₂ outside the drop.

Re-examination of Figures 1, 10, 11 and 12 substantiates the second conclusion made. The SO₄ concentrations observed in Figure 1 (the result of laboratory investigation) are generally ten times greater than SO₄ concentrations observed in precipitation for concentration of SO₂ one order of magnitude less. The maximum possible concentration of SO₄ in a drop resulting from a given concentration of SO₂ is achieved only after a long period of exposure, much longer than the fall time of a drop. Unless the maximum concentration of SO₂ is substantially greater than the concentra-
tion below that level is unlikely that gas desorption will occur and sub-maximum SO$_2$ concentration drop fall time will be of little significance.

**Drop Area**

Theoretically drop area will determine the amount of SO$_2$ contacted (Engelmann, 1966) and absorbed by a falling drop. Van den Heuvel and Mason (1963) found that the mass of SO$_4$ produced by a drop was proportional to its surface area.

Figure 14 illustrates the relationship between the total SO$_4$ supply and half drop area. Although a significant relationship does exist we are unable to conclude whether the observation is the result of increased collision efficiency or the ability of the drop to produce larger quantities of SO$_4$ or the dependence of drop area upon total precipitation.

Drop area was determined to be insignificant with respect to the SO$_4$ concentration for the strong ventilation and all case analyses. This observation would indicate that although the mass of SO$_4$ produced by a drop is related to drop size, variations in drop size do not significantly affect the concentration of SO$_4$ observed. A significant negative rank correlation was found to exist between drop size and SO$_4$ concentration for the weak ventilation cases. The range of half drop area for precipitation events following periods of poor ventilation was extremely large (4.85 mm$^2$ to 15.81 mm$^2$). For a small
FIGURE 15: TOTAL SO$_4$ SUPPLY vs. $\frac{1}{2}$ DROP AREA
sample size exhibiting great variation in drop area, drop size is negatively related to the SO$_4$ concentrations as hypothesized.

**Drop Temperature**

Mckay (1970) determined that variations in drop temperature will affect the rates of absorption and oxidation of SO$_2$ to form SO$_4$. The present analysis suggests that the effect of temperature variations on the total SO$_4$ supply and SO$_4$ concentration are insignificant.

**Synoptic Conditions**

It was determined in the previous chapter that the SO$_4$ concentrations observed were significantly higher when preceded by synoptic conditions resulting in poor ventilation of the study area (illustrated in Figures 8 and 9). Comparison of Figures 11 and 12 indicates that the SO$_4$ concentration observed in precipitation following periods of poor ventilation are higher than those observed in events associated with strong ventilation for similar concentrations of SO$_2$. This leads to the conclusion that plume dispersion equations are not suitable for the calculation of SO$_2$ concentrations during periods of poor ventilation. The build-up of SO$_2$ in the atmosphere under such conditions is of such a magnitude that SO$_4$ concentrations in precipitation are significantly higher.

It was also observed, although the difference was not
significant, that total SO$_4$ supplied by storms following periods of poor ventilation was generally greater. However, as was previously noted, the mean total precipitation for such events exceeded the overall mean precipitation received for each storm.

Conclusions

The results of laboratory investigations reported in the literature indicate that the washout of SO$_2$ from the atmosphere and the subsequent supply and concentration of SO$_4$ observed at the earth's surface will be a function of the atmospheric SO$_2$ concentration, total precipitation, precipitation duration, sub-maximum SO$_2$ concentration drop fall time, drop size and drop temperature.

The analysis of data collected during this study leads to the conclusion that total SO$_4$ supply is significantly related to total precipitation, precipitation duration and drop size. It was determined that total precipitation accounted for 79.8% of the variation in total SO$_4$ supply. The SO$_4$ concentration was found to be a function of the atmospheric SO$_2$ concentration which explained 53.23% of the variation observed in all cases and 75.36% of the variation in precipitation events associated with strong ventilation. SO$_4$ concentrations in precipitation were determined to be significantly higher following periods of poor ventilation.

In view of the findings of the present study we should
take care not to over estimate the possible effects of precipitation duration, sub-maximum SO₂ concentration drop fall time, drop size and drop temperature when considering the spatial or temporal variations in the supply and concentration of SO₄ observed at the earth's surface. Variations in total SO₄ supply are for the most part a function of the total amount of precipitation received while variations in SO₄ concentrations appear to be related only to the atmospheric SO₂ concentration.

The author wishes to caution against the interpretation of the results of the study in a predictive nature. The use of secondary data for the calculation of atmospheric SO₂ concentrations and drop area suggests that this research should be introduced to the field as offering explanation for as opposed to quantitative formulae for the prediction of variations in total SO₄ supply and SO₄ concentration.

Further research should include the use of on site instrumentation for the measurement of SO₂ concentrations, drop size and drop temperature which would allow for the construction of empirical equations which could be used for the calculation of total SO₄ supply and SO₄ concentrations. The study area for this research is a large urban area with a number of high volume, continuous point sources of SO₂. Comparison with the results of similar research conducted in an area where atmospheric SO₂ is present at "background" concentrations would be of interest. Finally, the author suggests that members of
the precipitation chemistry field concern themselves with expanding their explanatory and predictive capacities to include all mineral and nutrient parameters found in precipitation.
APPENDIX A

Turbidimetric Method for the Detection of Sulfate

A. General Discussion

1. Principle: Sulfate ion is precipitated in a hydrochloric acid medium with barium chloride under conditions favoring the formation of barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension is measured by a nephelometer or transmission photometer with the sulfate ion concentration being determined by comparison of the reading with a standard curve.

