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IMPACT OF AIR POLLUTANTS ON
TERRESTRIAL VEGETATION

(Sulfur dioxide, fluorides and metals)

A LITERATURE SURVEY

1976 ANNUAL REPORT

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TERRESTRIAL VEGETATION

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A LITERATURE SURVEY

by

Sagar V. Krupa, Boris I. Chevone, Steve Fagerlie,
Frank Russo and David S. Lang

Assistant Professor and Research
Scientists respectively,

Department of Plant Pathology
University of Minnesota
St. Paul, MN 55108

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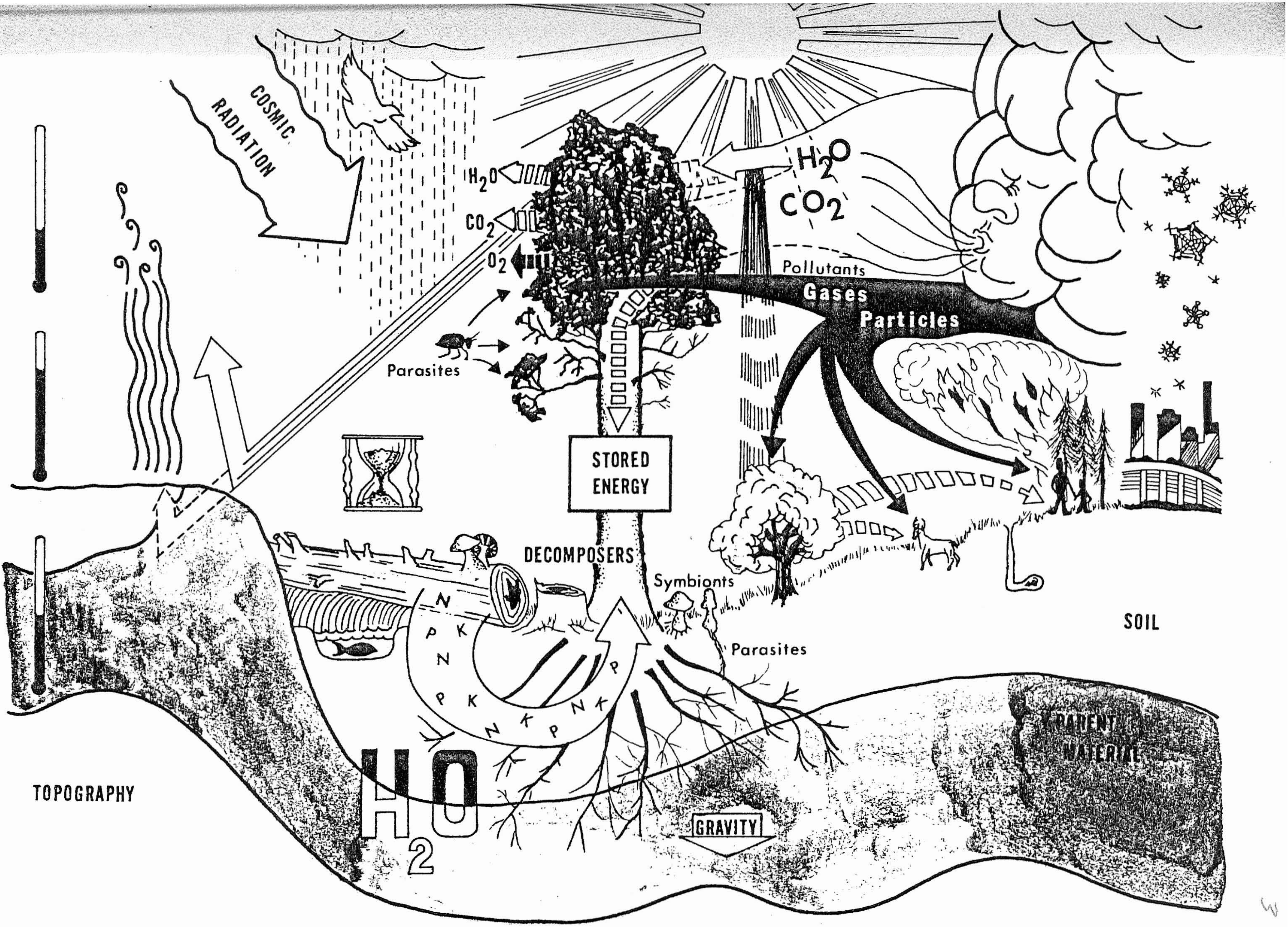
PREFACE

This review by no means constitutes an exhaustive compilation of all the published literature on the various aspects of air pollution discussed herein. It, however, represents a summation of our current knowledge on the various topics and the opinions of the authors. This document has been prepared to satisfy a specific need and the authors are deeply indebted to all the air pollution scientists from whose work information is drawn.

The Authors

Note to the reader

All the information presented in the Appendix of this report is organized and numbered in the same order as the various sections and subsections in the text.


COSMIC RADIATION
H2O
CO2
O2
H2O
CO2
Pollutants
Gases
Particles
Parasites
STORED ENERGY
DECOMPOSERS
Symbionts
Parasites
N P K N P K N K P N K P
SOIL
PARENT MATERIAL
TOPOGRAPHY
H2O
GRAVITY

Impact of Air Pollutants on Terrestrial Vegetation

1. General Background

An air pollutant in the present context can be defined as any gaseous, solid or liquid contaminant of the atmosphere that causes undesirable effects on plants. Some air pollutants such as sulfur dioxide and hydrogen fluoride are produced directly from a source as substances harmful to plants. These are known as primary air pollutants. Other atmospheric components under the class of secondary air pollutants, such as ozone and peroxyacetyl nitrate (PAN), are produced in the atmosphere secondarily through reactions involving sunlight and chemicals such as nitrogen dioxide and hydrocarbons from automobiles, etc.

The major sources of national air pollution are summarized in Table 1-1.

In an order of decreasing importance, plant pathogenic air pollutants in the United States can be listed as follows:

ozone
sulfur dioxide
fluorides
peroxyacetyl nitrate
particulates
oxides of nitrogen
ethylene
hydrogen chloride
chlorine
others

Table 1-1. Major Sources of National Air Pollution.*

Source	Percent
Transportation	60
Industry	18
Generation of electricity	14
Space heating	5
Refuse disposal	3

* From Middleton, J. (1967).

The major sources of some of these air pollutants and their individual contributions are listed in Table 1-2.

Air pollution is a source-transport-effect phenomenon. Air pollutants pathogenic to terrestrial vegetation, as mentioned previously arise from a variety of natural and man-related phenomena. The proposed copper-nickel mining is considered to increase the atmospheric loading of both primary and secondary particulates as well as aerosols. The chemical components expected are metals and the corresponding anions such as sulfates. Should a smelter be located in the region, then sulfur dioxide and gaseous fluorides may be the important components.

The regional copper-nickel study pertains to an area predominantly composed of a forest ecosystem (lake states forest - Weaver and Clements, 1938) in terms of the terrestrial vegetation.

The forest resources of the United States are under increasing pressure. The demand for traditional forest products to serve as building materials, pulp, stable watershed, forage and fuel has been intensified. Forests must also satisfy the growing psychological need of the urban man to seek refuge from the increasing stresses of his everyday environment. More and more of the commodity producing space of the forest is being transformed into recreation space for camping, vacation homes, etc. The successful management of both the developed and undeveloped forest is complicated due to certain insect pests and diseases, which become more prevalent on trees stressed by man's activities and by air pollutants (Miller and McBride, 1975).

Many examples of forest injury caused by air pollutants are based upon postmortem examinations. Only on rare occasions has a suitable

Table 1-2. Major Sources of Plant-Pathogenic Primary Air Pollutants.*

Pollutant	Transportation	Industry	Generation of electricity	Space heating	Refuse disposal
			10^6 tons/year		
Sulfur oxides	1	9	12	3	3
Fluorides		1			
Particulates	1	6	3	1	1
Nitrogen oxides	6	2	3	1	1
Hydrocarbons	12	4	1	1	1
Miscellaneous/ Others	1	2	1	1	1
Total	21	24	20	7	5
Percent	28	30	26	9	7

* From Wood, F. A. (1969).

unaffected control area been available to provide baseline description of the preexisting ecosystem and permit a more critical evaluation of the total injury

Based upon specific needs and land-use maps, according to Linzon (1973), the pre-pollution studies being carried out by the Ontario Ministry of Environment in the Nanticoke area consist of:

1. The determination of background concentrations of fluorides and sulfur in vegetation and soil before the industries become operational,
2. The determination of the endemic occurrence of insect, disease and oxidant injuries on vegetation,
3. The establishment of permanent sample plots comprised of existing wood lot and plantation trees for annual observation, measurement and sampling.
4. The establishment of planted plots of seedling trees and clonal ramets for annual observation and sampling,
5. The establishment of annual plots of indicator plant species for observation and harvesting, and
6. The correlation of vegetation data with air sampling records

According to Linzon (1973), the significance of these studies is that if ambient air records coupled with the vegetation data indicate that the biological component of the environment is in danger, then further abatement action is warranted.

Ambient air is never composed of a single air pollutant. Multitudes of chemicals and biological components in the air interact continuously in multiple ways resulting in a highly dynamic system. A specific pollutant (s) can, however, prevail in higher dosages at a specific location at a given time (s) ?t and thus its vegetational impact ? can be obvious.

Plants in general are sensitive to different air pollutants. They respond rapidly under acute stress. However, under conditions of chronic stress, long term vegetational decline is common. Variation in vegetational response to air pollutants exists at population, generic, species and varietal levels.

Vegetational injury due to air pollutants can occur through: 1) direct foliar absorption and/or deposition, 2) adverse changes in the soil physics and chemistry and 3) both 1) and 2). In addition to plant genetic properties, other parameters such as the aerial environment, stage of plant growth, edaphic factors, etc., play an important role in the overall effect.

In the following sections of this report our current knowledge on the vegetational effects of the following three pollutants is reviewed: sulfur dioxide, fluorides and metals.

2. Effects of Sulfur Dioxide on Vegetation

2.1 Introduction.

The movement of sulfur and its compounds throughout our environment on several scales (the "sulfur cycle") is a field of intensive study. The chief motivation is mankind's contamination of the atmosphere with sulfur compounds regionally and possibly even on a global scale (Cadle, 1975). It has been estimated that volcanoes emit sulfur dioxide (SO_2), their principal sulfur product, in a quantity some two orders of magnitude less than that added to the atmosphere by anthropogenic activity (1.5 vs 150 x 10^6 metric tons) (Gaspar, 1975). A lower estimate of man's total contribution to the atmospheric sulfur of 64.9 x 10^6metric tons has also been given (Friend, 1973).

2.2 Chemistry and Biology of Sulfur.

Sulfur occurs in a variety of compounds in the atmosphere. Many of these compounds take part in the Sulfur Cycle (Figure 2.2-1).

Hydrogen sulfide (H_2S) is believed to be emitted into the atmosphere in large but uncertain quantities, mainly from natural resources such as swamps and estuaries. Most of ~~is~~ it is rapidly oxidized to SO_2 and H_2SO_4, by a number of reactions involving 0, O_2, O_3 and possibly radicals (e.g. OH and HO_2) (Figure 2.2-2).

Sulfur dioxide is not only a product of H_2S oxidation, it constitutes about 95% of the sulfur compounds produced by the burning of sulfur-containing fossil fuels.

The major anthropogenic sources of sulfur dioxide are listed in Table 2.2-1.

The atmospheric chemistry of sulfur dioxide has most widely been studied. Sulfur dioxide in the atmosphere can undergo photochemical oxidation, but the rate has long been thought to be too slow (Gerhard and Johnstone, 1955) to be important. A much more rapid process is the oxidation of SO_2 in drops of catalytically active solutions suspended in air (Johnstone and Coughanour, 1958). At steady state, the rate of oxidation

Figure 2.2-1. Sources and sinks of sulfur compounds. Units are 10^6 metric tons per year calculated as sulfate. Based on Kellog _et al_. (1972) and Cadle (1975).

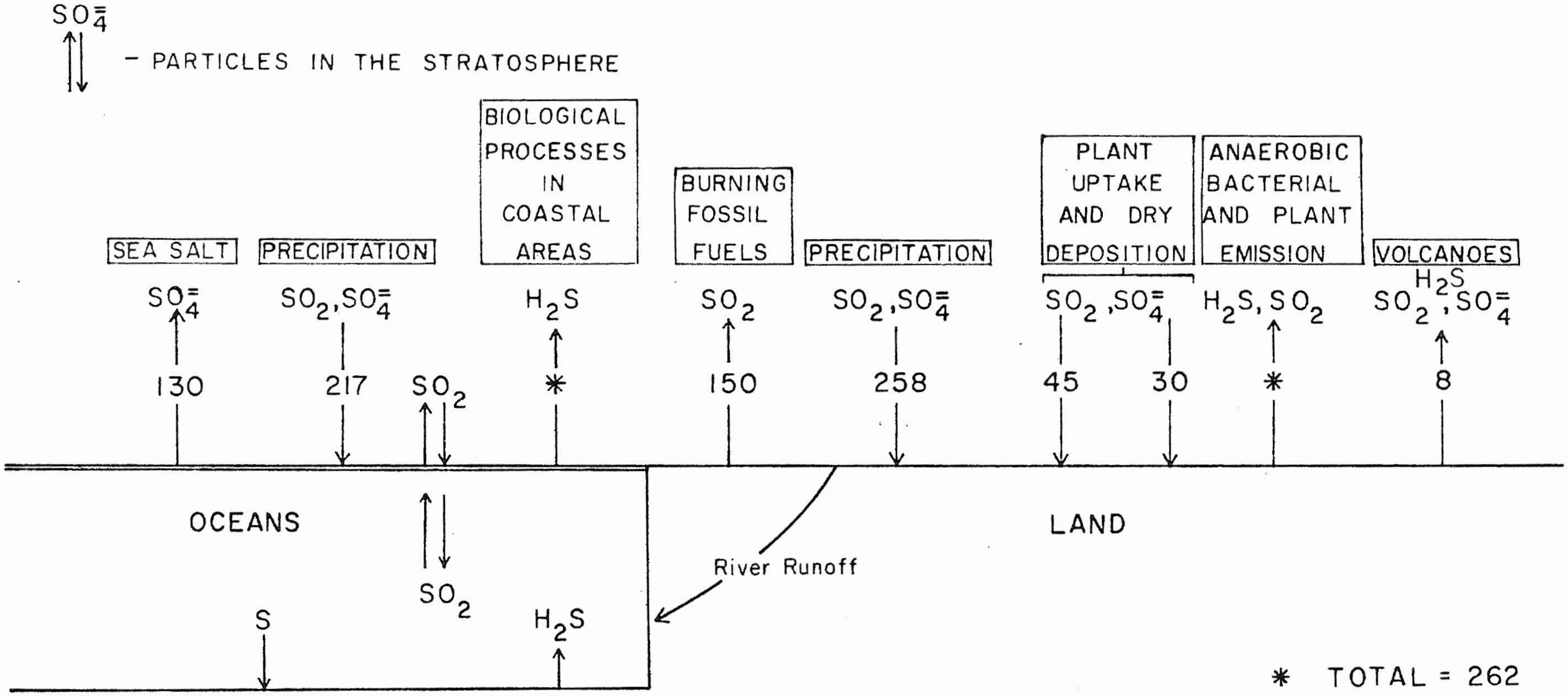
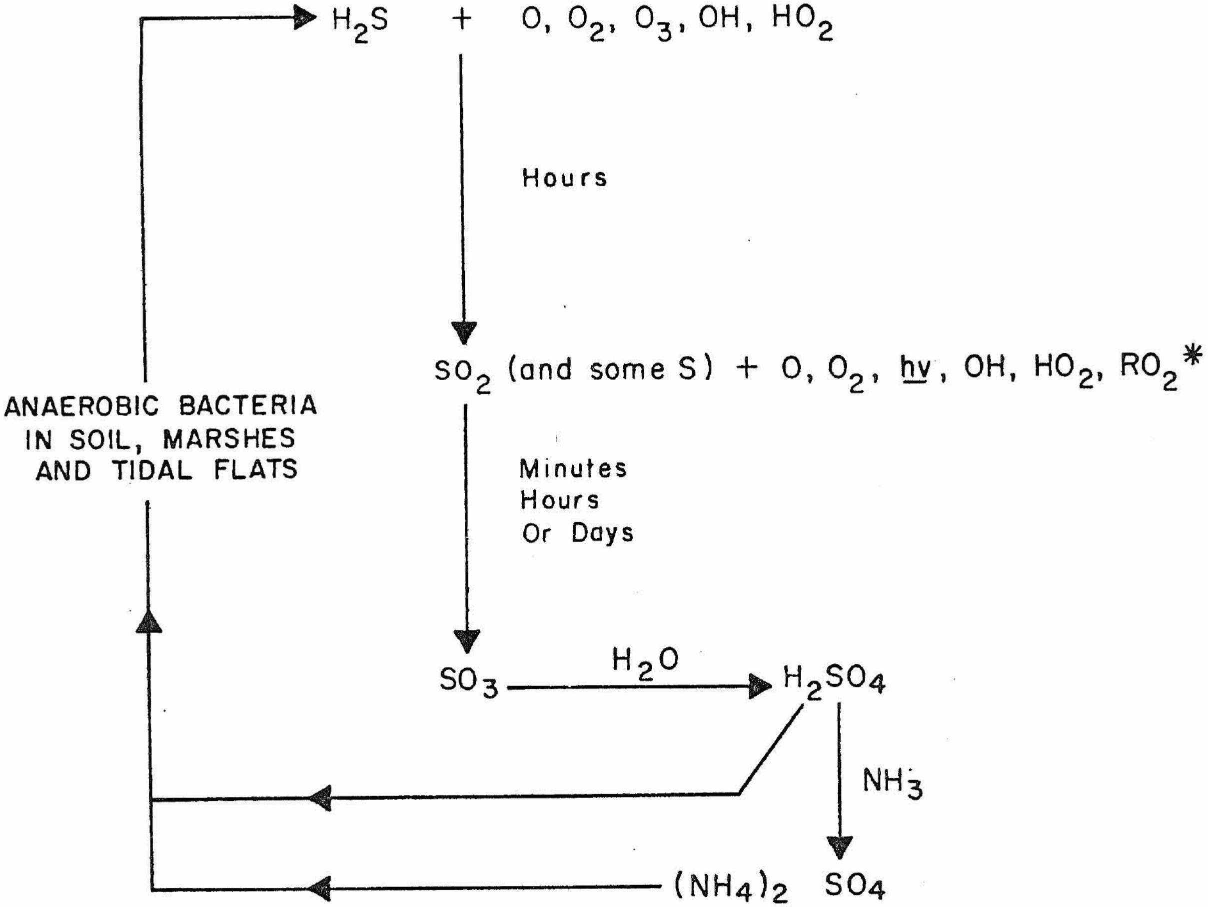

$SO_4^=$
- PARTICLES IN THE STRATOSPHERE
SEA SALT
$SO_4^=$
130
PRECIPITATION
$SO_2, SO_4^=$
217
SO_2
BIOLOGICAL PROCESSES IN COASTAL AREAS
H_2S
*
BURNING FOSSIL FUELS
SO_2
150
PRECIPITATION
$SO_2, SO_4^=$
258
PLANT UPTAKE AND DRY DEPOSITION
$SO_2, SO_4^=$
45
30
ANAEROBIC BACTERIAL AND PLANT EMISSION
H_2S, SO_2
*
VOLCANOES
H_2S
$SO_2, SO_4^=$
8
OCEANS
SO_2
S
H_2S
River Runoff
LAND
* TOTAL = 262

Figure 2.2-2. Diagram of the chemical and bacteriological processes involving sulfur, with indications of residence time. From Cadle (1975).



*Organic peroxy radicals

Table 2.2-1. Major Anthropogenic Sources of Sulfur Dioxide.

1. Combustion of coal
2. Production, refining and utilization of petroleum and natural gas
3. Industries using and manufacturing sulfuric acid and sulphur
4. Smelting and refining of ores

in droplets depends on the rate of catalyzed oxidation in solution. The oxidation process can be described as simultaneous absorption of two gases (SO_2 and O_2) by liquid aerosols accompanied by chemical reactions in the liquid phase. This complex system of mass transfer remains to be completely elucidated (Cheng et al., 1971).

It has been postulated that the ammonia content of the air "controls" the conversion of SO_2 to H_2SO_4 by its buffering action, i.e., by keeping the pH of droplets, within which oxidation takes place, high enough for oxidation to proceed until the ammonia (NH_3) is depleted by formation of ammonium sulfate $(NH_4)_2\ SO_4$ (Gaspar, 1975).

Metal ions, SO_2 and NH_3 have a synergistic effect on the formation of sulfuric acid, and hence on the sulfate-containing particulate matter in the atmosphere. If it is assumed that the rate of oxidation of SO_2 in a droplet is proportional to the concentration of SO_3^{2-}, use of equilibrium constants for $SO_2 - NH_3 - H_2O$ system indicates an initial oxidation rate enhanced 500-fold by the presence of NH_3 in concentrations similar to those found in the atmosphere (Scott and Hobbs, 1967).

There is a great deal of uncertainty concerning the details of the mechanisms for catalyzed oxidation of SO_2. The apparent reaction order for oxidation of SO_2 in aqueous aerosols seems to depend on the catalyst--SO_2 ratio (Gaspar, 1975). A four step model for the reaction mechanism has been proposed for the catalysis of manganese without invoking the oxidation of sulfite ion:

$$SO_2 + Mn^{++} \rightleftharpoons Mn{*}SO_2^{++}$$

$$2Mn{*}SO_2^{++} + O_2 \rightleftharpoons (Mn{*}SO_2^{++})_2{*}\ O_2$$

$$(Mn{*}SO_2{}^{++})_2 \; * \; O_2 \rightleftharpoons 2\ Mn{*}SO_3{}^{++}$$

$$Mn{*}SO_3{}^{++} + H_2O \rightleftharpoons Mn^{++} + HSO_4^- + H^+$$

Hydrolysis of SO_2 has been suggested to be the first step to the oxidation:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3$$

Half life of SO_2 with reference to hydrolysis is approximately 1 minute.

The formation of ammonium sulfate particles in the atmosphere is a significant process because of the quantity formed and the important effect of ammonium sulfate as a cloud condensation nucleating agent (Pruppachar, 1972). It has been suggested that no metal ion catalyst may be necessary for the SO_2 oxidation. However, no mechanism for this uncatalyzed oxidation has been proposed (Gaspar, 1975).

The possibility that a significant (approximately 75%) increase in the concentration of cloud condensation nuclei can occur during the short (roughly 4 minutes) time required for air to flow through a cloud was indicated by the calculations based on a model for ammonium sulfate formation. In this model, SO_2 dissolved in cloud droplets in the presence of ammonia, was oxidized to sulfate (Good and Thynne, 1967; Miller and de Pena, 1972). These calculations were carried out for SO_2 and NH_3 concentrations typical of unpolluted air, and indicate that the rate of ammonium sulfate production in clouds is sufficiently rapid that it is probably the major worldwide source of these particles. Total global sulfate production by this mechanism is estimated to be 6×10^{12} to 4×10^{13} moles per $year^{-1}$ compared with estimates of total sulfate production in the atmosphere of 4.2×10^{12} moles per $year^{-1}$ (Friend, 1973).

Insoluble particulate matter such as ferric oxide (Fe_2O_3), manganese dioxide (MnO_2) and carbon, can capture SO_2 by physical absorption, as well as by catalyzed oxidation (Corn and Cheng, 1972; Judeikis and Siegal, 1973; Smith et al., 1969).

Several different chemical states of sulfur can occur in ambient pollution aerosols: SO_3, SO_4^{2-}, SO_2, SO_3^{2-}, S^0 and R_2S. Many of these can occur together in a single sample (Gaspar, 1975).

A considerable fraction (15 - 25%) of all particulates in the atmosphere consists of sulfates formed by the oxidation of natural H_2S or man-made SO_2 (Schneider and Kellogg, 1973). In many areas ammonium sulfate is the principal component of the atmospheric aerosol (Newell, 1970). Much of the sulfate-containing particulate matter is initially very small in diameter and grows by coagulation.

2.3 Concentrations of sulfur in the environment.

Some atmospheric concentrations of H_2S reported are:

1.02×10^{-5} ppm to 2.04×10^{-5} ppm in Colorado and 3.4×10^{-5} to 6.8×10^{-5} ppm in Missouri (Breeding et al., 1973).

Ambient SO_2 concentrations for the most part vary from 3.4×10^{-4} ppm to 17×10^{-4} ppm.

According to Georgii (1970) SO_4^{2-} concentrations range from about 1.7×10^{-4} to 17×10^{-4} ppm at locations remote from major pollution sources.

2.4 Residence times for S compounds.

The residence time or the average life-time of an atmospheric constituent can be defined as the concentration of that constituent divided by its removal rate. Kellog et al. (1972) gave the following rough estimates of the global tropospheric residence times for several atmospheric sulfur compounds: $H_2S < 1$ day; $SO_2 < 1$ hr to a few days, SO_4^{2-} several days to a week respectively. These estimates may vary in specific locations.

2.5 Effects of SO_2 on Plants.

Sulfur dioxide is one of the most extensively studied plant pathogenic air pollutants. According to Robinson and Robbins (1968), the major anthropogenic sources of SO_2 consist of smelting of ores (10%), refining of petroleum (4%) and the combustion of oil (16%) and coal (70%).

The major identified sinks for SO_2 are precipitation scavenging, chemical conversion, and absorption by soil, water, rocks and plants.

Sulfur is an element needed by plants for complete nutrition. At one time it was thought that plants satisfied their sulfur requirements only by absorbing sulfur from the soil. However, it has been demonstrated by Bromfield (1972) and Fried (1948), that atmospheric sulfur can and does play a major role in satisfying a plant's sulfur requirements. Atmospheric SO_2 enters the leaf primarily through the stomata. Once inside the leaf, SO_2 is transformed into sulfite followed by oxidation to sulfate. Both sulfite and sulfate can be toxic to plants. However, according to Thomas et al. (1943), sulfite ion is 30 times more toxic than the sulfate.

The effects of SO_2 on plants can be divided into two major categories: visible and subtle effects. Visible effects are produced on foliage by alterations in cellular pigmentation or by the development of characteristic foliar patterns and colorations as the result of death of cells. Subtle effects are not as readily identifiable and can usually be recognized only by monitoring plant growth, productivity or selected physiological parameters.

Visible effects may be divided into acute and chronic injury. Although the mechanism by which vegetation is injured by SO_2 is not fully understood, the rate of sulfite accumulation appears to be important. Acute SO_2 injury is characterized by cell death as a result of exposure to high concentration of SO_2 for short periods of time (few to several hours). In this instance, there is a rapid accumulation of toxic sulfite ions beyond the plant's conversion ability to form sulfate. Acute SO_2 injury on broadleaf plants is characterized by areas of necrotic tissue located between veins, (interveinal necrosis) (Figure 2.5-1). These areas of necrotic tissue are usually ivory colored at first, but with time may turn brown to reddish-brown. With conifers, acute SO_2 injury usually appears first at the needle tip and subsequently extends toward the base. The affected tissue appears reddish-brown in color (Figure 2.5-1).

Chronic injury develops from long-term exposure (several days to weeks) to low levels of SO_2 with intermittent peak concentrations. In this case, the rate of accumulation of sulfite is slow and does not exceed the plant's ability to oxidize it to sulfate. No injury is visible until sufficient sulfate accumulates to produce an effect. Chronic injury is characterized by a bleaching of chlorophyll resulting in chlorosis or yellowing of the leaf without the cells being killed. Under certain conditions, the leaves may appear to be experiencing normal senescence, but resulting in premature leaf drop.

Figure 2.5-1. Symptoms of acute injury induced on broadleafed and coniferous vegetation by sulfur dioxide and fluoride.

A: Acute injury on broadleafed aster induced by sulfur dioxide. Note the typical interveinal necrosis.

B: Acute injury on larch induced by sulfur dioxide. Note extensive needle necrosis.

C: Acute injury on bigtoothed beech induced by fluoride. Note the typical marginal and tip necrosis.

D: Acute injury on loblolly pine induced by fluoride. Note extensive needle necrosis.

A

B

C

D

FIGURE 25-1

Subtle injury is usually difficult to detect and is characterized by reduced growth, yield or reproduction without the appearance of visible foliar symptoms. Reduced growth without the development of visible foliar symptoms have been reported by Tingey et al. (1971), Reinert et al. (1969) and Bleasdale (1952).

2.5.1 Dose-response relationships.

Relationships between SO_2 dosages and the occurrence of visible symptoms of injury on higher plants have been adequately described in the EPA criteria document (EPA-R3-73-030,1973). Data for SO_2 dosages that produce threshold injury to vegetation has been summarized by Heggestad and Heck (1971) and by EPA (1973). This information is presented in Table 2.5-1. These data, for the most part, are based on continuous exposure of vegetation under controlled conditions to the given concentrations of SO_2 for a particular time period. Under ambient conditions, vegetation is exposed to fluctuations in SO_2 concentrations that can vary considerably in intensity. The data in Table 2.5-2 (Jones et al., 1974) are based on observations of visible injury on over 120 species of vegetation growing in the vicinities of coal-fired steam plants in the southeastern United States over a 20-year period (Jones, unpublished) and around smelters in Canada (Dreisinger and McGovern, 1970). In comparing the dat~~e~~a in Tables 2.5-1 and 2.5-2, the range in values for threshold injury in both the intermediate and the resistant groups of plants under controlled condition exposures tends to be considerably higher than those exposed to SO_2 under ambient conditions.

Table 2.5-1. Projected sulfur dioxide concentrations that will produce threshold injury to vegetation for short-term exposures[a] (From "Effects of Sulfur Oxides in the Atmosphere on Vegetation," Revised Chapter 5 for *Air Quality Criteria for Sulfur Oxides*. EPA-R3-73-030, September 1973)

Time (hours)	Concentration Producing Injury in Three Susceptibility Groups of Plants					
	Sensitive		Intermediate		Resistant	
	ug/m^3	(ppm)	ug/m^3	(ppm)	ug/m^3	(ppm)
0.5	2620 to 10,480	(1.0 to 4.0)	9170 to 31,440	(3.5 to 12)	26,200	(10)
1.0	1310 to 7860	(0.5 to 3.0)	6550 to 26,200	(2.5 to 10)	20,960	(8)
2.0	655 to 5240	(0.25 to 2.0)	3930 to 19,650	(1.5 to 7.5)	15,720	(6)
4.0	262 to 2620	(0.1 to 1.0)	1310 to 13,100	(0.5 to 5)	10,480	(4)
8.0	131 to 1310	(0.05 to 0.5)	524 to 6550	(0.2 to 2.5)	5240	(2)

---

[a] Values were developed from subjective evaluations of injury reported in the literature where both time and concentration were considered. In most cases the concentrations and times shown for each susceptibility grouping are reasonable only when the plants are growing under sensitive environmental conditions.

Table 2.5-2. Sulfur dioxide concentrations causing threshold injury to various sensitivity groupings of vegetations[a]

Maximum Average Concentration	Sensitivity Grouping		
	Sensitive ($ppm\ SO_2$)	Intermediate ($ppm\ SO_2$)	Resistant ($ppm\ SO_2$)
Peak	1.0-1.5	1.5-2.0	2.0
1-Hour	0.5-1.0	1.0-2.0	2.0
3-Hour	0.3-0.6	0.6-0.8	0.8
	Ragweeds	Maples	White Oaks
	Legumes	Locust	Potato
	Blackberry	Sweetgum	Upland Cotton
	Southern Pines	Cherry	Corn
	Red and Black Oaks	Elms	Dogwood
	White Ash	Tuliptree	Peach
	Sumacs	Many Crop and Garden Species	

---

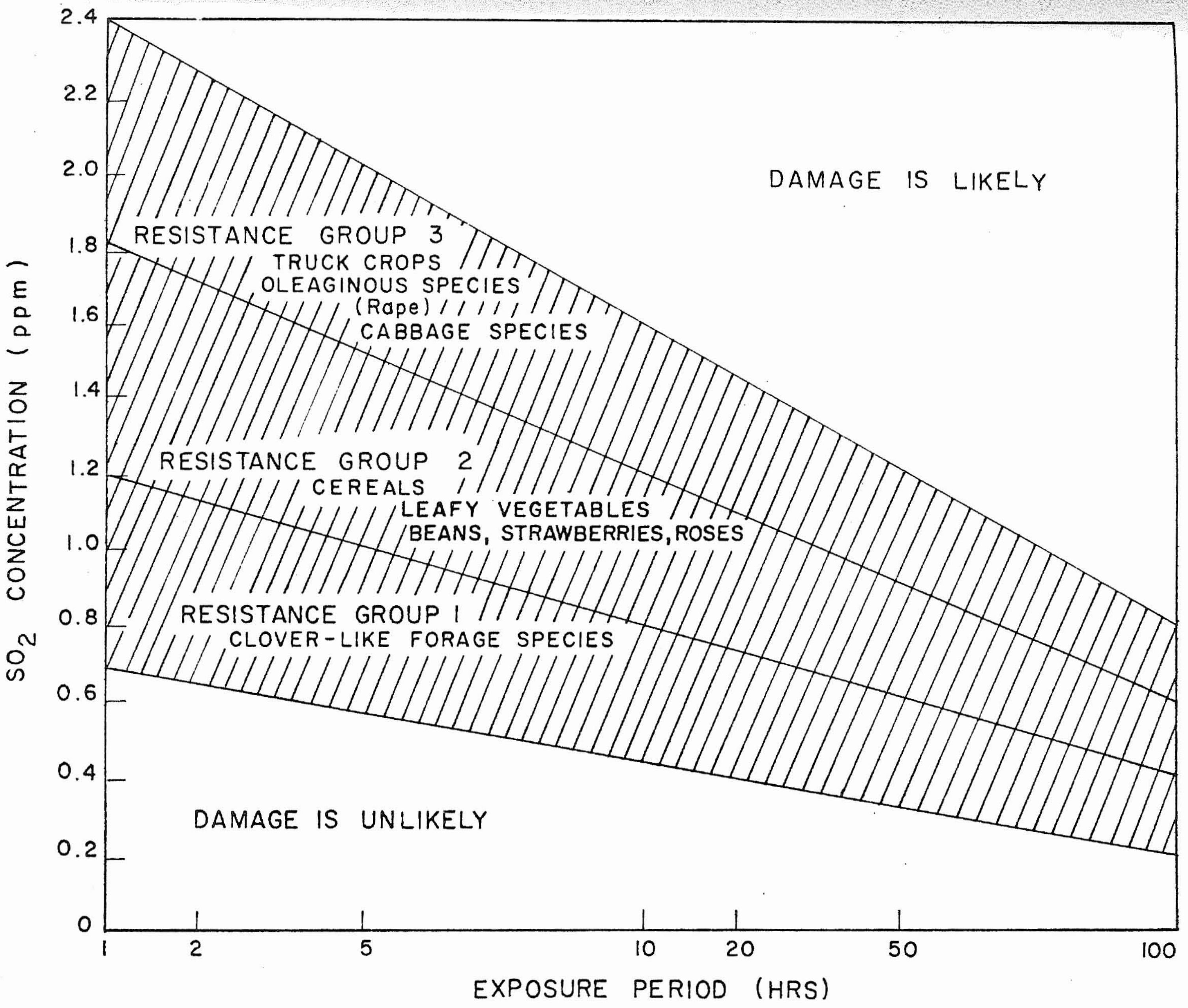
[a] Based on observations over a 20-year period of visible injury occurring on over 120 species growing in the vicinities of coal-fired power plants in the southeastern United States.

According to Jones et al. (1974) threshold injury to sensitive vegetation may be produced by relatively short-term exposures in which the maximum 1-hour average SO_2 concentration equals or exceeds 0.5 ppm. However, some species and some genetically sensitive individuals within species, particularly among the legumes and confiers, may be injured by SO_2 expsoures that exceed 0.25 ppm, maximum 30-minute average for several hours (Materna et al. 1969; Linzon, 1971). On the other hand, it appears that native desert species require exposure to more than 2.0 ppm SO_2 for 2 hours to be significantly affected (Hill et al. 1974).

For most field investigations of damage to vegetation in the ambient environment, such as those conducted at Trail, British Columbia (National Research Council of Canada, 1939), Sudbury, Ontario (Dreisinger and McGovern, 1970; Linzon, 1971; Dreisinger, 1965), and Biersdorf, Germany (Gudarian and Stratmann, 1962 and 1968; Gudarian, 1960; Stratmann, 1963), the SO_2 exposures that caused damage were frequent, sometimes were of long duration, and contained maximum 30-minute peak concentrations that frequently exceeded 1.0 ppm.

Zahn (1961), using Stratmann's equation for calculating "irritant" threshold values (Stratmann, 1958) for plants summarized data (Figure 2.5-2) relating SO_2 dosages to visible injury and damage in a graphic form. The threshold values are consistent with published data, and the graph appears to be useful as a general guide for estimating SO_2 dosages that could potentially cause visible injury and damage. Zahn cautioned, however, that there is considerable scatter over the range of the data, and that these data are only valid for continuous SO_2 exposures without long interruptions, which tend to mitigate injury or damage.

Figure 2.5-2. Sulfur dioxide concentrations that may produce threshold injury (hatched area) to vegetation with continuous exposure for various periods of time. (From Zahn, 1961).


DAMAGE IS LIKELY
RESISTANCE GROUP 3
TRUCK CROPS
OLEAGINOUS SPECIES
(Rape)
CABBAGE SPECIES
RESISTANCE GROUP 2
CEREALS
LEAFY VEGETABLES
BEANS, STRAWBERRIES, ROSES
RESISTANCE GROUP 1
CLOVER-LIKE FORAGE SPECIES
DAMAGE IS UNLIKELY
SO_2 CONCENTRATION (ppm)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
1
2
5
10
20
50
100
EXPOSURE PERIOD (HRS)

As far as subtle effects are concerned, with the current state of our knowledge, it would be difficult to establish definite general relationships between effects and reported low SO_2 dosages.

2.5.2. Plant response to SO_2.

The response of a plant to SO_2 is a function of the dosage, plant's genetic constitution, its growth stage and the environmental conditions of exposure. Genetic constitution controls both inter and intraspecific differences in susceptibility. Related species and varieties within a species may show considerable variation in response. Even within a variety, individual members will often show a high degree of variation in their response to SO_2. For example in a cross-pollinated white pine stand, under ambient conditions, in general only 12% - 20% may show visible symptoms of injury.

Setterstrom et al. (1939) and Webster (1969) have shown that in general, plant leaves are most sensitive to SO_2 just after full expansion. On the other hand, older and younger leaves are more resistant to injury.

The environmental conditions under which a plant is exposed to SO_2 affect symptom development, primarily through their influence on stomatal opening, photosynthesis and other physiological activities. Moisture stress or drought conditions reduces vegetational response to SO_2 (Thomas et al., 1943; Zimmerman and Crocker, 1934). Zimmerman and Crocker (1934) found that plants exposed in the dark were not injured by SO_2 dosages which produced injury during exposures in light. Light also affects plant sensitivity through photosynthesis. Exposure to SO_2

at temperatures below 40° F were reported by Setterstrom and Zimmerman (1939) to produce less injury than exposures at higher temperatures.

Even though it is difficult to compare the results of various researchers each of whom has employed a different experimental design and injury evaluation system, generalized list of SO_2 sensitive species have been developed from laboratory and field observations.

Some examples are listed in Table 2.5.2-1.

2.5.3. Interactions between SO_2, other pollutants and vegetational effects.

Menser and Heggestad (1966) were the first to report that exposure of Bel W-3 tobacco to mixtures of SO_2 and ozone caused more injury than exposure to either of the pollutants alone. Since then other investigators (Dochinger *et al.* 1970; Jaeger and Banfield, 1970; Tingey *et al.* 1971) have presented data that suggest that exposures to SO_2 in combination with either O_3 or NO_2 may produce more pronounced effects on several species of vegetation than would exposure to any of the single pollutants. Interactions were generally observed at concentrations of SO_2, O_3, or NO_2 up to 0.5, 0.1 and 0.2 ppm, respectively. Data for effects caused by interactions of pollutants can be considered only preliminary, because considerably more research is needed, particularly in demonstrating the occurrence of such interactions in field situations.

2.5.4. Effects on lichens and bryophytes.

Most of the research involving lichens and bryophytes has been oriented toward the survival of particular species within regions of differing concentrations of SO_2. The influence of SO_2 and other environmental parameters as related to the decrease in the abundance of

Table 2.5.2-1. Some Plant Species Known to Be Sensitive to SO_2

American elm	(*Ulmus americana*)
Beech	(*Fagus sylvatica*)
Bigleafed aster	(*Aster macrophyllum*)
Bind weed	(*Convolvulus arvensis*)
Birch	(*Betula* spp)
Bromegrass	(*Bromus* spp)
Clover	(*Melilotus* and *Trifolium* spp)
Curly Dock	(*Rumex crispus*)
Dandelion	(*Taraxacum officinale*)
Eastern White Pine	(*Pinus strobus*)
Fleabane	(*Erigeron canadensis*)
Gooseberry	(*Ribes* spp)
Lamb's quarters	(*Chenopodium album*)
Larch	(*Larix* spp)
Pigweed	(*Amaranthus retroflexus*)
Plantain	(*Plantago major*)
Ragweed	(*Ambrosia* spp)
Saskatoon serviceberry	(*Amelianchier alnifolia*)
Smartweed	(*Polygonum* spp)
Sorrel	(*Rumex* spp)
Wild grape	(*Vitis labrusca*)

these organisms has been reviewed by Barkman (1968); Gorham and Gordon (1960); LeBlanc and DeSloover (1970) and LeBlanc and Rao (1975). Evidence has been presented that SO_2 ~~was~~ is the primary agent responsible for the impoverishment of lichens and bryophytes near areas of industrialization. Numerous reports have related reductions in the number of species with mean SO_2 concentrations over various averaging periods (Table 2.5.4-1). It is generally accepted that low concentrations over long periods are more deleterious to lichens and bryophytes than higher concentrations for short periods. However, little evidence has been presented to support this view.

2.6 Effects of Atmospheric Sulfur on Forest Ecosystems.

Atmospheric sulfur may affect the health and efficiency of a forest ecosystem in various ways (Linzon, 1975). Forest communities have evolved and become established through the selective pressures of the environment. The addition of a new pressure, such as increased atmospheric sulfur, can alter the delicate balance of the ecosystem. This alteration may be deleterious or beneficial depending on both the magnitude of the addition and the state of the receptor.

According to Smith (1974) there are three types of forest ecosystem effects arising from exposure to various dosages of atmospheric air pollutants: I. Under low dosages, the vegetation and the soil of the ecosystem may act as a sink, with no detectable effects occurring except for an increase in nutrient levels, possibly accompanied by a stimulatory-fertilization effect. II. Under conditions of intermediate dosages, individual trees may be adversely or subtly affected by the

Table 2.5.4-1. Average sulfur dioxide concentrations resulting in a decrease in the number of epiphytic lichen and bryophyte species.

SO_2 Concentration (ppm)	Averaging Period	Research Area	Reference
0.015	Annual	Stockholm, Sweden	?
0.020	Winter (Oct.-April)	Newcastle, England	
0.015-0.03	Annual	Belfast, Ireland	
0.005-0.01	Summer (May-Oct.)	Sudbury, Canada	

nutrient stress, reduced photosynthetic rate, and predisposition to diseases caused by fungi, insects, etc. III. Under conditions of high dosages, acute morbidity or mortality of specific trees occurs, which may seriously alter the structure and function of the ecosystem.