2. Interference: Color or suspended matter may be removed by filtration. If both are small in comparison with the sulfate ion concentration, interference is corrected for as indicated below. Silica in excess of 500 mg/l will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate barium sulfate satisfactorily.

There are no ions other than sulfate in normal waters that will form insoluble compounds with barium under

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1 Taken from Standard Methods for the Examination of Water and Wastewater, 13th Edition; A.P.H.A., Washington, D.C.
strongly acid conditions. Determinations should be made at room temperature, which may vary over a range of 10 °C without causing appreciable error.

The minimum detectable concentration is approximately 1 mg/l sulfate.

B. Apparatus

1. Magnetic Stirrer: It is convenient to incorporate a timing device to permit the magnetic stirrer to operate for exactly 1 min. The stirring speed should not vary appreciably. It is also convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate the speed of stirring. If more than one magnet is used, they should be of identical size and shape. The exact speed of stirring is not critical, but it should be constant for each run of samples and standards, and should be adjusted to about the maximum at which no splashing occurs.

2. Spectrophotometer: Any spectrophotometer set at 420 μm, while providing a light path of 4-5 cm, is satisfactory.

C. Reagents

1. Conditioning Reagent: The conditioning reagent is made by mixing 50 ml glycerol with a solution containing 30 ml conc HCl, 300 ml distilled water, 100 ml 95% ethyl or isopropyl alcohol, and 75 g sodium chloride.

3. Standard Sulfate Solution: The standard solution is prepared by dissolving 147.9 mg anhydrous sodium sulfate, \( \text{Na}_2\text{SO}_4 \), in distilled water and diluting to 1,000 ml.

D. Procedure

1. Formation of Barium Sulfate: Measure 100 ml sample, or a suitable aliquot made up to 100 ml, into a 250 ml erlenmeyer flask. Add exactly 5.00 ml conditioning reagent and mix in the stirring apparatus. While the solution is being stirred, add a spoonful of barium chloride crystals and begin the timing immediately. Stir for exactly 1 min at a constant speed.

2. Measurement of barium sulfate: Immediately after the stirring period has ended, pour some of the solution into the absorption cell of the photometer and measure the turbidity at 30-sec intervals for 4 min. Since maximum turbidity usually occurs within 2 min and the readings remain constant thereafter for 3-10 min, consider the turbidity to be the maximum reading obtained during the 4-min interval.

3. Preparation of Calibration Curve: Estimate the sulfate concentration in the sample by comparing the turbidity reading with a calibration curve prepared by carrying sulfate standards through the entire procedure. Space the standards at 5 mg/l increments in the 0 to 40 mg/l
sulfate range. Above 40 mg/l the accuracy of the method decreases and the suspensions of barium sulfate lose stability. Check the reliability of the calibration curve by running a standard with every three or four unknown samples.

4. Correction for Sample Turbidity: Correct for the color and turbidity present in the original sample by running blanks from which the barium chloride is withheld.

5. Calculation:

\[
\text{mg/l } SO_4 = \frac{\text{mg } SO_4 \times 1,000}{\text{ml sample}}
\]

6. Standard Deviation: The standard deviation of the method was determined in the laboratory through replicate analysis of concentrations of 10 mg/l. It was determined to be .4295 mg/l.
APPENDIX B

The Effect of Storage on Samples

It is noted in Standard Methods that in the presence of organic matter, certain bacteria may reduce sulfate to sulfide. This may be avoided if samples are stored at low temperatures. Georgii and Weber (1960) found that after a period of ten days the concentration of SO₄ fell to 85% of the original concentration. It should be noted that their presentation of the effect of storage on sample concentration reflects a high degree of variability which is likely due to variations in analytical procedures.

The purpose of this appendix is to determine if any variation in SO₄ concentration took place over a storage period of ten days under conditions similar to those experienced during the sampling program. For this investigation an actual precipitation sample "spiked" with 5 mg/l SO₄ was analyzed daily using the method described in Appendix A. Figure 16 illustrates that no variation beyond the standard deviation of the method could be attributed to the storage method or period.
FIGURE 16: EFFECT of STORAGE on SAMPLE CONCENTRATION
APPENDIX C

The Effect of Sample Size on the Analytical Method

The accuracy of analyses involving the use of photometric equipment will vary according to the reading on the standard curve. Analyses resulting in very high readings of transmittance tend to overestimate the actual concentration of contaminant present.

In a program where precipitation sampling is necessary, the only control of sample volume is through variation of the collection orifice area. Sampling control purposes prohibit frequent alterations of the collection unit and maintenance determines that the collection orifice should not be too large.

The collection area of the sampling unit used in this study was 410.25 cm². A sample volume of 39 ml was obtained from 1 mm of rainfall. The purpose of this appendix is to determine the volume of sample required to obtain reliable results from the analytical method described in Appendix A. Standard concentrations of 5 and 10 mg/l of SO₂ were analyzed in aliquots ranging from 10 ml (the sample volume collected from .25 mm of rain fall) to 100 ml.
It was observed that sample volumes of 50 ml or greater (Figure 16) provided results within the standard deviation of the method as determined by replicate analysis of samples of identical concentrations. Since samples used in this study are limited to volumes of 50 ml or greater, rainfalls must provide at least 1.25 mm of precipitation for reliable analysis.
FIGURE 17: EFFECT of SAMPLE VOLUME on SAMPLE CONCENTRATION
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