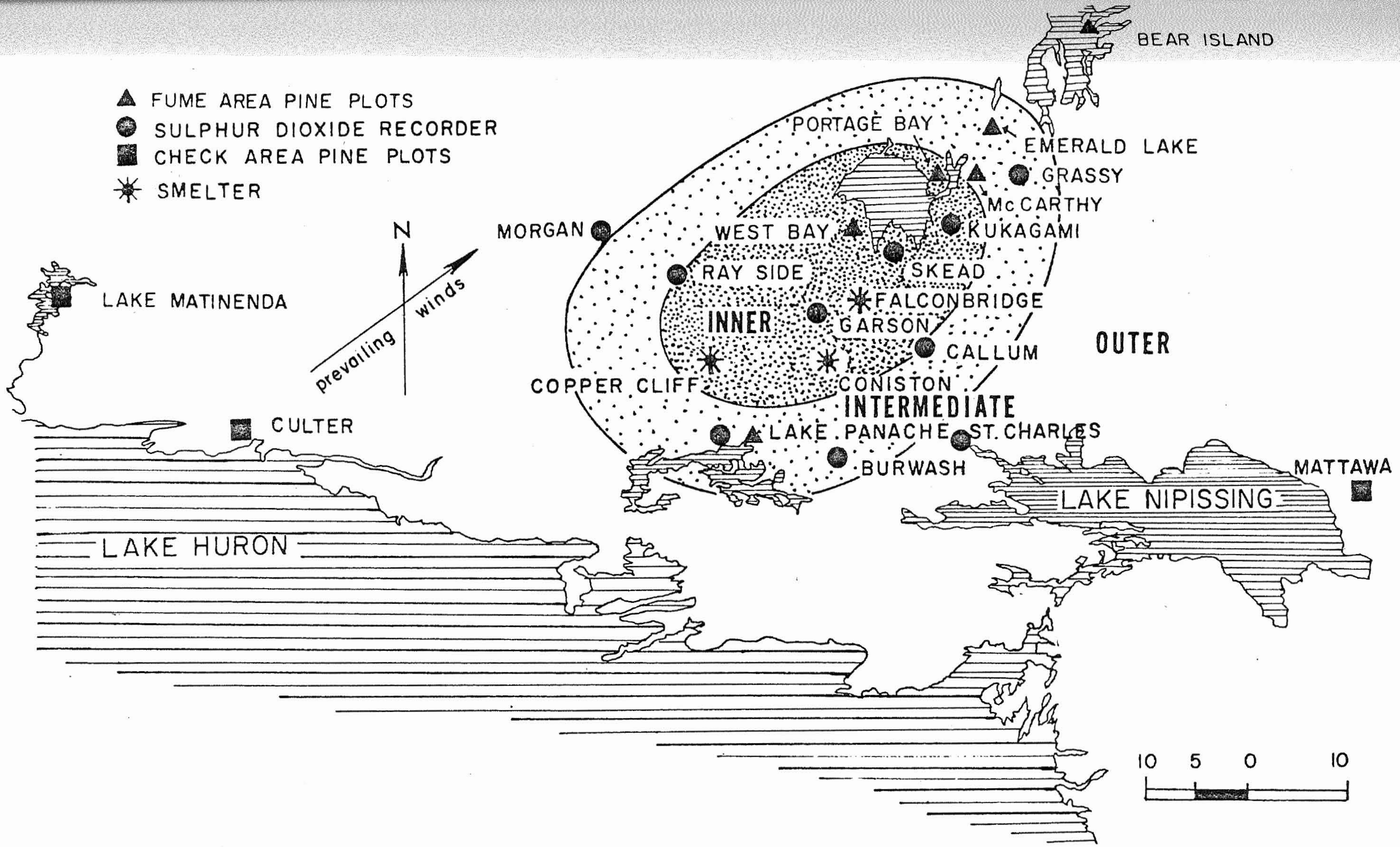
Acute injury has been found to develop on forest trees in the presence of the following SO_2 doses: 0.95 ppm for 1 hour, 0.55 ppm for 2 hours, 0.35 ppm for 4 hours and 0.25 ppm for 8 hours (Dreisinger, 1965; Linzon, 1958). Excessive chronic effects on forest growth have been reported from Canada in areas where air concentrations exceeded 0.017 ppm SO_2, the arithmetic mean for the total measurement period (5 month growing season) (Linzon, 1973). Numbers of epiphytic lichens on balsam poplar (*Populus balsamifera*) were drastically reduced in Canada in zones where the seasonal mean levels of SO_2 were over 0.02 ppm (LeBlanc *et al*. 1972). Similar results have also been reported from Sweden (Skye, 1964) and England (Gilbert, 1968).

2.6.1. Forest ecosystem effects in the vicinity of copper and nickel smelters.

In the Sudbury area of Ontario, three large nickel and copper smelters had discharged roughly 7000 tons of SO_2 per day into the surrounding atmosphere by the 1960's. Forest damage was highly significant in the area, with acute injury on trees occurring up to 25 miles northeast of Sudbury (Linzon, 1958).

Based on studies over a 10-year period, the Sudbury area of Ontario was segregated into three fume zones: inner, intermediate and outer (Linzon, 1966). In the inner fume zone (Figure 2.6.1-1), an area of roughly

Figure 2.6.1-1. Forest damage survey: Sudbury, Ontario sulfur fume damage area. The hatched area is subject to frequent SO_2 fumigations and severe tree damage. The elliptical area surrounding the inner fume zone is subject to less frequent SO_2 fumigations and little tree damage. From Linzon (1975).


FUME AREA PINE PLOTS
SULPHUR DIOXIDE RECORDER
CHECK AREA PINE PLOTS
SMELTER
N
prevailing winds
BEAR ISLAND
PORTAGE BAY
EMERALD LAKE
GRASSY
McCARTHY
KUKAGAMI
MORGAN
WEST BAY
RAY SIDE
SKEAD
FALCONBRIDGE
INNER
GARSON
OUTER
CALLUM
CONISTON
COPPER CLIFF
INTERMEDIATE
LAKE MATINENDA
CULTER
LAKE PANACHE
ST. CHARLES
BURWASH
MATTAWA
LAKE NIPISSING
LAKE HURON
10 5 0 10

720 square miles, white pine (Pinus strobus) trees displayed acute and chronic injury resulting in reduced radial and volume growth and in excessive tree mortality. In the intermediate fume zone, an area of 1600 square miles, minimal SO_2 damage was found, while in the outer fume zone, atmospheric contamination was too dilute to cause visible injury.

Chronic injury symptoms develop slowly on coniferous foliage, with the greatest increase in the injury in Sudbury area occurring on the one year old needles of eastern white pine (Linzon, 1971).

Chemical analysis of vegetation (Table 2.6.1-1) in the Sudbury area shows the accumulation and build-up of sulfur in the foliage of vegetation close to the sources (Linzon, 1973).

The comparative sensitivity or resistance of various tree species to SO_2 has been noted in forest damage studies in North America since the turn of the century (Katz et al. 1939; Scheffer and Hedcock, 1955). Table 2.6.1-2 lists a selection of trees according to their comparative sensitivity to SO_2 compiled by Linzon (1975) from results obtained by various investigators.

It has been observed in the Sudbury area that other biological effects can occur as a result of atmospheric contamination. Blister rust of white pine (Cronartium ribicola) was found to be practically non-existent in areas close to the sulfur source, and the incidence of weevil insect injuries was less compared to the control areas (Linzon, 1958; 1971). In addition it has been observed that felled trees persist on soil surface for lengthy periods with little subsequent decay.

Studies conducted on the occurrence of lichens in the Sudbury area (LeBlanc et al. 1972) showed that in zones where the seasonal mean

Table 2.6.1-1. Results of Chemical Analyses for Total Sulphur (%) in Foliage at Various Distances from Sudbury Smelters--1971.

Location	Collection Month -1971	Current Foliage	Jack Pine 1-yr.-old Foliage	White Birch Foliage
Skead	June	-	0.19	0.33
	July	-	0.20	0.61
	August	0.23	0.28	0.68
	Average	0.23	0.22	0.54
Kukagmi Lake (27 miles NE)	June	-	0.15	0.21
	July	-	0.22	0.26
	August	0.15	0.14	0.40
	Average	0.15	0.17	0.29
Grassy Lake (40 miles NE)	June	-	0.13	0.26
	July	-	0.11	0.22
	August	0.14	0.15	0.25
	Average	0.14	0.13	0.24
Blind River (100 miles W)	June	-	0.10	0.13
	July	-	0.07	0.12
	August	0.12	0.12	0.16
	Average	0.12	0.10	0.14

Table 2.6.1-2. Sensitivity of Trees to SO_2

Sensitive	Intermediate	Tolerant
Black Willow	Austrian Pine	Balsam Poplar
Chinese Elm	Balsam Fir	Carolina Poplar
Douglas Fir	Basswood	Grand Fir
Eastern White Pine	Catalpa	Little-leaf Linden
Jack Pine	Choke Cherry	Lodgepole Pine
Largetooth Aspen	Eastern Cottonwood	London Plane
Manitoba Maple	Engelmann Spruce	Red Oak
Ponderosa Pine	Mountain Maple	Silver Maple
Trembling Aspen	Red Pine	Sugar Maple
Western Larch	Western Hemlock	Western Red Cedar
White Ash	Western White Pine	White Cedar
White Birch	White Elm	White Spruce

Trees listed in alphabetical order.

levels of SO_2 were over 0.02 ppm, the number of epiphytes growing on balsam poplar were drastically reduced. Lichen prevelance observed in zones around the study site related to their sensitivity to SO_2. Bacidia chlorococca, Lecanora saligna, and Parmelia sulcata were found in all pollution zones, but none of these were recorded within a radius of 4 miles from Sudbury. Xanthoria fallax, X. polycarpa, Physcia orbicularis and Parmelia rudecta were first encountered beyond 21 miles from Sudbury.

A study conducted in the northeasterly direction from the Falconbridge smelter in the Sudbury area (Gorham and Gordon, 1960) revealed strong sulfate accumulation in the surface soils up to one mile; and in pond and lake water up to two miles from the source. Floristic studies showed a reduction in the number of terrestrial plant species close to the smelter. Climbing buckwheat (Polygonum cilinode) and red-berried elder (Sambucus pubens) were the most tolerant herbaceous plant species, and red maple (Acer rubrum) and red oak (Quercus rubra) were the most tolerant tree species, occurring within one mile of the source. The most sensitive herbaceous and tree species were sour-top blueberry (Vaccinium myrtilloides) and white pine, respectively. These species were not encountered until a distance of 16 miles northeast of the smelter.

2.6.2. Forest ecosystem effects in the vicinity of an iron sintering plant.

In the Wawa area of Ontario, an iron sintering plant emitted annually about 200,000 tons of SO_2 into the atmosphere. Since the prevailing winds are southwesterly during the vegetational growing season, the forest toward the northeast was found to be affected.

Three categories of vegetational damage were mapped based on the effects on white birch and these were "total kill", "heavy kill" and "light damage". In 1970 the areas in square miles for the three categories were 41.9 (total kill), 73.8 (heavy kill), and 227.4 (light damage), for a total of 343.1 square miles of affected forest (Linzon, 1975) (Figure 2.6.2-1).

In studies conducted by the Phytotoxicology section of the Ontario Air Resources Branch, significant correlations were found between sulfur levels in the air as detected by sulfation candles and sulfur levels in the vegetation (Table 2.6.2-1).

An ecological survey was conducted in the Wawa area in 1960 (Gordon and Gorham, 1963). Within about 10 miles northeast from the sinter plant, ground flora declined markedly from about 20-40 species per 40 square meter quadrat beyond this distance to 0-1 species within 2 miles of the source. The most sensitive tree species was white pine, not being observed within 30 miles of the source, while white spruce (Picea glauca), black spruce (P. mariana), and trembling aspen (Populus tremuloides) were not observed within 15 miles. As was the case in Sudbury, climbing buckwheat and red-berried elder were the most tolerant herbaceous plant species.

During the summers of 1965 and 1966 a study of epiphytic flora was conducted in the Wawa area (Rao and LeBlanc, 1967). No epiphytes were recorded within 16.1 kilometers northeast of the source. Beyond that point, epiphytic "desert" corticolous lichens and bryophytes

Figure 2.6.2-1. Forest damage survey Wawa sulfur fume area 1970. Control plot 7 is NNE and control plot 8 is SW of the illustrated area. From Linzon (1975).

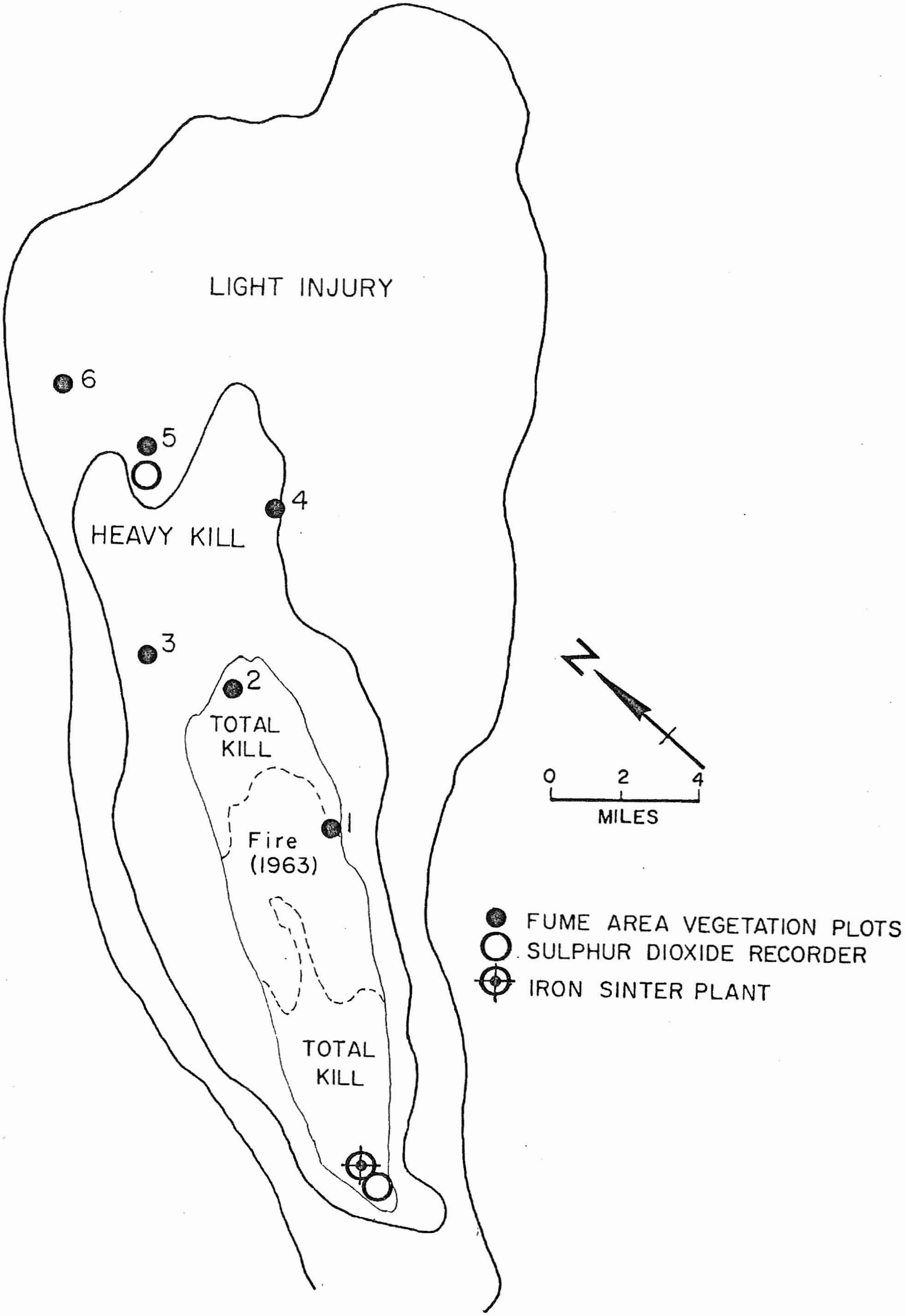

LIGHT INJURY
6
5
4
HEAVY KILL
3
2
TOTAL KILL
1
Fire (1963)
TOTAL KILL
N
0
2
4
MILES
● FUME AREA VEGETATION PLOTS
○ SULPHUR DIOXIDE RECORDER
IRON SINTER PLANT

Table 2.6.2-1. The Correlation Coefficient and Regression Equation of the Air Candle Sulphation Rate and the Total Sulphur (5) in Vegetation Samples - Wawa 1970, 1971 and 1972.

Plot No.	Distance and Direction from Sinter Plant	Average Sulphation Rate mgm $SO_3/100\ cm^2$/day			Average Concentration of Total Sulphur (%) in Vegetation		
		1970	1971	1972	1970	1971	1972
1	10 mi. NE	1.03	1.48	1.55	0.24	0.44	0.51
2	12 mi. NE	0.61	0.88	0.87	0.25	0.36	0.44
3	16 mi. NE	0.57	0.36	0.42	0.22	0.27	0.36
4	19 mi. NE	0.25	0.39	0.38	0.19	0.30	0.28
5	22 mi. NE	0.35	0.26	0.35	0.22	0.30	0.34
6	24 mi. NE	0.25	0.20	0.19	0.17	0.25	0.26
7 (Control)	38 mi. NE	0.08	0.12	0.11	0.17	0.21	0.23
8 (Control)	35 mi. NW	0.04	0.04	0.02	0.18	0.26	0.21

Correlation Coefficient	$r = 0.84^*$	$r = 0.96^{**}$	$r = 0.95^{**}$
Regression Equation	$Y = 0.08x + 0.17$	$Y = 0.14x + 0.23$	$Y = 0.20x + 0.23$

**Significant at 1% level
*Significant at 5% level

Note: data for Betula papyrifera? (see p. 41) gradually appeared. Nearest to the source *Bacidia chlorococca* and *Cladonia coniocraea* were the only species and appeared only on the bases of trees. At greater distances, they gradually appeared on the trunks of trees. There appeared to be a sequence of increasing sensitivity from crustose to foliose to fru~~ct~~ticose lichens and bryophytes. The maximum number of species found on one tree occurred at 43.5 Km northeast.

2.7 SO_2 - Vegetational injury evaluation techniques.

The following criteria play an important role in evaluating SO_2 effects on vegetation:

a. Assessment of the type (s) of source (s) in the study area.
b. Meteorological conditions of the study area with emphasis on geography and topography.
c. Selection of study plot design and distribution.
d. Selection of existing vegetational species for study.
e. Vegetational injury surveys including growth increment studies and expression of injury data.
f. Foliar-total sulfur-analysis procedures including sampling.
g. Soil-available sulfur-analysis procedures including sampling.
h. SO_2 fumigation studies under known environmental conditions in the laboratory.
i. Field fumigation studies including open-top chambers and fumigation of vegetational parts.
j. Introduction of bioindicators.
k. Correlations and interpretations.

The objective of this section is not to review in depth all the aforementioned criteria but to mention some salient points under each category. For details, the reader is referred to Krupa et al. (1977).

a. Prepollution background studies are an asset to evaluating the effects of SO_2 from point sources on vegetation. The type of pollutant source (s) in the study area must be evaluated. The strategy of investigation should be devised to suit single point source, multiple point sources, area or regional source or a line source, depending on the need. In addition to SO_2, potential major primary and secondary phytopathogenic air pollutants in the study area should be identified.

b. In terms of pollutant dispersion, transport, deposition and vegetational effects, an understanding of the regional and local weather conditions and patterns are critical. Severe vegetational injury from point source plumes occur under fumigation and trapping conditions. In terms of vegetational injury, as mentioned previously, weather parameters such as temperature, relative humidity, cloud cover, radiation, etc., are important. Experimentally verified dispersion models and reverse trajectory data are extremely valuable in evaluating vegetational impacts around point sources. In many instances wind direction and velocity data coupled with isopleths are used in air monitoring studies. While experimentally verified isopleths are useful in the case of in-land study sites, wind trajectories and corridor pollutant dispersion systems should be considered in cases of land areas adjoining large water masses (Lyons, 1974). Due to frequent variations in vertical and horizontal mixing, deviations in the path of corridor dispersion of point source plumes are difficult to predict within the general direction. In addition, in all cases wind dispersion as influenced by the given topography should not be ignored. For details, the reader is referred to Hoydish and Sabetta (1975) and Bessemoulin et al. (1975).

c. Selection of study plot design and distribution is extremely critical in evaluating SO_2 effects on vegetation.

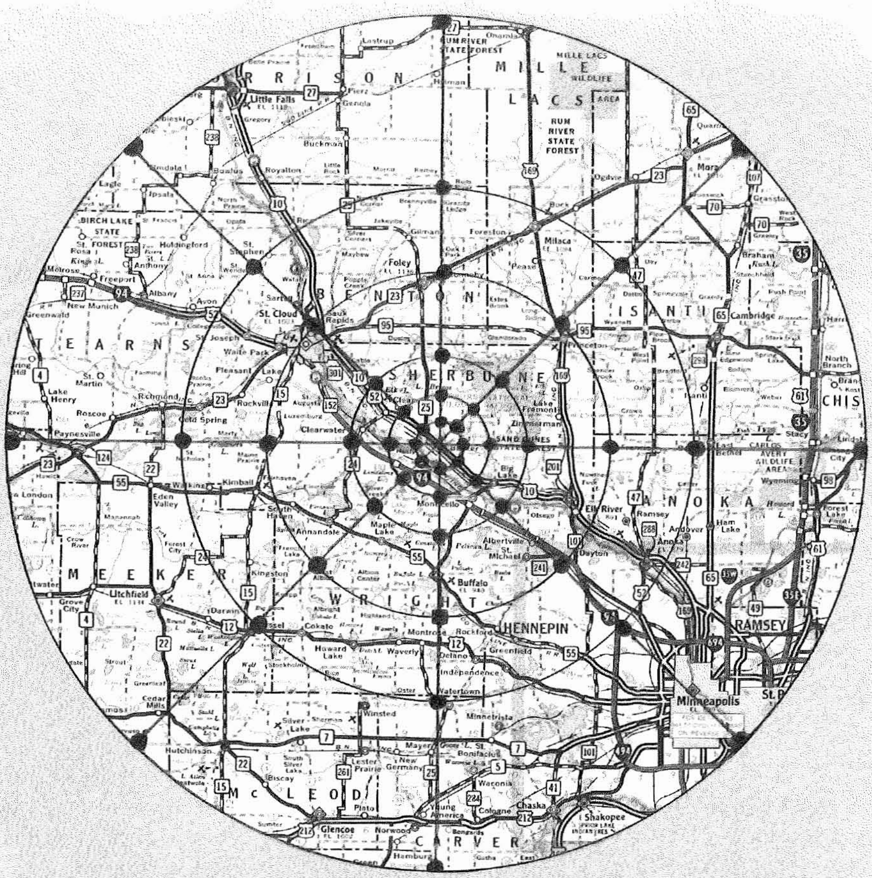
With single point sources, the most frequently used study plot distribution consists of the radial gradient design (ref. Krupa and Kohut, 1976) (Figure 2.7-1). In many cases, as a modification of this, greater numbers of plots have been differentially distributed in the predominant wind direction during the vegetational growth season or in the direction of observed injury zones in the post-operative studies.

In cases where multiple point sources are separated by distances of, for example, 5 to 10 miles, there may be a need to use a disproportionate grid system (Figure 2.7-2). This is in contrast to a uniform or proportionate grid system used to evaluate area sources.

The aforementioned distribution patterns are by no means universal. Several other approaches have been used by other investigators.

As far as the selection of study plot design is concerned, both circular and rectangular plots have been used. Sizes varying from 1 m x 1 m quadrat to 1/2 acre plots have been used. In terms of vegetational sampling for foliar analysis, in many cases plot size is dictated by the availability within close proximity to each other, of a sufficient number of replicates of a given plant species. However, where plant community and population studies are being conducted, it is advisible

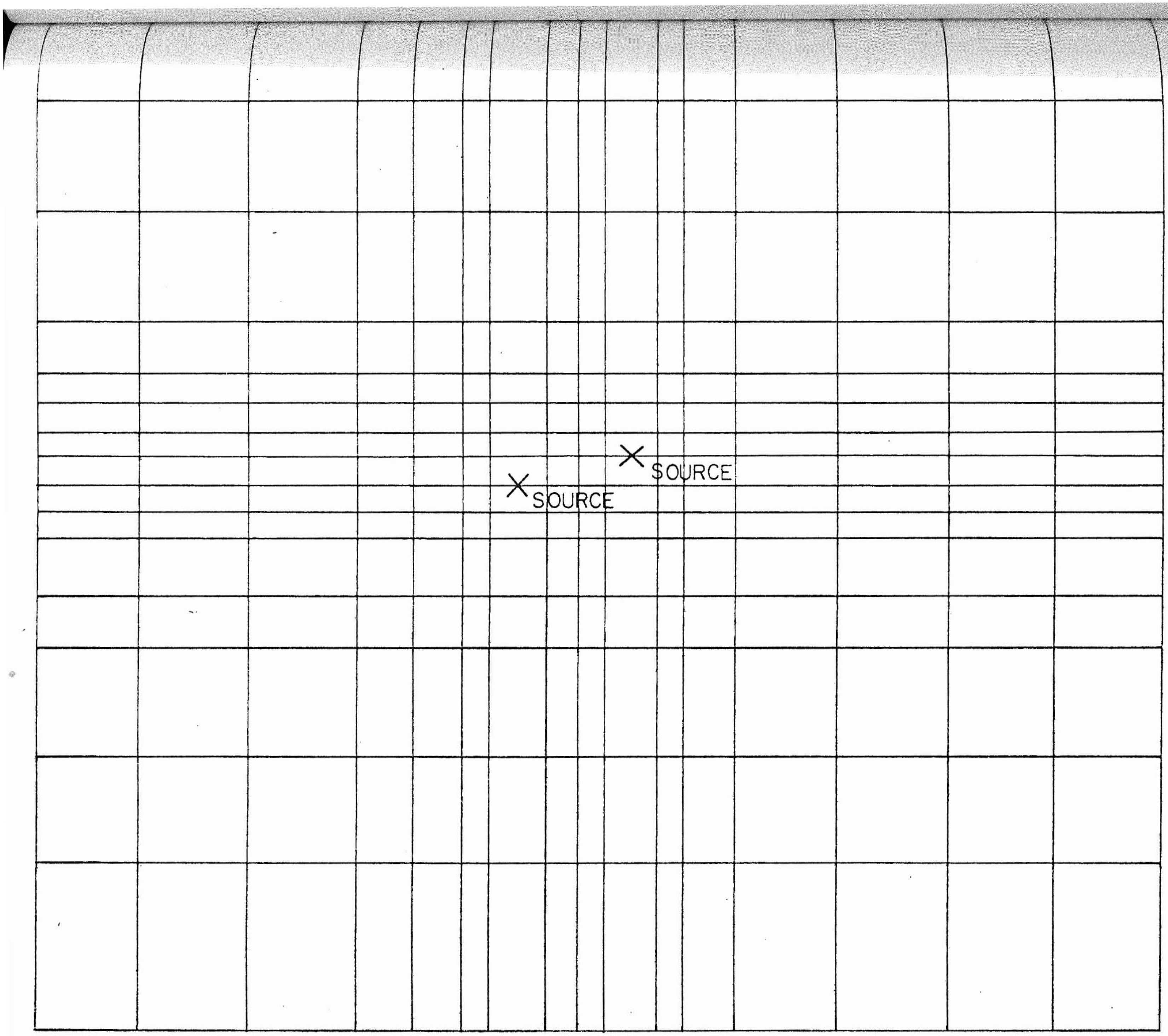
Figure 2.7-1. Radial gradient study plot distribution design around a single point source. Black dots in the figure represent study plots located at 2.5, 5, 10, 20, 40 and 50 miles from the point source in 8 different directions. From Krupa and Kohut (1976).



Study areas within a 50mile radius of

Sherburne County Power Plant, Becker, Minnesota

Figure 2.7-2. Disproportionate grid study plot distribution design around closely located multiple point sources.



N

SCALE
1cm =
Roughly
5
Miles

PLOTS ARE LOCATED
IN THE CENTER OF
EACH SQUARE

to work with small plots. Variation is known to increase in soil and foliar chemical composition with increase in size of the study plot, beyond a threshold. what? ref.? ?

d. Selection of proper plant species within the available vegetational population is dependent upon ~~some~~ criteria such as:

1. Pollutant (s) in question (SO_2).
2. Plant species known to be sensitive to (SO_2) the pollutant (s) under study.
3. Type of response expected--short-term acute effects vs long-term decline.
4. Accumulators vs sensitive plant species, etc.
5. Annuals vs perennials.
6. Abundance within the study area.
7. Presence or absence of other stress problems on the vegetation selected for study.

e. Vegetational injury surveys should be performed ~~during~~ several times within a growing season and over several growing seasons. This should include both established study plots as well as others at random within the total study area and should include all major plant species. In an ideal situation, in most geographic areas, the evaluation should be performed by an entomologist-virologist, a plant pathologist, a forest pathologist and a soil scientist. As much as possible, evaluation should be supported by photographs, proper identifications and descriptions, laboratory examination and other substantiative procedures.

Increment boring studies should be performed on trees free of any visible stress other than air pollution. Enough replicates should be used at each study site to facilitate statistical analysis. This may mean as many as 30 to 60 trees at each site. Weather, soil and biological data on an annual basis, should be available for the study sites. In addition, air quality monitoring data ~~is~~ are needed. Boring studies should be performed on a site system as closely identical as possible to the vegetational sampling program.

For the expression of SO_2 injury on plants, features such as disease indices, for example (ε - specific type of injury x % leaf area showing that type of injury / number of plants evaluated), number of leaves or needles annually maintained, degree of annual internodal growth, annual ring data, annual needle extension, per cent of plant area showing visible symptoms, etc., have all been used. For details on some of these, refer to Drummond and Pearson (1977).

f. Total sulfur and other elemental analysis of the foliage has been performed by many investigators (ref. Linzon, 1975, Krupa and Kohut, 1976). It is important that the foliage be sampled at a minimum of two points during the growing season: at the stage of full expansion of the leaf (about 5 weeks after budbreak) and at the stage of peak metabolic activity (about 5 - 6 weeks before the onset of fall colors). In an ideal case more sampling and analysis points are warranted. Same branch on a given tree in comparable position with the branches of all the replicative trees of visually comparable condition should be sampled during a growing season and during all other seasons. While individual tree analysis may involve as many as 30 or more replicates to determine the individual plant variation, due to economic restrictions, this may be circumvented by compound sampling with the use of as many as 30 trees over several sampling points during the growing season over at least a minimum of two growing seasons.

? ref ? conflicts with comment, top of page 52!

It is vital to preserve foliar samples in a dry condition for foliar sulfur analysis. Preservation of foliar samples in plastic bags on ice is a totally negative factor. Paper bags and ambient or room temperature for preservation are highly advisible. For foliar total sulfur analysis, refer to Krupa and Kohut (1976) and the Appendix of this report.

g. Available sulfur and other elements have been analyzed in the soil by many investigators (ref. Krupa and Kohut, 1976). It is important that the soil be sampled at least twice during the growing season. In areas with significant particulate fallout, samples will have to be collected more often. It is advisible to coordinate the location and time of soil sampling with foliar sampling. While it would be ideal to analyze several individual soil samples in a given study plot, in many cases it is sufficient to analyze compound samples. The compound samples will consist of 12 or more individual samples from a given plot, pooled together and serving as a composite for that plot. Generally top 6" of the soil is obtained as a core for analysis. Where more information, such as leaching, etc., are needed, it is advisible to obtain 6" - 12" soil cores also.

? ref. ?

While foliar samples should be preserved in paper bags until analysis, soil samples should be preserved in tightly sealed plastic bags. For elemental analysis of the soil, refer to Krupa and Kohut (1976) and the Appendix of this report.

In soil sampling, it is advisible to establish a specific point within the study plot and sample from that point at set locations at each sampling time and every growing season. For example, in the regional copper-nickel study, the center point of each study plot was identified with a stake and soil samples were obtained at 50 ft., 100 ft. and 150 ft. radial points in four directions (N, S, E and W).

h. Almost all the air pollution-vegetation research groups in the United States conduct exposure studies of vegetation to air pollution. Air pollutant fumigation chambers of assorted sizes, shapes and designs are currently in use. The basic requisites include the following criteria: a) temperature, relative humidity and light control. Temperature and relative humidity should be continuously recorded. b) in some cases a certain volume of air is exchanged every minute inside the exposure chamber for fresh filtered air to maintain acceptable CO_2 concentrations within the chamber to facilitate the normal photosynthetic activity of the plants. More recently continuous higher rate air flow or exchange systems have been employed in exposure chambers. It is highly advis~~i~~able to monitor CO_2 concentrations within the chamber on a continuous basis throughout the fumigation. c) there are several types of pollutant dispensing systems currently in use: both manual and self-controlling or automatic. The pollutant (s) concentration (s) should be monitored continuously throughout the exposure. Several types of SO_2 monitors are currently available in the market. These operate on principles such as: wet bubbling (West and

Gaeke), flame photometric, gas chromatography-flame photometric, coulometric, conductimetric, colorimetric and more recently pulsed fluorescence. In the recent years flame photometric and coulometric units have been highly popular. The pulsed fluorescence technique came into vogue in 1975 and is still fairly untested. The purpose of this section is not to review the merits and demerits of various instruments. For details, the reader is referred to the final report from the EPA (contract No. CPA 70-101, 1972) and evaluation papers in the Journal of the Air Pollution Control Association (1974-1976).

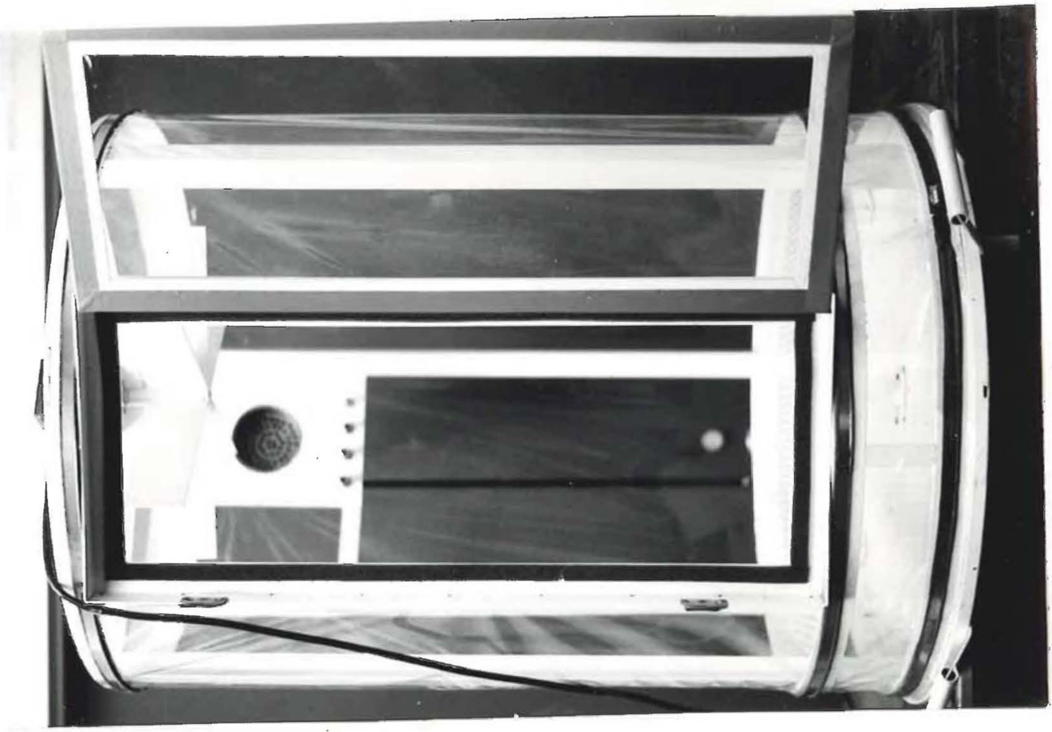
In addition to the aforementioned considerations, plants to be exposed to the pollutant (s) should be allowed to adapt to the exposure chamber conditions at least 2 - 3 days in advance of the exposure and should be allowed to remain in the chamber for a similar period after exposure. Injury evaluation procedures have been previously discussed. Figure 2.7-3 illustrates two different types of laboratory plant-pollutant exposure chambers. For details regarding the information discussed in this section, the reader is referred to Heagle and Philbeck (1977).

Plant growth and care before and after exposure to the pollutant are also important. Fertilizer addition, certain chemical sprays, drought vs.sufficiency of water, etc., affect plant injury. This subject has been reviewed by Brennan and Leone (1977). Other parameters such as stage of growth, varietal variation, etc., have been discussed previously in this report.

Figure 2.7.3. Laboratory plant exposure chambers to air pollutants.

Left - Controlled environmental air pollution exposure chamber, walk-in type. Model M2 Environmental Growth Chambers, Inc. Ohio.

Right - Circular teflon pollutant laboratory or greenhouse exposure chamber. Model developed at North Carolina State University.



i. Several investigators have performed air pollutant fumigation of vegetation under field conditions. Individual tree branches have been fumigated by Gerhold (1972) and more recently by Legge (1976) to study their responses to SO_2. In these studies either branches have been bagged and fumigated or cuvette type cells have been used through which the branch is inserted and sealed for exposure. F. A. Wood and his co-workers at Penn State University have used a system similar to that described for acid aerosols under Section 3.2 and Figure 3.2-1 of this report. More recently open-top chambers have come into vogue and have been utilized for field air pollutant fumigation (Mandl et al. 1973; Heagle et al. 1973). Figure 2.7-4 illustrates a modified open-top chamber (nozzle-top chamber) currently being used by the air pollution-vegetation effects group at the University of Minnesota. In these chambers the top is open but the outside air is substantially prevented from entering the chamber through the top, by introducing filtered or unfiltered air at the bottom through a plenum, thus creating a positive air flow from the bottom upwards. Known concentrations of a given pollutant (s) can be introduced into the chamber through the air flow system. While these chambers do not reproduce natural field conditions 100% due to a chamber effect, they offer the best available workable field study system at this time. These chambers have the advantage of being erected around already existing tree seedlings or crops. Alternatively vegetation can be planted within the chambers for exposure to pollutants in the ambient air or to artificially and additionally added pollutant (s). For details concerning these chambers, refer to the

Figure 2.7.4. University of Minnesota nozzle - open - top field chambers. For details, refer to Appendix 2.7.i.

Appendix of this report. EPA is currently experimenting with a field fumigation system for SO_2, known as the "ZAPP" (Zonal air pollution plots). In these studies tubes with holes at preset distances, are placed between rows of pre-planted vegetation. The holes in the tubes go through only one wall of the tube and face toward the foliage of the vegetation. Sulfur dioxide is dispensed through these tubes and the vegetation is fumigated throughout or periodically during the growth season under field condition. EPA is currently experimenting with 1 acre field plots. Criticism offered consists of: a) great variations exist in the SO_2 concentrations within small areas due to variations in microclimatology and b) economically unreal numbers of SO_2 monitors are required to monitor these variations so that appropriate corrections and interpretations can be made for dose-response relationships. These features become particularly critical in evaluating chronic and subtle vegetational effects.

j. Introduction and monitoring of responses of plants considered to act as biological indicators to a given pollutant, ~~has~~ have been performed by a number of scientists. This simply involves, in this case for example, introducing and maintaining a number of plants considered to be sensitive to SO_2. Care should be taken to introduce plants known to be native to the study area. One idea of plant introduction is to avoid the selection pressures that the native vegetation growing already in the study area might have survived and thus possible acquired resistance to the given pollutant (s). For details regarding this refer to Feder and Manning (1977). Plants considered to be sensitive to SO_2, which are suitable for the regional copper-nickel study are listed in Section 2.5.2 in this report.

k. Correlations and interpretations are vital to any research, particularly those oriented to field and environmentally oriented studies. In field studies involving SO_2 the following information is correlatable and is vital: a) ambient SO_2 dosages, b) weather conditions, c) stage of growth and varietal characteristics, d) soil chemistry including available S concentrations, e) foliar total sulfur concentrations, f) acute, chronic or subtle injury data, g) laboratory and field fumigation data and finally h) source characteristics.

Proper statistical design and analysis are vital. Procedures such as multiple factorial, correlative and regression analysis have been used by several investigators.

more details!!

3. Acidic Rain and Acid Aerosols.

3.1. Acidic rain.

3.1.1. Introduction.

Presently a phenomenon known as "acidic rain" is arousing a great deal of interest. Evidence has been presented to show that in some geographic areas, the acidity of rainfall has been increasing in recent years. This increase is largely attributed to atmospheric inputs of SO_2 and NO_2 from anthropogenic sources (Likens, 1972; Likens and Bormann, 1974; Likens *et al*. 1975).

Many scientists believe that rain in an unpolluted atmosphere should have a pH of 5.7 (this is the pH of a solution of CO_2 in water in equilibrium with the partial pressure of CO_2 in the atmosphere). Increase in acidity below ~~beyond~~ pH 5.7 is generally attributed to atmospheric loading of substances arising from: 1) combustion of fossil fuels in industrial, transportation, agricultural, and residential heating operations; 2) use of fertilizers and other chemicals in intensive agriculture; and 3) decomposition of industrial, urban and agricultural wastes.

Data for pH of rain are lacking for most of the United States, and those that are available are insufficient for evaluating long term trends (Jones, 1974). Johnson *et al.* (1972) reported that rain and snow at Hubbard Brook, New Hampshire, averaged pH values of 4.1 from 1963 through 1969, while Pearson and Fisher (1971) found that pH of precipatation over the Northeast averaged ~~to~~ 4.4. Similarly, Likens *et al*. (1972) reported weighted annual average pH values ranging from 4.0 to 4.3 for precipitation in the Northeast. Various investigators have reported much higher annual average pH values for precipitation along the Pacific Coast (pH 5.0 - 8.5) (Whitehead and Feth, 1964; Tarrant et al. 1968) and in Florida (pH5.0 - 6.8) (Brezonik et al. 1969) where prevailing airflow is predominantly toward shore. During the summer of 1974, pH of rain in the Minneapolis-St. Paul area ranged from 4.0 to 5.6 (Krupa et al. 1976). The lowest reported pH for rain in the United States is 2.1 (Likens and Bormann, 1974).

Review of the current literature indicates that acidic rain can cause the following effects: 1) material damage, 2) alterations in the growth and development of terrestrial vegetation, 3) alterations in soil physics and chemistry and 4) alterations in the chemistry and biology of aquatic systems.

Almost all of our current knowledge of rain composition and chemistry is based on inadequate sampling and collection procedures as well as questionable analytical procedures and interpretations. At this time the basis or bases for the acidity of rain is a subject of intense debate (Likens and Bormann, 1974; Newman, 1975; Frohliger and Kane, 1975; Krupa et al. 1976). Atmospheric chemists generally agree that our present knowledge of rain chemistry and associated aspects is insufficient.

The major components known to be present in acidic rain are listed in Table 3.1.1-1.

3.1.2 Sampling and analytical procedures for the study of acidic rain.

Till recently rain samples have been collected in open containers of different types (metal containers, stainless steel pots,

Table 3.1.1-1. Major Components in Acidic Rain*

Organic -- Inorganic

1. Insoluble particulates

    - spores
    - pollen
    - pesticides
    - complex inorganics

2. Soluble fraction

    A. Acids

    - Volatile weak
        - CO_2
        - organics
        - unknowns
    - Non-volatile weak
        - HF
        - Hydrolysable salts
        - organics
    - Non-volatile strong
        - H_2SO_4, HNO_3, HCl, S_2O_6

    B. Salts

    - Complex
        - unknowns
    - Simple
        - cations
            - NH_4, Pb, Fe, Mn, Zn, Cu, Ca, Na, K, etc.
        - anions
            - SO_4, NO_2, NO_3, Cl, PO_4, F, HCO_3, etc.

---

*After Krupa (1976).

polyethylene pots, bulk "garbage-can", etc.). These types of collectors trap both dry and wet fallout. More recently many investigators have made an effort to collect wet fallout or rain only (devices that remain open only during the rain). For details on some of these points, the reader is referred to NOAA report (Miller, 1976).

Most of the literature on rain composition pertains to bulk precipitation samples--weekly, bi-weekly or monthly. Individual rainfalls vary in their pH, chemical composition and background for acidity (Krupa et al. 1976). Furthermore, the same rainfall, collected at different but closely located sites are different in their chemical composition (Krupa et al. 1976). Currently it is believed that even a given rain at an individual sampling site, collected as fractions against time, may vary in its composition (Krupa and Coscio, unpublished).

Sampling surface plays an important role in the composition of rain. Surfaces such as metal, glass, polyethylene, polyvinyl chloride, teflon, etc., have all been used. Because of the presence of microquantities of certain elements in rain, adsorption-absorption-leaching properties of the collection surface pose~~s~~ serious problems in chemical analysis. Thus a serious evaluation of the collection surface to be used, is warranted. Robertson (1968) has summarized comparative concentrations of different trace elements in sea water on ? and various types of collection surfaces. According to Robertson, teflon appeared to be relatively free from trace metal impurities and should prove useful.

Some of the characteristics of the sample are critical in the study of rain chemistry. For example, samples allowed to stay too long in the field or stored at warm temperatures are subject to microbial growth and chemical alterations (ref. Proc. I. Int. Symp. Acidic Precip. Forest Ecosystems). Similarly, samples stored in containers with space between the liquid phase and the cap of the container, allow gas exchange between the aqueous system and the gas phase above it. These aforementioned considerations are summarized in Table 3.1.2-1.

Techniques for the analysis of several rain components are still in the developmental stage. For example no acceptable technique is available to distinguish the SO_4^{2-} originating from a soluble salt versus the portion originating from H_2SO_4. Techniques used in the analysis of the particulate fraction in rain or organic acids in rain are complex and time consuming. Nevertheless, an integrated analytical approach and evaluation of as many components as possible ~~is~~ are necessary to assess the biological impact of acidic rain.

Some of the techniques currently available to analyze different rain components are summarized in Table 3.1.2-2.

Almost all the procedures summarized in Table 3.1.2-2 are currently being used by the ~~A~~air pollution-vegetation effects group at the Department of Plant Pathology, University of Minnesota. An integrated approach using these procedures to study the chemistry of rain are presented in Figure 3.1.2-1. For details on specific procedures, refer to the Appendix in this report.

3.1.3. Chemistry of rain.

The ionic components of rain that are frequently discussed in the literature include:

Table 3.1.2-1. Parameters in Sampling and Collection of Rain for Chemical and Biological Studies*

1. Sampling
    - A. Specificity
        - wet and dry
        - wet
    - B. Time
        - Bulk
        - Single events
        - Sequential sampling within single events
    - C. Surface
        - Metal
        - Glass
        - Polyethylene
        - Polyvinyl chloride
        - Teflon
    - D. Characteristics
        - Dead volume
        - Biocides
        - Preservation

*After Krupa (1976).

Table 3.1.2-2. Some Rain Components and Analysis Techniques*

1.	Free acidity (pH)	Electrode
2.	Electrical Conductivity	Conductivity bridge --Potentiometer
3.	Total acidity	Alkali titration
4.	Molarities of Acid Types	Coulometry
5.	Total organic matter	Combustion
6.	Particle morphology and composition	Scanning electron microscopy--x-ray analysis
7.	Organic acids	Gas or high-pressure liquid chromatography--mass spectrometry
8.	Dithionate	Column--ion exchange and colorimetry
9.	Cations**	Atomic absorption, emission spectrography, plasma spectrography, ion-chromatography
10.	Anions**	Colorimetry, specific ion electrode, turbidometry, ion-chromatography, etc.

*From Krupa (1976)

**Free and Total

Figure 3.1.2-1. Flow chart showing the integrated analytical procedure used to study the chemistry of rain. For details on the techniques, refer to Krupa et al. (1975, 1976) and the Appendix of this report.

ANALYSIS OF RAIN CHEMISTRY

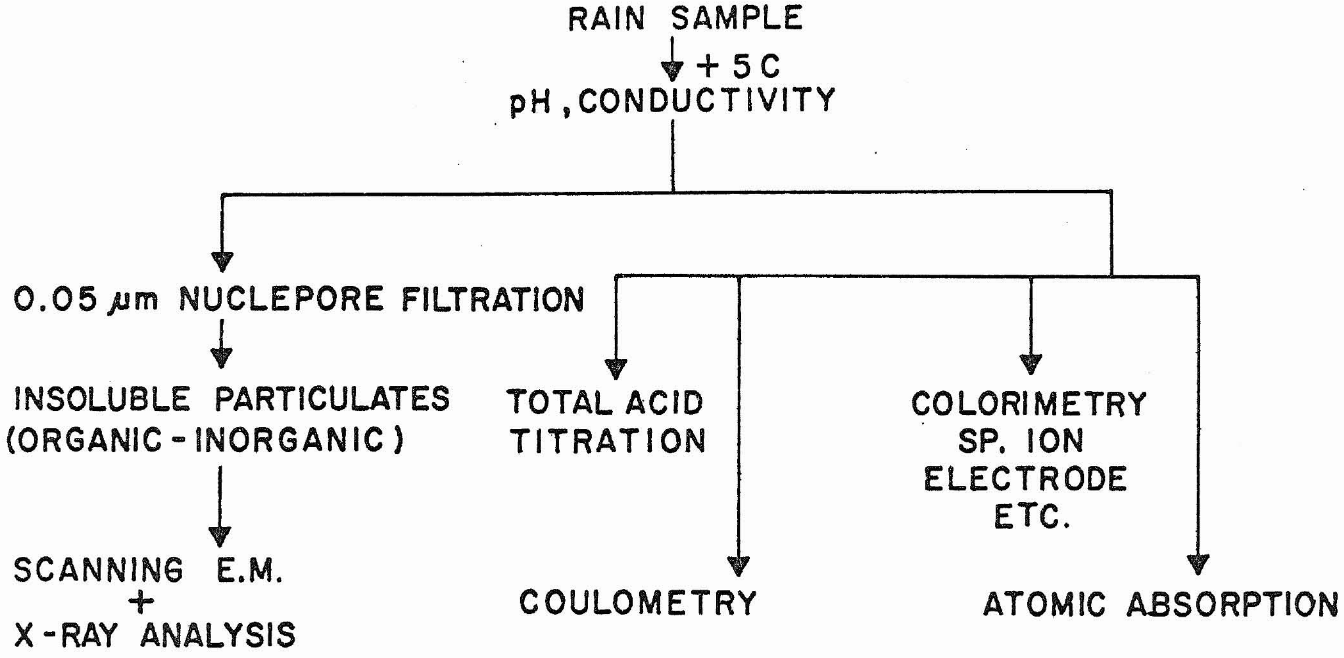


FIGURE 3.2 — 4

(-): Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, HCO_3^-

(+): Na^+, Ca^{++}, K^+, Mg^{++}, NH_4^+

Electrical conductivity and pH are also included. Rarely determined components include PO_4, I, F, H_2O_2, CH_2O, other than the aforementioned cations, and total organic and insoluble material. Although the insoluble and organic material in rain may be as abundant as the soluble constituents, the latter fraction has been more intensively studied.

a. Nitrogen: NH_4^+, NO_3^-, NO_2^-

Nitrogeneous compounds are vital plant nutrients. It is generally agreed that the source of nitrogen in the air may be attributed primarily to the soil, but some investigators attribute use of fertilizers and combustion of coal as significant factors (Likens et al. 1975). Commoner (1970) states that natural processes including photochemical N_2 fixation cannot account for the observed values found in precipitation, and with the notable increase of the nitrogen levels in precipitation in the last 25 - 30 years, fertilizer and combustion processes may be correlated as the source. NH_4^+ is found at levels of 0.01 - 1 mg/l (Junge, 1963). Its distribution shows no obvious relationships to industrial areas (Junge, 1963). However, according to Eriksson (1952) ammonia concentrations in precipitation in industrial centers is high and the only net source of NH_4^+ in the air seems to be that released during the combustion of fuels. In Israel calcareous soil sources contribute 4 - 20 kg/NH_4^+/ha/year (Yaalon, 1964). Ratios of NH_4^+:NO_3^- have been examined with the conclusion that the consistency of the ratio for an area implies a real association between the two components and opens speculation for a common source (Jones, 1971). Leland (1952) reported a ratio~~n~~ of Ca. 4:1 while Jones (1971) reported 0.8:1.6.

According to Gambell and Fisher (1964) NO_2 appears to be the most likely source for NO_3^-. Odén (1968) noted that the use of fertilizers mapped over Sweden was "fairly congruent" with that of NO_3 fallout. However, unexplained discrepancies exist in his data. The low ratio of NO_2:NO_3 (Ca. 1) indicates that NO_2 is probably oxidized rapidly in rain or in aerosols (Junge, 1963).

b. <u>Chlorine</u>:

Junge (1963) notes that Gorham found a highly significant correlation between the chloride ion and acidity for a pH of less than 5.7 in urban precipitation samples in England. This was not the case for SO_4 despite its large concentrations. Junge believes that anthropogenic chloride may be of regional importance in highly populated areas, while Eriksson (1952) and Odén (1964) believe the oceans and ~~the~~ volcanic eruptions to be the only sources. It is generally believed that HCl is not a contributor to the acidity in precipitation.

c. <u>Sulfur</u>:

Wilson (1926) studied nitrogen and sulfur in rainwater in New York. According to him "there appears to be a direct relationship between the concentration of sulfur in the rainfall and the quantity of smoke in the atmosphere." Since then investigators have followed the role of sulfur in our environment with zeal. Some of the typical sulfate concentrations reported in rain are as follows:

1 - 10 mg/l U.S. (Junge, 1963)
3 mg/l - Average ? refs ?
5 mg/l - Europe and England
2 ± 1 mg/l - U.S. (Gambell and Fisher, 1966)
(Bulk precipitation)

Although sulfur is an essential plant nutrient, studies indicate that the amounts contained in precipitation make only a minor contribution to crop requirements (USDA Tech. Bull. #1179). Sulfur in precipitation is estimated as sulfate and there appears to be only a single instance in the literature where sulfur oxidation states were examined: Crowther and Ruston (1911), after initial sulfate precipitation by bromine-water digestion of the sample, determined the amount of total sulfur in a state less oxidized than sulfate. In the polluted area of Leeds, England, they found ca. 25% of the total sulfur in such a state.

There is controversy as to the existence of a seasonal fluctuation of sulfate in precipitation due to fossil fuel combustion. According to Gambell and Fisher (1966) average monthly sulfate concentrations indicate that sulfur from man's activities is not the controlling factor, as low winter concentrations do not reflect the increases in the production of SO_2 during these months. Leland (1952) and others report consistently higher sulfate levels in the winter and attribute this to larger quantities of coal and oil burned.

Several investigators have commented on the concentration of sulfate in precipitation as a function of the type of precipitation. Herman and Gorham (1957) noted that snow contained much lower concentrations of most substances than did rain collected over a similar period. Khemani and Murty (1968) studied the concentrations of anions and cations in different situations and found that sulfate was only as half abundant in rain from cold stratus cloud types as in that from cold convective clouds. Gatz and Dingle (1971) studied the effect of shower cells on the concentration of pollen, β-radioactivity, and inorganic ion counts and found that marked variations were produced by individual shower cells. The concentration profiles were loosely inverse to rainfall rates and duration. Junge (1963) states that large variation may exist in rainfalls which are small, due to washout-pickup of gas by falling rain and evaporation of the descending drops, while in large rains, rainout-pickup of material in cloud formation becomes the controlling factor.

Several investigators from Scandinavia suggest that sulfur in precipitation originates from global upper air atmosphere (Oden, 1964). They suggest that the sulfur in the precipitation originates from 1 - 4 km of the atmosphere that is not appreciably affected by local emissions. Estimates of the contribution of SO_2 and particulate sulfur components to the sulfate content of rain have varied. Bielke and Georgii (1968) presented data in a case where the concentration of SO_2 in the lowest kilometer of the atmosphere exceeded that at higher altitudes:

	SO_2	Aerosol SO_4^{2-}
Rainout (cloud contribution)	5%	20%
Washout (sub-cloud contribution)	70%	5%

This suggests an important gaseous contribution to total sulfate in rain. Gambell and Fisher (1964) found that the concentration of sulfate remained at high levels throughout the course of rainstorms, suggesting that the source of sulfate was not appreciably affected by washout. Petrenchuck and Selezneva (1970) analyzed rains in the U.S.S.R. and found that in the clean northern regions, the cloud contribution (rainout) constituted 55% of the total precipitation mineralization, whereas in the industrialized southern regions, with heavy pollution of the atmospheric boundary layer, the washout in the subcloud layer was the predominant process (only 20% cloud contribution). Miller and dePena (1972) measured the contribution of scavenged gas (rainout and washout) to the sulfate content of rain using a model system in which a "plume" was introduced beneath the cloud layer (SO_2 at 50 ppm). They found that the concentration of total sulfur in rain reflected the peak concentration of the plume (highest trajectory of the broadest plume) and depends little on the vertical profile below. They concluded that the sulfate content of rain reflects particulate washout rather than gaseous washout. Miller and dePena found 80% of the sulfur to be in the particulate fraction collected in the first 1 hour. Only 20% was in the gaseous washout. They noted that upon evaporation, a droplet allowed to remain for a reasonable time in a cloud with partial pressures of SO_2 and NH_3 characteristic of polluted areas, produced a particle of cloud nucleus size.

why? ? contradicts Bielke + Georgii p. 76 (not clear)

d. SO_2 oxidation and sulfate formation:

It is generally believed that catalytic oxidation is the main cause of sulfate formation (Georgii, 1970; Junge, 1960; Meszaros, 1970;

Rodhe, 1970). In a study of the sulfate particles in the air, Wagman (1967) found that the principal sulfate forming mechanism at relatively low SO_2 levels, involves interaction with water in the vapor phase, whereas sulfate-containing particles increase in size by vapor condensation. Photochemical reaction rates do not seem to explain adequately the concentrations of oxidation products of sulfur found in the atmosphere. To date, the most probable method of sulfur oxidation might be termed the "SO_2 - NH_3 - H_2O" system. Scott and Hobbs (1967) found that at SO_2 and NH_3 levels typical of those in the earth's atmosphere, the formation of the sulfate after 24 hours was two-fold that occurring without NH_3. While NH_3 is considered to be the primary catalyst, NO_2 as well as alkaline earth metals have been implicated (Gambell and Fisher, 1964). Miller and dePena (1972) report that in the production of sulfate in a power plant plume, as much as 80% of the SO_2 can be recovered in the particulate fraction within 1 hour.

? consistent with comment on p 77?

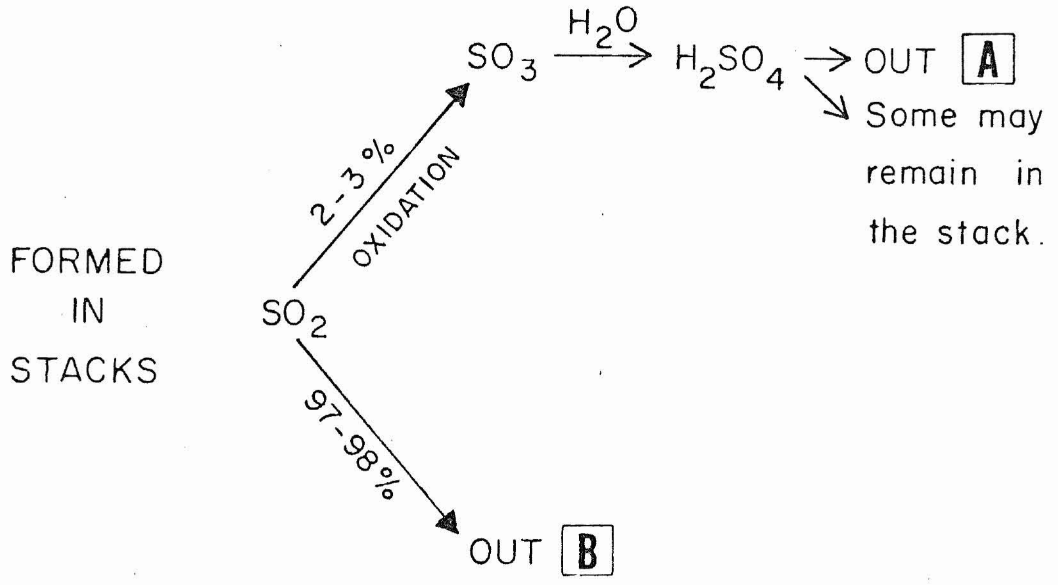
e. Acidity in precipitation

Several investigators have observed pH values for rain to be below 5.6 - 6.1. Barrett and Brodin (1955) reported "since SO_2 is one of the major constituents of pollution, it is likely that sulfuric acid is the controlling factor of the pH of rain." Since then, almost all the studies on acidic rain have been based on correlation of pH maps and sulfur depositions. According to Johnson et al. (1972) 3 - 4 mg/l sulfate will lower the pH of rain to 4.4 - 4.1. It should be remembered that while the pH scale is linear, the SO_4 content increases logarithmically with decrease in pH. Krupa et al. (1976) presented correlations between single systems of SO_4, NO_3 and Cl and pH (refer to the Appendix of this report for details). Based on their data SO_4 concentrations required to reach pH 3.0 or below are unreal in terms of the reported values.

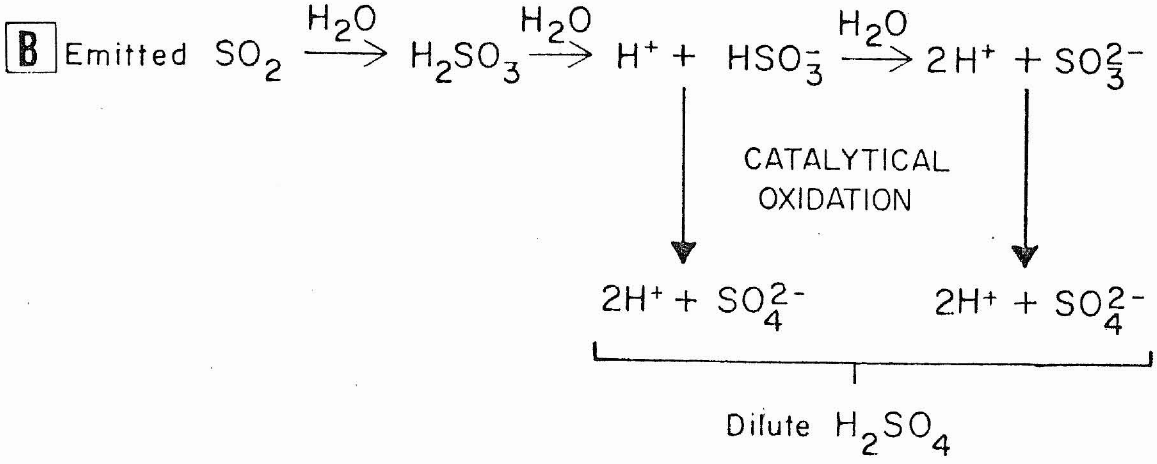
According to Likens et al. (1972) strong acids destroy the carbonic acid buffering system in rain. Odén from Sweden, has been perhaps the foremost proponent of the sulfuric acid theory of precipitation. However, according to Odén (1968) "The available quantitative material does show that one cannot directly correlate the acidity in air or precipitation with the industrial release of sulfur." Other factors such as the "climatic pump" might outweigh a direct relationship. Mrose (1968) states that the type of pollution may account for the difference in the reports concerning pH trends: coal combustion creates dust which may partly neutralize the acid, while with oil combustion H_2SO_4 remains unchanged. Sulfate analysis of precipitation is not especially useful as it cannot be determined as to how much of the SO_4^{2-} was present as acid and how much was present as salt. Similarly pH values reflect the negative logarithm of the free hydrogen ion concentration, but does not identify the parent source (s) of the hydrogen ions. Free H^+ originating from strong and weak acids will be modified by soil derived cations, and the final pH should in the end be adjusted by reversible absorption of CO_2 and NH_3. Brossett (1973) was the most recent to attempt to relate acid production to pollutant sources (Figure 3.1.3-1).

According to Anderson (1969) data collected in the vicinity of Uppsala, Sweden, show that geographic distribution of sulfur and pH do

Figure 3.1.3-1. Relationship between sulfuric acid production and pollutant sources of sulfur. From Brossett (1973).



$$\boxed{\mathbf{A}}\ \text{Emitted}\ H_2SO_4 \xrightarrow{H_2O} H^+ + HSO_4^- \xrightarrow{H_2O} \underbrace{2H^+ + SO_4^{2-}}_{\approx 5M\ H_2SO_4}$$



not reflect good correlation. Krupa et al. (1976) were unable to find correlation between changes in the pH and changes in the SO_4^{2-} concentration in the Minneapolis-St. Paul area during the summer of 1974.

Much criticism exists in the literature toward assumptions based on measured pH values. Whitehead and Feth (1964) note that pH tends to change in storage and the change is especially significant in water with low mineral content and weak buffering system (rain). They state that the amount and direction of pH change is unpredictable for any single water sample and, therefore, values reported for pH taken at the time of sample analysis do not accurately represent the pH of rain. However, more recent studies by Krupa and Coscio (unpublished) indicate that rain samples collected in chemically inert containers, without dead volume which otherwise facilitates gas exchange and stored at refrigeration temperatures prevents changes in pH for periods as long as several weeks. This becomes particularly effective if a proper biocide is utilized.

The current practice in many laboratories is to determine the free acidity (pH) and total acidity (alkali titration). Few studies exist where the molarity of total acids have been determined (Askne and Brossett, 1971; Liberti et al. 1968). More recently, Krupa et al. (1976) reported on a coulometric procedure for the determination in molarities of both strong and weak (volatile and non-volatile) acids (refer to the Appendix in this report).

According to Likens et al. (1976) both sulfates and nitrates contribute to the acidity of rain as sulfuric and nitric acids. However, by

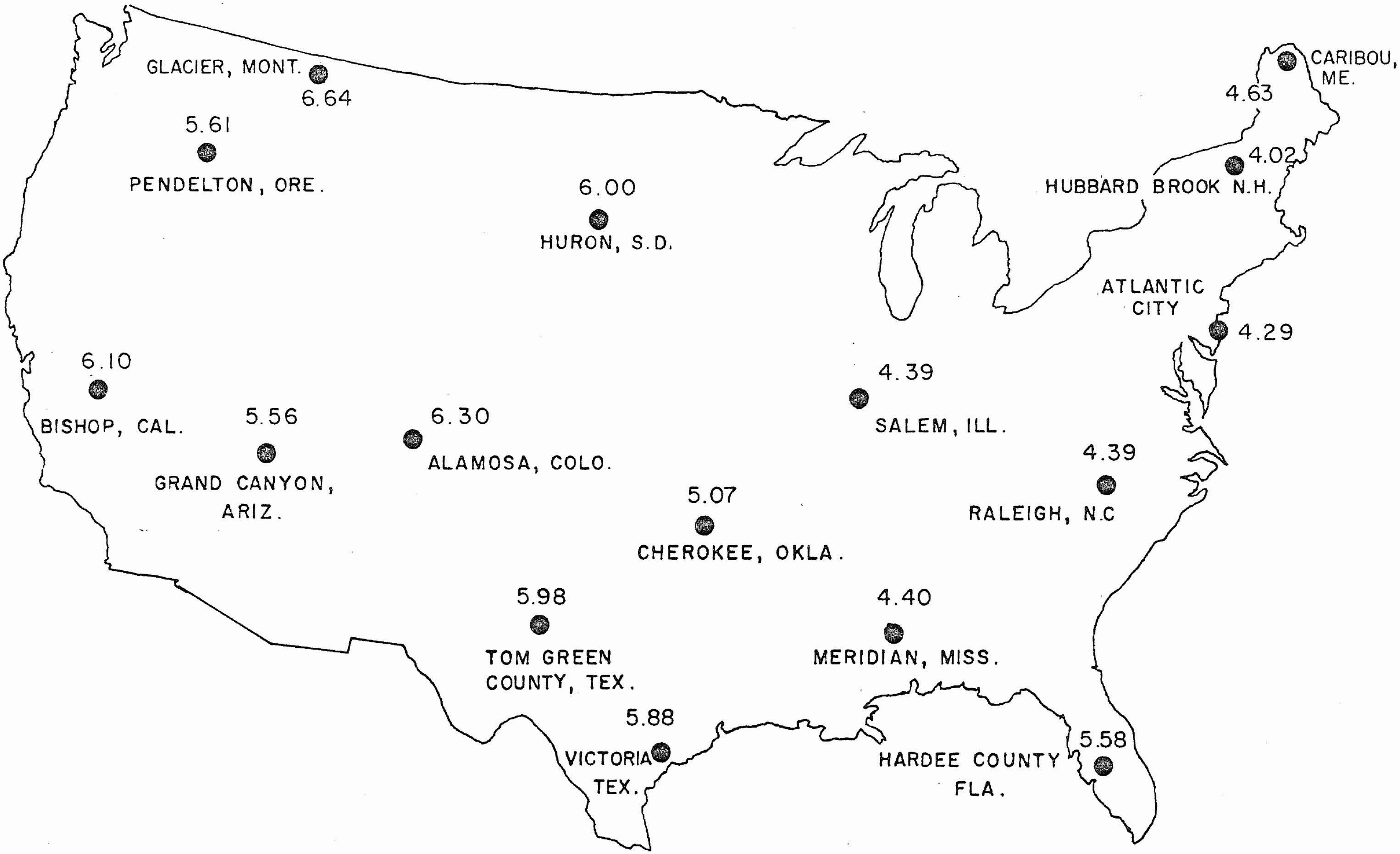
Frohliger and Kane (1975), a comparison of the free hydrogen ion concentration and the total hydrogen ion concentration of rain samples shows that rain is a weak acid. Frohliger (1976) presented pk values on rain in support of its weak acid nature. Krupa et al. (1976) presented evidence to show the presence of a multiple hydrogen-ion donor system in the Minneapolis-St. Paul area. The hydrogen-ion donor system consisted of strong as well as volatile and non-volatile weak acids. The proportion of these different acid species varied between sampling sites and between rain events. The weighted mean pH of rainfall over the United States during 1972-1973 is presented in Figure 3.1.3-2.

f. Residence and transport of sulfur.

As the persistence of pollutant constituents of the atmosphere governs their accumulation and redistribution in the atmosphere as well as their ultimate dispersion over the earth's surface, this problem has received continued scrutiny by investigators. According to Martell and Poet (1970) residence time of tropospheric aerosol is about 6 days. Rhode (1972) states that the residence time for sulfur in the atmosphere is 30 - 70 hours. However, Weber (1970) deduced from his stack plume studies that 50% of the SO_2 is lost within 20 minutes to 1 hour under neutral or stable meteorological conditions in the winter period. Högström (1973) cites 5 case studies around Uppsala, Sweden which indicate the residence time for sulfate as well as the strong acid to be 1 - 2 hours, corresponding to a distance of travel in the range of 50 - 100 km. His comment~~s~~ that 50% of the sulfate is precipitated as strong acid is made without any supportive data other than correlations of fallout mappings for acidity and sulfate. Some of these comments should suffice

? P78 Miller & dePena, 80% in 1 hr

Figure 3.1.3-2. The weighted mean pH of precipitation over the United States for 1972-1973 (Miller, J. Personal Communication).


GLACIER, MONT.
6.64
5.61
PENDELTON, ORE.
6.00
HURON, S.D.
CARIBOU, ME.
4.63
4.02
HUBBARD BROOK N.H.
ATLANTIC CITY
4.29
6.10
BISHOP, CAL.
5.56
GRAND CANYON, ARIZ.
6.30
ALAMOSA, COLO.
4.39
SALEM, ILL.
4.39
RALEIGH, N.C
5.07
CHEROKEE, OKLA.
5.98
TOM GREEN COUNTY, TEX.
4.40
MERIDIAN, MISS.
5.88
VICTORIA TEX.
5.58
HARDEE COUNTY FLA.

to indicate that there is a great deal of controversy regarding the half life of SO_2 in the atmosphere. Various investigators have estimated it to vary from 20 minutes to 7 days. The actual atmospheric residence times for SO_2 at specific locations are probably highly variable and dependent on the particular environmental factors at those sites.

3.1.4. Vegetational effects of acidic rain.

Acidic rain has been implicated in the increased leaching of nutrients from soils (Overrein, 1972), decreased pH values of lakes and streams (Odén and Ahl, 1970). Little is known, however, of the effects of acidic precipitation on terrestrial vegetation. To our knowledge, there are no published reports demonstrating vegetational injury due to naturally occurring acidic rainfall. Several investigators, however, have reported direct injury of various plant species by artificially applied acid mists and acid solutions (Ferenbaugh, 1976; Shriner et al. 1974; Wood and Bormann, 1974). According to Wood (1975) changes acidic rain may induce in natural ecosystems are likely to be widespread but difficult to detect over short periods of time.

From the available literature, the phytological implications of the effects of pollution in rainfall may be categorized as follows:

a. direct injury to foliage

b. effects on host-parasite relationships

c. deleterious effects on the soil

d. deposition of other harmful substances on the plant tissue

Gordon (1972), inoculating developing pine needles with sulfuric acid solutions, found that needles subjected to solutions more acidic than pH 4.0 grew to only 50% of the length of the control needles. Shriner (1974) noted marked erosion of the cuticle on oak and bean leaves subjected to artificial rains of pH 3.2. Wood and Bormann (ref. Wood, 1975) observed foliar spot necrosis and irregular leaf development on yellow birch and sugar maple seedlings misted in a laboratory with acidic solutions of pH 3.0. At pH 2.3, these hardwood seedlings also suffered decline in productivity, assimilating only 60% of the biomass of seedlings grown under less acidic conditions.

Recently Wood and Pennypacker (unpublished) demonstrated with different concentrations of sulfuric acid that the acid concentrations of 10^{-3}M and 10^{-2}M were injurious (necrosis) to Scotch pine needles. This injury was also produced by similar concentrations of phosphate buffered sulfuric acid.

Shriner (1974) studied the effects of simulated acidic rain (sulfuric acid) on host-parasite interactions. Five host-parasite systems studied by Shriner were affected by simulated rain (sulfuric acid) at pH 3.2. Acid treatments resulted in: an 86% inhibition in the number of telia produced by the oak-pine rust (*Cronartium fusiforme*) on willow oak (*Quercus phellos*); a 66% inhibition in the reproduction of root-kno~~w~~t nematode (*Meloidogyne hapla*) on field-grown kidney beans (*Phaseolus vulgaris* Red kidney); a 29% decrease in the percentage of leaf area of field-grown kidney beans affected by the rust *Uromyces phaseoli*; and either a stimulation or inhibition in the developmentof halo blight (*Pseudomonas phaseolicola*) on kidney bean. In the last case, the effect was dependent upon when the acid treatment was applied in relation to the disease cycle.

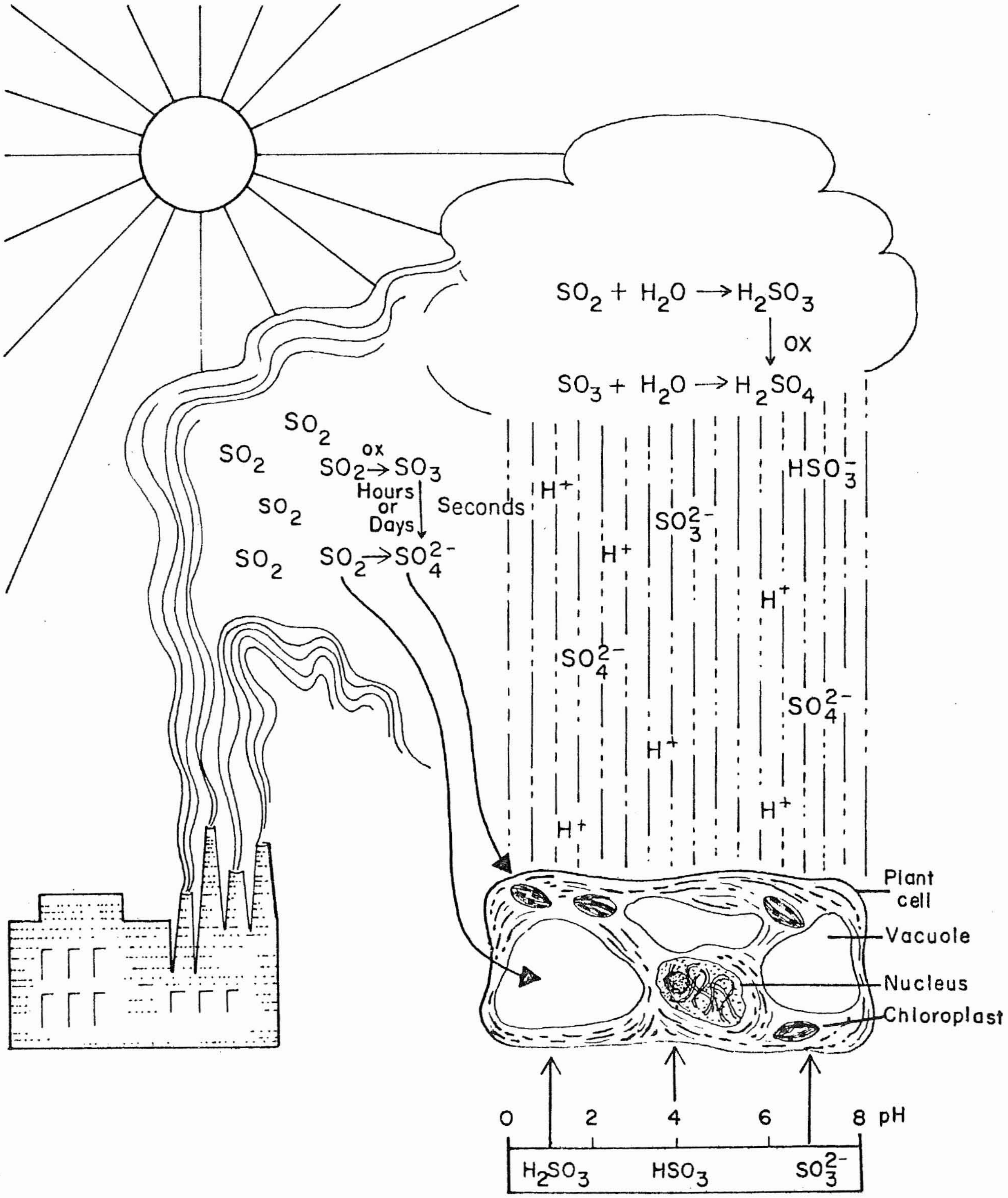
Use of acidic solutions to induce plant injury and symptom development cannot be considered valid in light of the inadequacies concerning what is actually known about the acidic nature of natural precipitation. The biological effects of strong and weak acids are not the same. Furthermore, mixtures of strong and weak acids and their biological effects have not been properly understood. Rain is a complex mixture of numerous inorganic and organic components which interact in multiple ways. While most investigators seem to attribute effects to H^+ ions, the studies of Wood and Pennypacker (unpublished) indicate that anions (in the case of H_2SO_4, HSO_4^-, and SO_4^{2-}) may be highly significant in biological effects.

Crowther and Ruston (1911) were the earliest investigators to ascribe plant damage to the acidic nature of polluted precipitation in Leeds, England. They described direct leaf toxicity and "less nutritious timothy grass" as manifestations of the pollution in rain. Syratt and Wainstall (1968) suggest that degradation of chlorophyll is a result of the acidic nature of SO_2 at high humidity (sulfurous acid). Odén (1963) asserts that plant damage due to the acidic nature of most sulfurous compounds may be manifest as plasmolysis of the cells at high concentrations and chlorophyll destruction at lower concentrations. Odén also cited a rather cryptic metabolic protection mechanism of "Base-rich vegetation" whereby SO_2 is ~~to~~ oxidized to H_2SO_4 and then liberated by plants. According to Odén acidic rain effects are more significant on coniferous vegetation because of the accumulative properties of the needles. Likens <u>et al.</u> (1972) report that Sweden sustains an annual reduction in forest growth as a result of acidic rainfall. The authors of this report (Krupa <u>et al.</u>) find it difficult to understand ~~as to~~ how one separates biological effects due to gaseous, aerosolic and dry fallout pollutants, which occur continuously before and after rain, from those effects suggested to be caused by the pollutants in rain.

Much of the discussion o~~n~~f the action of SO_2 damage to plants has arisen from studies on lichens and bryophytes. In a discussion by Sundström and Hallgren (1973) relative to lichen (phycobiont) sensitivity and sulfur pollution, the authors portray the "probable" picture of the relationship between the plant cell and the sulfur pollution (Figure 3.1.4-1). Of this relationship, they state "It is reasonable to suppose that in the event of sulfurous pollutions, the transport of SO_2 or H_2SO_3 and HSO_3^- through the membranes is much more rapid than the uptake of the more charged SO_3^{2-} ion. This selective uptake of undissociated molecules, and to some degree HSO_3^-, is followed by their dissociation in the cell, resulting in an accumulation of charged HSO_3^- and SO_3^{2-} ions and an acidification of the cell."

In terms of soil effects, mounting acid inputs may cause decreases in the fertility of forest soils. It has been suggested that increased rain acidity accelerates the leaching of potassium, magnesium and calcium (Overrein, 1972). Field studies in Sweden correlate increased acidic rain inputs with decreases in soil pH and per cent base saturation (Odén et al. 1972). Increased soil fertility may also result from

Figure 3.1.4-1. Emissions and transformation of SO_2 and SO_3. The figure shows the probable transformations of SO_2 in air and water. The arrows into the cell give an approximate picture of the permeability of the various sulfurous compounds. The distribution of the various dissociation states of H_2SO_3 at different pH values is shown in the pH scale below the cell. From Sundstrom and Hallgren (1973).


$SO_2 + H_2O \rightarrow H_2SO_3$
ox
$SO_3 + H_2O \rightarrow H_2SO_4$
SO_2
SO_2
ox
$SO_2 \rightarrow SO_3$
Hours or Days
Seconds
SO_2
SO_2
$SO_2 \rightarrow SO_4^{2-}$
H^+
SO_3^{2-}
HSO_3^-
SO_4^{2-}
Plant cell
Vacuole
Nucleus
Chloroplast
0
2
4
6
8
pH
H_2SO_3
HSO_3
SO_3^{2-}

acidic rain, due to for example, additions of nitrate and sulfate ions, common components of chemical fertilizers. In fact, Wood and Bormann (refer Wood, 1975) found that mean productivity of white pine seedlings subjected to artificial rains containing sulfuric, nitric and hydrochloric acids was 20% greater at pH 2.3 than at lower acid concentrations.

One interesting example of the deposition of potentially harmful materials on plant surfaces was described by Francis *et al*. (1968). They ascribe the entry of polonium 210 into tobacco plants to deposition by precipitation, rather than by soil uptake as was previously believed.

Plants constitute rather effective air filters. Bach (1972) states that Aitken nuclei (0.1μ) in the atmosphere are reduced by 34% for a coniferous forest and 19% for a deciduous forest. According to Eaton *et al*. (1973), forest canopies have been found to filter 90% of the hydrogen ion from pH 4.0 rain water falling on the landscape during the growing season. As a result, less acid solutions (pH 5.0) reach the forest floor.

At present our knowledge of the chemistry of acidic rain as well as its biological effects is incomplete and inadequate. Intensive research is required in the future to answer the questions and the concern that is being expressed at this time regarding this problem, on a global basis.

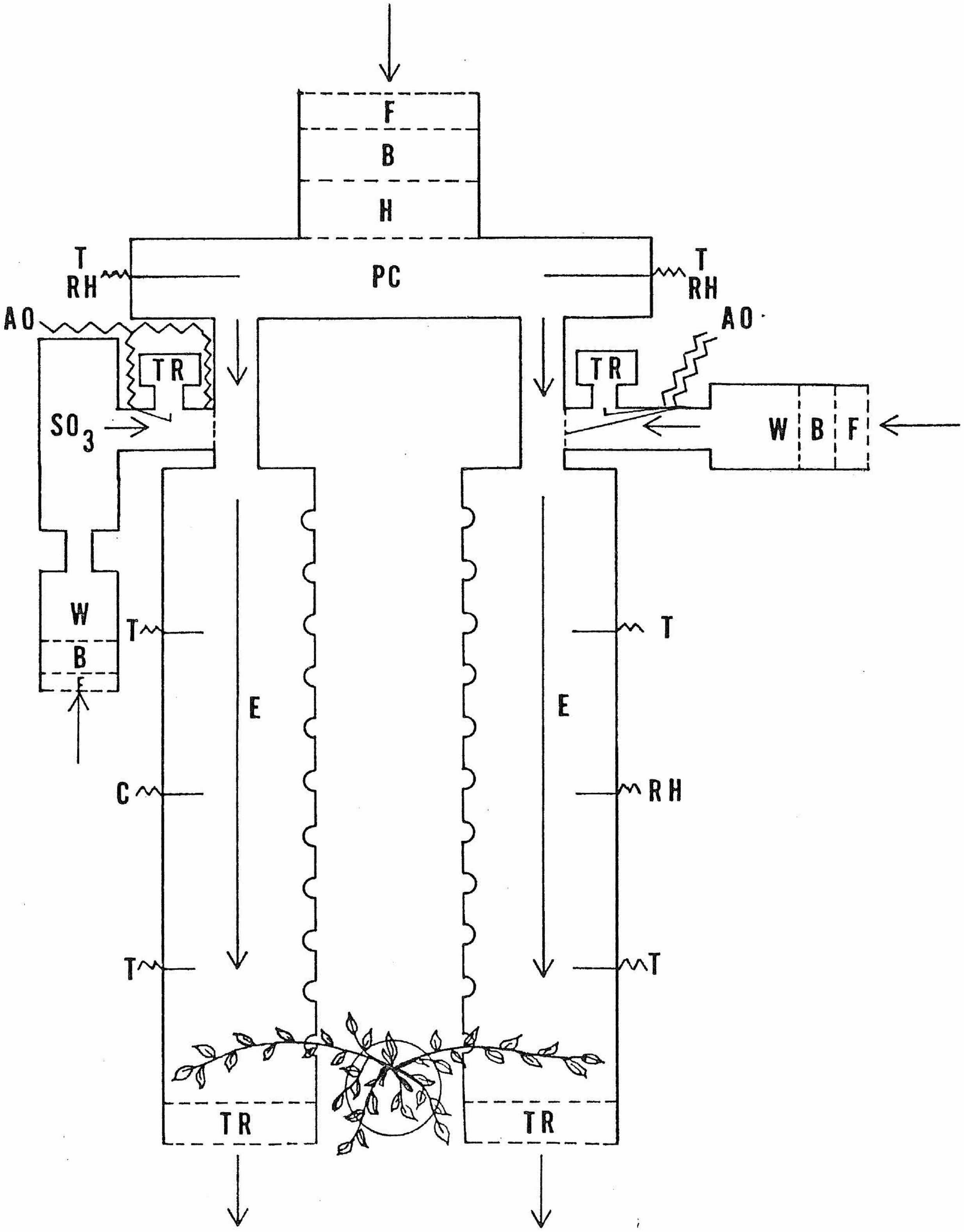
3.2 Acid aerosols.

As opposed to the projected regional effects of acidic rain, acid aerosols are known to be a serious problem on a local basis around point sources under unusual conditions. Acid aerosol in the present context is defined as the suspension of an acid molecule (s) in a vapor phase. Acid aerosols are highly reactive. While sulfuric acid molecules dissociate fast in liquid droplets, aerosols seem to preserve their integrity until reacted with other surfaces or atmospheric components. As opposed to sulfuric acid droplets, aerosols are much smaller in size. Sulfuric acid aerosols are known to occur between 0.02 $\overset{\mu m}{m}$ and 0.6 m μm ? in size. Most sulfuric acid aerosols seem to result from the reaction between SO_3 and water. To date little research has been conducted on the effects of H_2SO_4 aerosols of the low condensation size, on terrestrial vegetation.

Currently several research groups in the United States, including the University of Minnesota are investigating acid and saline aerosol effects on vegetation. A design of the H_2SO_4 aerosol-vegetation exposure facilities is presented in Figure 3.2-1.

Figure 3.2-1. Plant exposure chamber to H_2SO_4 aerosol. F: total air filter, B: blower, H: humidifier, PC: pre-conditioning chamber, T: temperature probe, RH: relative humidity probe, AO: adjustable orifice, TR: aerosol trap, SO_3: SO_3 source, C: coulometry sampler, E: exposure chamber. The left side tubular chamber serves to expose plant parts to H_2SO_4 aerosol while the right side chamber serves to expose plant parts to humid air (control) After Krupa and Shrum (1976).

W = ?


F
B
H
PC
T
RH
T
RH
AO
AO
TR
TR
SO_3
W
B
F
W
B
F
T
T
E
E
C
RH
T
T
TR
TR

4. Effects of fluorides on vegetation.

4.1 Introduction

Fluorine chemically bound as fluoride is widely distributed in the earth's crust. It occurs in both igneous and sedimentary rocks and is estimated to constitute between 0.06% and 0.09% by weight of the upper layers of the lithosphere (Leech, 1956). The chief fluorine containing minerals are fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_{10}F_2(PO_4)_6$).

The industrial sources of fluoride in the environment are listed in Table 4.1.1.

4.2 Environmental fate and transformation of fluoride.

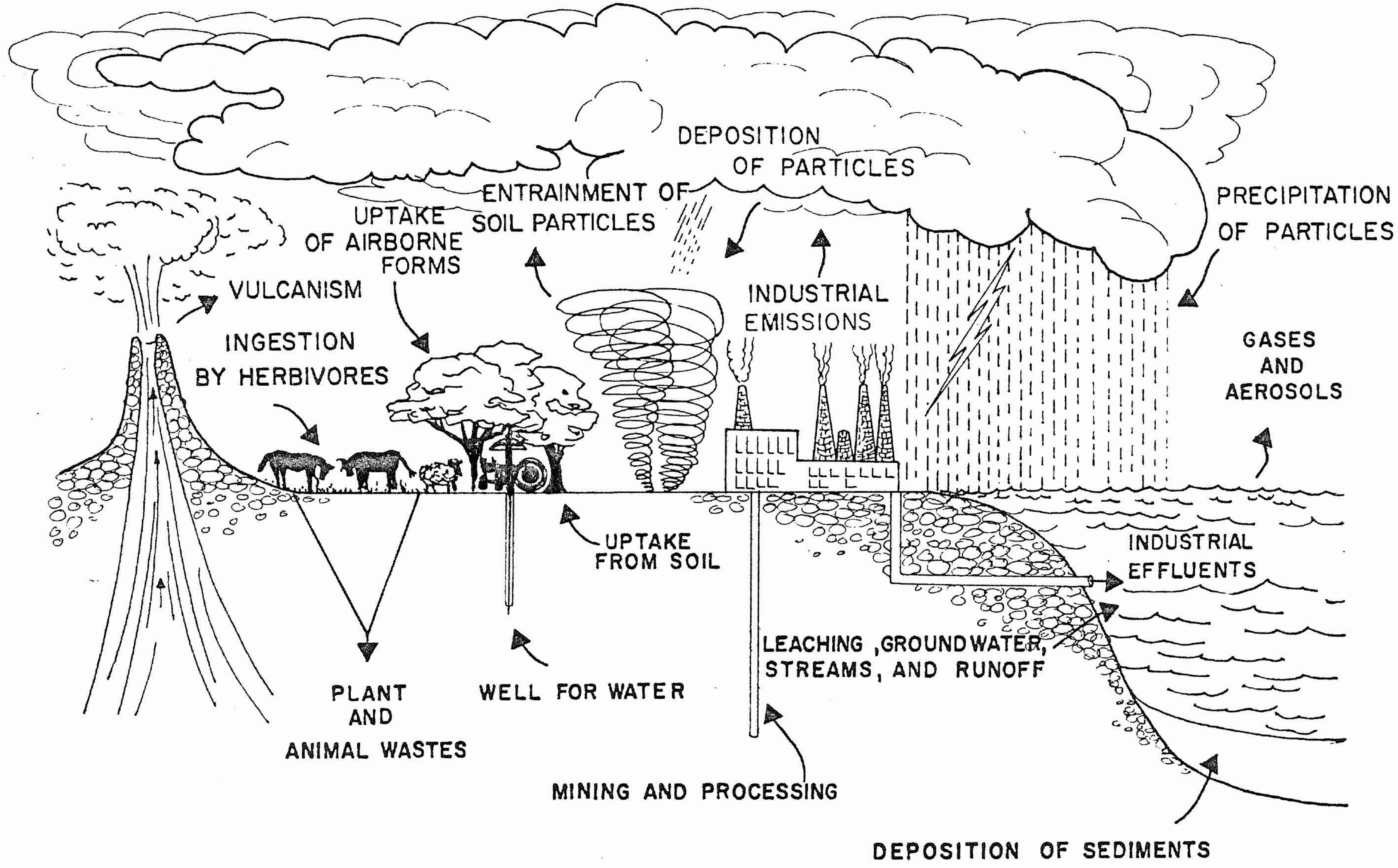
A simple summary of the transfer of fluoride in the environment is depicted in Figure 4.2-1, where the various routes by which fluoride passes to and from the atmosphere, hydrosphere, lithosphere, and biosphere are illustrated (refer Fluorides - National Academy of Sciences, 1971). Both the natural pathways and those due to man's activities are shown, but their relative magnitudes are not indicated.

Vulcanism and the entrainment of soil particles are the natural routes by which gaseous and particulate fluorides pass from the lithosphere to the atmosphere; vaporization and aerosol formation are possible routes from the hydrosphere. By deposition of particulate materials or through precipitation, atmospheric fluoride returns to the hydrosphere or lithosphere. The transfer of fluoride from the lithosphere to the hydrosphere can occur through the leaching of minerals or the addition of particulate matter to ground water and streams.

Table 4.1-1. Industrial Sources of Fluoride.

1. Manufacture of phosphate fertilizers.
2. Manufacture of phosphorus and phosphate feed supplements.
3. Manufacture of aluminum.
4. Manufacture of brick, tile, pottery and cement.
5. Manufacture of glass, enamel and fiber glass.
6. Combustion of coal.
7. Manufacture of fluorides.
8. Petroleum refining.
9. Metal casting, welding, etc.
10. Taconite industry.
11. Rocket fuels.

Figure 4.2-1. Environmental transfer of fluoride. From Fluorides, National Academy of Sciences, Washington, D. C. (1971).


DEPOSITION OF PARTICLES
ENTRAINMENT OF SOIL PARTICLES
UPTAKE OF AIRBORNE FORMS
PRECIPITATION OF PARTICLES
VULCANISM
INDUSTRIAL EMISSIONS
INGESTION BY HERBIVORES
GASES AND AEROSOLS
UPTAKE FROM SOIL
INDUSTRIAL EFFLUENTS
LEACHING ,GROUNDWATER, STREAMS, AND RUNOFF
PLANT AND ANIMAL WASTES
WELL FOR WATER
MINING AND PROCESSING
DEPOSITION OF SEDIMENTS

The return route would be the deposition of sediments. The terrestrial portion of the biosphere is an intermediate stage in the passage of the atmospheric fluoride to the lithosphere. Fluoride accumulation by vegetation can pass to the soil through plant wastes or enter the food chain through herbivores or ultimately through animal wastes. When fluoride is taken up from vegetation from the soil solution, its passage through the biosphere represents a recycling of lithosphere fluoride.

When industrial and other human activities are superimposed on the natural mechanisms of fluoride transfer, they result in new routes of transfer or an increased flow through pre-existing ones. For example, the emission of particulate and gaseous fluorides in the mining and industrial processing of fluoride-bearing minerals represents a path from the lithosphere to the atmosphere; this increased fluoride is removed from the atmosphere by natural means.

4.3 Chemistry of airborne fluorides.

The range and dispersal of a fluoride in the atmosphere is determined not only by the meteorological conditions but also by the chemical stability and the physical state of the fluoride (gas, aerosol, smoke or dust).

Many inorganic fluorine compounds are rapidly hydrolysed by water vapor in the air and converted to less volatile compounds, which are removed from the atmosphere by condensation and nucleation processes.

For example, silicon tetrafluoride, a major industrial pollutant, reacts with water vapor in air to form hydrated silica and fluorosilicic acid (Byrns, 1966; Lange, 1950).

$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$ Fluorosilicic acid is highly soluble in water and is readily absorbed by plants (Hitchcock et al.1962; Brewer et al.1960). The vapor phase above an aqueous solution of fluorosilicic acid contains both hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4), the ratio of the first to the second decreasing with increasing concentration of fluorosilicic acid (Byrns, 1966; Munter et al. 1947).

Anhydrous hydrogen fluoride, which is emitted by many industries, combines readily with water vapor in the atmosphere to produce an aerosol or fog of aqueous hydrofluoric acid. Both the anhydrous and aqueous forms are easily absorbed by plant and animal tissues.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

$$nHF\ (aq.) + SiO_2 \rightarrow (n - 6)\ HF\ (aq.) + H_2SiF_6\ (aq.) + 2H_2)$$

Elemental fluoride (F_2 and some halogen fluorides (ClF_2, ClF_3, ClF_5, BrF_3, BrF_5, and IF_7) can produce injury in plant and animal tissues.

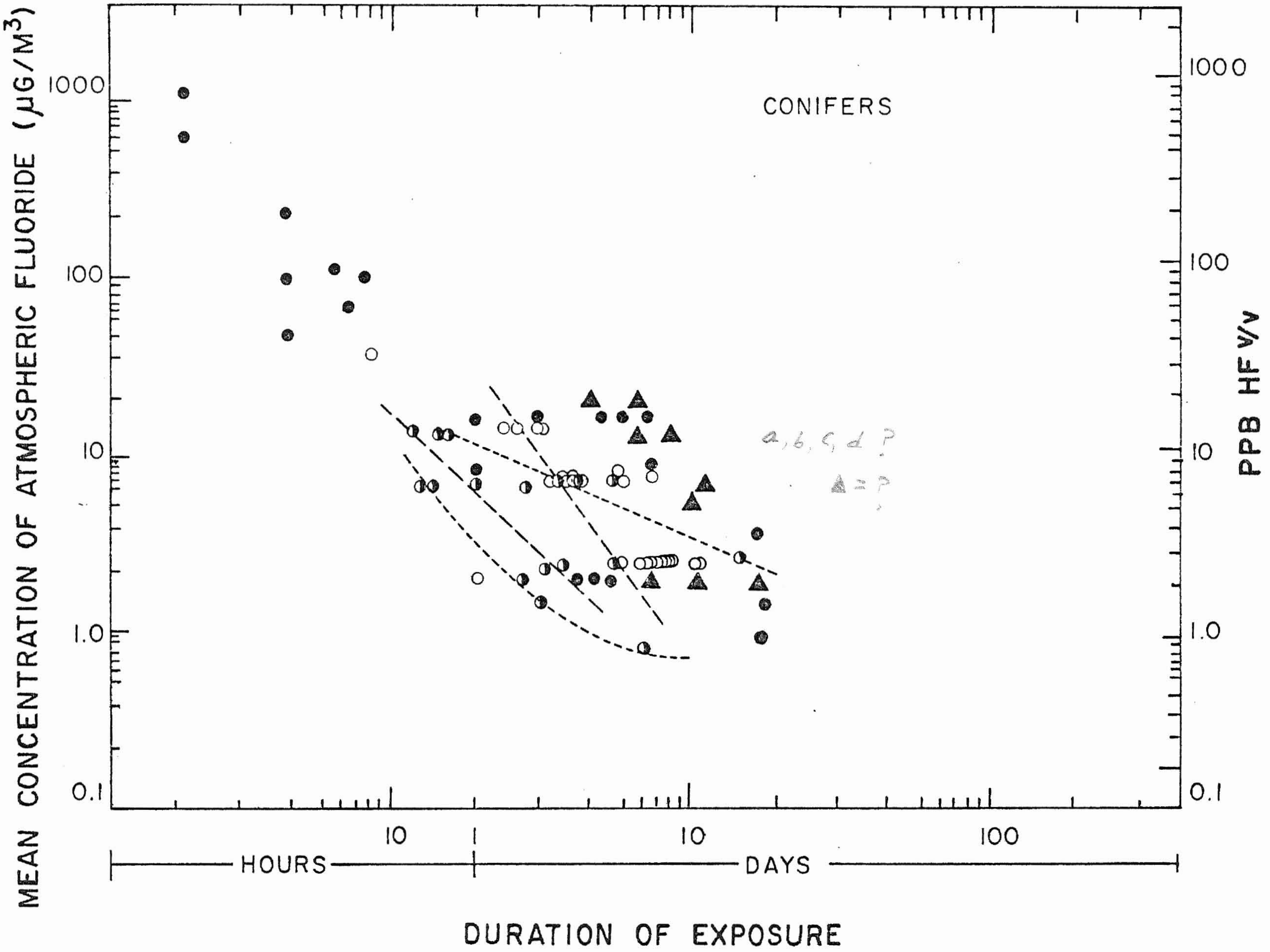
4.4 Effects of fluorides on plants.

According to the National Academy of Sciences document on fluorides (1971), plants are receptors of fluorides from three sources in their environment: soil, water and air. There is no distinction for a plant between soil and water as sources of fluoride, in that both contribute fluoride to the soil solution, the microenvironment of the roots. The phytotoxicity of fluoride from the soil or water is relatively unimportant, although the form and amounts of fluoride in or on a plant may be consequential for foraging animals. Phytotoxicity of fluorides are usually attributable to airborne forms like hydrogen fluoride, silicon tetrafluoride, and soluble particulates such as sodium fluoride and aluminum fluoride. Other forms of fluoride are less toxic but are of concern when accumulated by plants and transmitted to foraging animals.

Fluorides in the soil and water, with some exceptions generally do not accumulate in plants to toxic concentrations. Natural fluoride concentrations in plants are generally in the order of 20 ppm on a dry weight basis. Exceptions occur, however. Gaseous fluorides enter plants primarily by foliar uptake through the stomata. After entering the intercellular spaces, fluorides are absorbed by the mesophyll cells. Romell (1941) found that the fluorides subsequently move through the leaf in the transpirational stream. This movement carries the fluorides to the tips and margins of the leaves where it accumulates to several times the average concentration found in the whole leaf. Injury on broad leafed plants is generally evident as marginal and tip necrosis (Figure 2.5-1) and in conifers as necrosis of the needles, starting at the tip and spreading downwards (Figure 2.5-1).

Jacobson et al. (1966) believe that fluoride in the plant generally remains in the soluble form and maintains the properties of inorganic fluoride. The aforementioned authors observed that some fluoride can be removed from foliage by mild washing procedures. This has been interpreted as indicating that fluorides can move from the interior to the exterior of the leaf and that some of the fluorides could be subsequently lost from the leaf by rainwashing or foliar abrasion. The production of visible injury by fluorides i~~n~~s the result of their gradual accumulation over time until a toxic concentration is reached in the tissues. Figure 4.4-1 from McCune (1969) illustrates the relationship

Figure 4.4-1. Relation of concentration and duration of exposure to effects of atmospheric fluoride on conifers. O: no foliar markings observed, ●: markings present, ◐: threshold or point at which markings first appear. Curves represent possible thresholds for slight needle injury: a - larch, b - western white pine, lodgepole pine, arborvitae and spruce, c - mature needles of ponderosa pine, and d - young needles of ponderosa pine. From McCune (1969).



a, b, c, d ?

▲ = ?

incomplete

ppb = µg/m³ ?

between concentration and duration of exposure and effects of atmospheric fluoride on conifers. The time required to reach a certain foliar fluoride concentration is a function of the atmospheric fluoride concentrations. This is represented to some degree in Figure 4.4-2. It should be noted, however, that the duration of individual exposures, the influence of modifying environmental factors and the relative genetic sensitivity of the plant to the fluorides are all significant factors. The genetic control of a plant's sensitivity to fluorides can be seen in the great differences in the susceptibility which are found not only between species but also between varieties of the same species. Certain extremely sensitive species such as Chinese apricot and certain varieties of gladiolus will express visible symptoms when foliar fluoride concentrations are 30 - 50 ppm, while resistant species will not show visible symptoms at foliar concentrations of substantially greater values (excess of 100 ppm).

While foliar analysis for fluoride is a highly useful and confirmative tool, research has shown that there is no strong correlation between foliar fluoride concentrations and symptom expression in the species studied. This is an important consideration to keep in mind when evaluating and comparing lists of fluoride sensitive species which have been compiled. These lists may be based on the degree of injury produced by a given dose of fluoride, the dosage of fluoride required to reach the threshold for foliar injury, or the amount of fluoride present in foliage showing fluoride injury. The lack of correlations among these criteria often lead to variations in the sensitivity lists produced through their use. Table 4.4-1 lists

Figure 4.4-2. Relation of fluoride concentration in orchard grass to concentration of hydrogen fluoride and duration of exposure. From Hitchcock *et al.* (1971).

? units

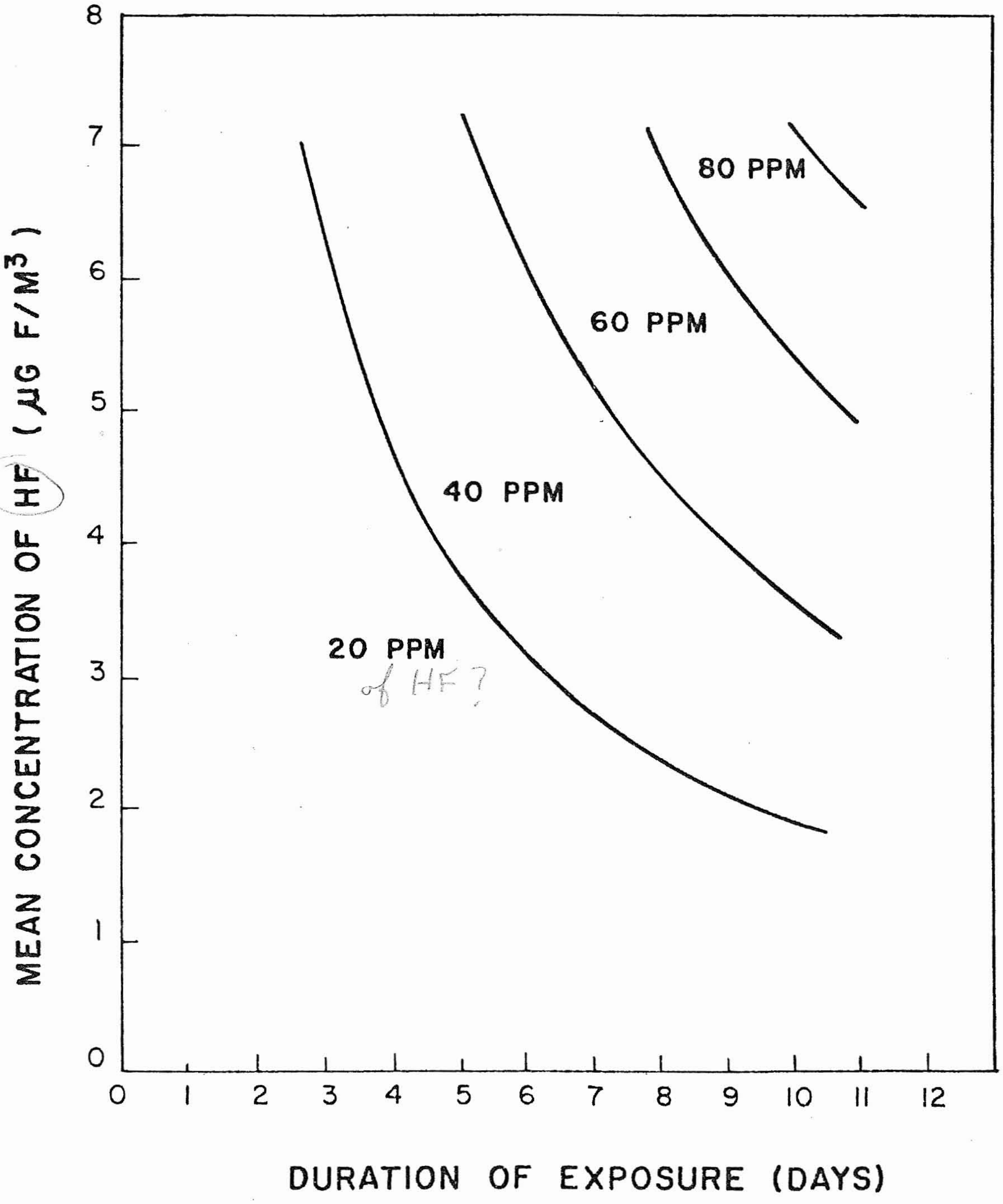

MEAN CONCENTRATION OF HF (μG F/M³)
F
0
1
2
3
4
5
6
7
8
0
1
2
3
4
5
6
7
8
9
10
11
12
DURATION OF EXPOSURE (DAYS)
20 PPM
of HF?
40 PPM
60 PPM
80 PPM

Table 4.4-1. Some Plant Species Known to Be Sensitive to Fluorides.

Blue spruce	(*Picea pungens*)
Blueberry	(*Vaccinium* spp)
Boxelder	(*Acer negundo*)
Dock	(*Rumex* spp)
Eastern White Pine	(*Pinus strobus*)
Iris	(*Iris* spp)
Smartweed	(*Polygonum* spp)
St. John's-wort	(*Hypericum perforatum*)
Western Larch	(*Larix occidentalis*)

fluoride sensitive plant species, derived from the compilation of Treshow and Pack (1970).

Injured areas on the leaves are the result of the gradual accumulation of fluorides to toxic concentrations in the tissue. If the concentration of the atmospheric fluorides is extremely high, fluoride may be taken into the leaf faster than it can be translocated to the leaf margin. In this instance, fluorides will accumulate rapidly in the central portions of the leaf with the subsequent development of interveinal areas of necrotic and chlorotic tissues. Needle necrosis in conifers has been discussed previously. In rare instances, a band of necrotic tissue will appear along the length of the needle. This banding is followed by the death of that portion of the needle distal to the band. There is frequently a sharp line of demarcation between healthy and necrotic tissue on broad leafed plants injured by fluoride. This line is an abscission layer which has been formed by cellular differentiation of the leaf mesophyll. The necrotic tissue outside this abscission layer will often drop off leaving the leaf with an irregularly shaped margin as the only indication of fluoride injury. The margin of the necrotic area may at times be characterized by the accumulation of red-brown resins or tannins. When the exposure to fluorides are intermittent, these zones of materials will be formed in succession giving a banded, stratified effect to the necrotic areas.

looks like SO_2 damage?

While foliar symptoms are characteristic of fluoride injury, they are not specific and can be mimicked by injury produced by other agents. This is particularly true of needle tip burn of conifers which can be produced by ozone, sulfur dioxide and moisture stress. On broad leafed species injury produced by chlorides, moisture stress and low temperatures will often resemble fluoride injury. The accurate diagnosis of fluoride injury requires a degree of familiarity with the symptoms produced by fluorides, the relative sensitivity of the plant species at the site, and an understanding of the local biotic and abiotic agents which may be affecting the vegetation being examined. In cases like this, foliar analysis of fluorides can often be a useful aid in the diagnosis. While such analysis can indicate the current level of fluoride in the tissue, the results must be compared with foliar fluoride levels on the same site prior to exposure or with fluoride levels at comparable control sites.

The impact of fluorides on vegetation is known to be conditioned by environmental and physiological variables. It is generally assumed that immature leaf tissues are most susceptible to fluoride. This has been observed in Ponderosa pine by Adams (1956) where the needles emerged from the fasicles were shown to be more sensitive than the mature needles. It is difficult to build a strong association between tissue age and sensitivity, since the accumulation of fluoride is often such a gradual process that foliar tissues frequently reach maturity before developing symptoms. The accumulation of fluorides is also influenced by environmental factors. Laboratory exposures by Daines et al. (1952) and Zimmerman and Hitchcock (1956) have indicated that plants experiencing a moisture stress will not be injured as severely as plants which are well watered when exposed. In the field, however, Treshow and Pack (1970) observed that those sensitive species growing under adverse edaphic conditions are consistently more severely injured than are plants growing under optimum conditions. The roles of other environmental factors, including other air pollutants, in conditioning a plant's response to fluoride have not been examined to any extent.

Subtle effects produced by fluoride, growth or yield reductions without the production of visible symptoms, have been examined. Reduced growth, leaf size and yields have been reported by Brewer and Chapman (1959) for some citrus species. Studies by Hill *et al*. (1958) and Applegate and Adams (1960) have shown that without symptom production, tomato and bush beans show no changes in growth and productivity. In some studies, fluorides have been observed to stimulate growth. This stimulatory response has been observed in Douglas fir needles and shoots by Treshow *et al*. (1967), in bean internode elongation by Adams and Sulzbach (1961) and in the growth of alfalfa by Treshow and Harner (1968).

These responses represent the findings of a variety of experimental procedures employing different pollutant concentrations, exposure times, plant materials and exposure environments. These draw attention to the range of effects which fluorides can produce on vegetation. However, the importance and relationship of these effects to the responses of vegetation exposed to fluoride in the field is still unclear.

4.5. Effects of fluorides on forest ecosystems.

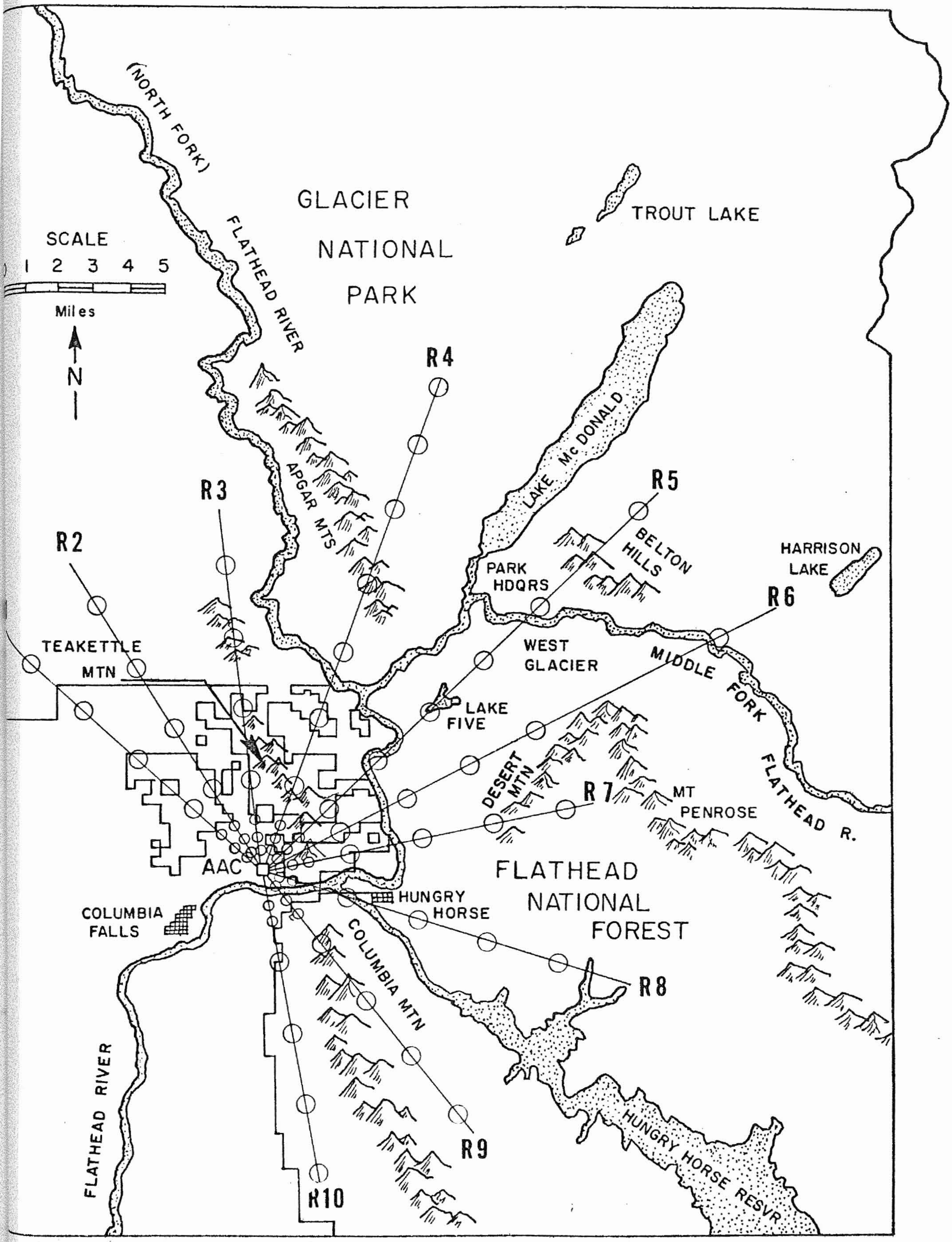
According to Carlson and Dewey (1971), the U. S. Forest Service initiated a study in 1969 to determine: 1) the major cause of vegetational injury and damage on forest lands proximal to the Anaconda Aluminum Company at Columbia Falls, Montana, 2) the source of the cause, 3) the area affected, 4) whether insects were accumulating fluorides, the suspected pollutant, and 5) if insect populations were being affected by fluorides.

Figure 4.5-1 shows the location of the Anaconda Aluminum Company reduction plant, 2 miles east of Columbia Falls, Montana and the sampling radii and plot locations. Ten radii, numbered consecutively 1 to 10, were established extending from the aluminum plant into the adjacent forested lands. The direction of each radius was based on the criteria: 1) it must transect National forest land, and 2) it should follow suspected wind channels. On each radius, basic plots 1/100 acre in size (6.6 ft. wide by 66 ft. long, oriented longitudinally) were established at 1/4, 1/2, 1, 2, 4, 6 and 8 miles from the plant. Since radii 4, 5 and 6 (Figure 4.5-1) intercepted Glacier National Park, additional plots were established at 10, 12 and 14 miles on radii 4 and 5 and at 14 miles on radius 6 to sample vegetation.

Topography of the study area varied from 3100 ft. (mean sea level) at the Anaconda plant, rising abruptly to 5936 ft. immediately east of the plant, to 8000 - 9000 ft. at the highest mountain peaks. Because of the variable topography, a number of different habitat types are represented. The more common are: Pseudotsuga menziesii, Abies lasiocarpa and Pinus albicaulis. A large variety of fauna, from grizzly

Figure 4.5-1. Fluoride study area. Note location of Columbia Falls, Anaconda Aluminum Company (AAC), Teakettle and Columbia Mountains, Glacier National Park, Apgar Mountains, Belton Hills and Lake McDonald. Note also sampling radii and plot locations (ovals).

From Carlson and Dewey (1971).


(NORTH FORK)
FLATHEAD RIVER
GLACIER
NATIONAL
PARK
TROUT LAKE
SCALE
0 1 2 3 4 5
Miles
N
R4
APGAR MTS
LAKE McDONALD
R5
R3
R2
BELTON
HILLS
HARRISON
LAKE
PARK
HDQRS
R6
TEAKETTLE
MTN
WEST
GLACIER
MIDDLE FORK
FLATHEAD R.
LAKE
FIVE
DESERT
MTN
R7
MT
PENROSE
AAC
FLATHEAD
NATIONAL
FOREST
HUNGRY
HORSE
COLUMBIA
FALLS
COLUMBIA MTN
R8
FLATHEAD RIVER
R9
R10
HUNGRY HORSE RESVR

bear and elk to small rodents, proliferate in the area (Carlson and Dewey, 1971).

According to Carlson and Dewey (1971), during 1969 and early 1970, the Anaconda Company reported that fluorides were emitted at a rate of nearly 7600 lbs. per day but were reduced to about 5000 lbs. by September, 1970. By early May 1971 emissions were reported to be reduced to 2500 lbs. per day.

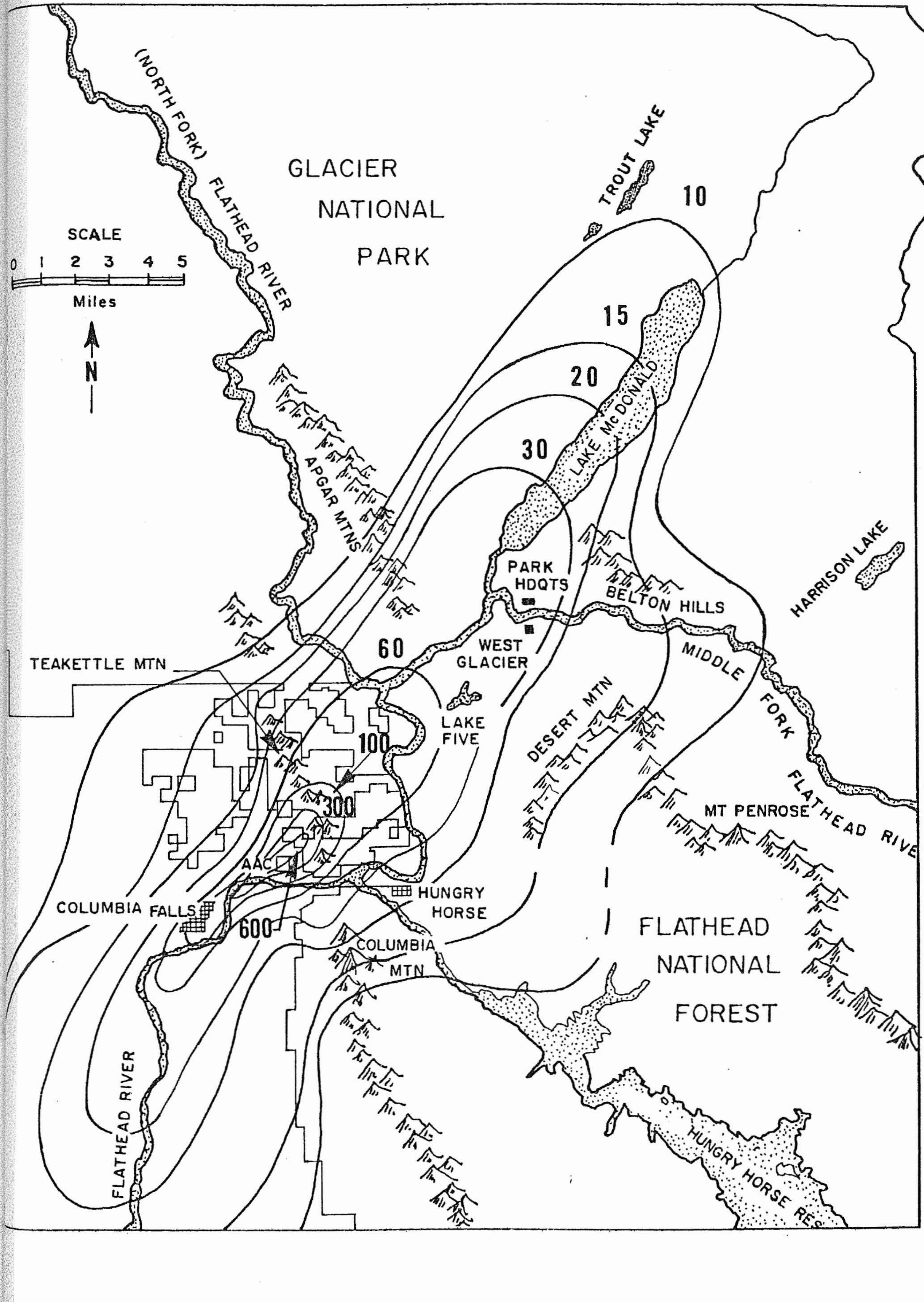
The following parameters were used in the evaluation of the pollution problem: 1) foliar fluoride content, 2) evaluation of the gross amount of foliar injury during a given year, and 3) possible relationship between injury index and foliar fluoride content.

The concept of injury index (I.I.) was developed after the field data were collected. P equals proportion of different needles showing fluoride burn symptoms for a given sample and R equals the ratio of length of burn on burned needles of the same sample. The product of PR would then be an estimate of the gross amount burned for foliage of a given year. A similar value can be computed for broadleafed plants.

Figure 4.5-2 depicts the extent of pollution. From the graphs of all radial profiles and vegetation sample data, distances at which average vegetational fluoride concentration equalled the arbitrarily established levels of 10, 15, 20, 30, 60, 100, 300 and 600 ppm were interpreted. These distances were plotted on the radii, and then equal pollution (fluoride concentration) levels were connected by lines and these lines of equal pollution were termed "isopols".

Figure 4.5-2. Isopols of fluoride pollution at Columbia Falls, Montana. 69,120 acres are included within the 30 isopol.

From Carlson and Dewey (1971).


(NORTH FORK) FLATHEAD RIVER
GLACIER
NATIONAL
PARK
TROUT LAKE
10
SCALE
0 1 2 3 4 5
Miles
N
15
20
LAKE McDONALD
30
APGAR MTNS
PARK
HDQTS
BELTON HILLS
HARRISON LAKE
TEAKETTLE MTN
60
WEST
GLACIER
MIDDLE
FORK
FLATHEAD RIVE
LAKE
FIVE
DESERT MTN
100
300
MT PENROSE
AAC
COLUMBIA FALLS
HUNGRY
HORSE
600
FLATHEAD
NATIONAL
FOREST
COLUMBIA
MTN
FLATHEAD RIVER
HUNGRY HORSE RES

Carlson and Dewey (1971) observed a constant increase in scale insects on lodgepole pine with increasing fluoride concentrations. This is depicted in Figure 4.5-3. Lodgepole pine that had scale counts exceeding 50 per 600 needles contained 23 to 401 ppm fluoride (average 133 ppm) in all vegetation, compared to a range of 6 to 160 ppm fluoride (average 35 ppm) for pines with less than 50 scales per 600 needles. A similarity in these patterns was also observed for ponderosa pine.

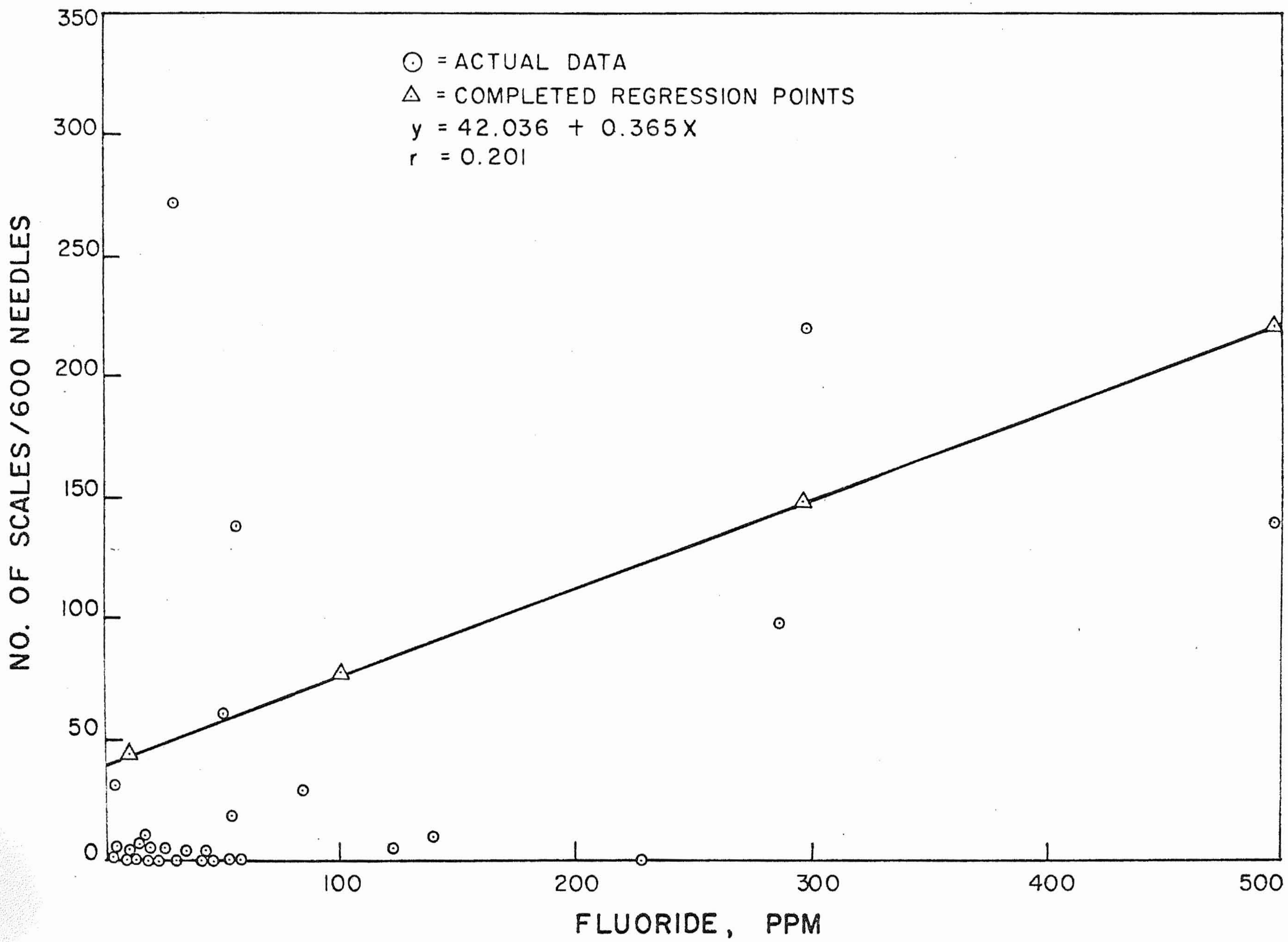
Histological and chemical analyses showed that vegetational injury was definitely associated with fluoride as a major factor. High injury indices were always associated with values of fluoride concentration above 100 ppm. The most serious vegetational injury occurred within the 60 ppm isopol (ref. Figure 4.5-2). A positive correlation was obtained between foliar fluoride level and injury index.

Apparent differences existed in species susceptibility to fluoride injury. Of the conifers, white pines were most susceptible followed by ponderosa pine, lodgepole pine and Douglas-fir, respectively. Spruces, western red cedar and subalpine fir most tolerant. Of the shrubs, chokeberry and serviceberry showed symptoms of fluoride injury quite readily while buffalo berry was the most tolerant. Lily of the valley and disporum were highly sensitive compared to other forbs. These classifications are based on field data and observations only.

According to the aforementioned authors, ecologically, western white pine is regarded as a seral or temporary species in the trend

Figure 4.5-3. Relationship between the number pine needle scales/600 needles to fluoride content, ppm. Lodgepole pine.

From Carlson and Dewey (1971).


⊙ = ACTUAL DATA
△ = COMPLETED REGRESSION POINTS
y = 42.036 + 0.365 X
r = 0.201
NO. OF SCALES/600 NEEDLES
350
300
250
200
150
100
50
0
100
200
300
400
500
FLUORIDE, PPM

towards a climax community. This species occurs on the east side of the Teakettle Mountain (ref. Figure 4.5-1) as an integral part of the forest community. However, due to severe fluoride injury, this species is dying or dead. This unnatural selection is considered to hasten the trends towards climax. The same sort of rationale may be valid for lodgepole pine.

According to the authors, previous research has shown that livestock will develop fluorosis if feeding is done on vegetation containing more than 35 ppm fluoride. The area with the 30 isopols (refer to Figure 4.5-2) contains several thousand acres of grazing lands that should not be utilized. The United States Forest Service is continuing to study this pollution problem.

4.6 Fluorides - vegetational injury evaluation techniques.

Almost all the criteria discussed for SO_2, apply for fluorides. Therefore, the reader is referred to Section 2.7 of this report for details. In addition, Sections 4.4 and 4.5 should be consulted for fluoride sensitive biological indicators and for some field techniques respectively.

Foliar fluoride analysis and soil available fluoride analysis procedures are included in the Appendix of this report.

As for ambient air monitoring of fluorides, for a long time bubbler trains have been used for trapping the particulate and gaseous fluorides from the atmosphere. In the last few years, double tape samplers have been available. These are capable of trapping both types of fluorides as separate fractions. The tapes are analyzed in the laboratory using appropriate extraction procedures and quantification methods such as the specific ion electrode. Recently, an all automated ambient fluoride monitor has been developed. This unit, however, is largely untested in the United States.