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COMPARATIVE UPTAKE OF SULFUR IN SULFUR DIOXIDE AND ACID RAIN BY CORN (*Zea Mays* L.)

A Dissertation Presented

By

James Edward Simon

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IN SULFUR DIOXIDE AND ACID RAIN
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ABSTRACT

Comparative Uptake of Sulfur In Sulfur Dioxide and Acid Rain By Corn (*Zea mays* L.)

(February,1984)

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While much is known about sulfur pollution *per se*, little is known about the form of atmospheric sulfur that can best be absorbed and neutralized by plants. This study has compared and evaluated the absorption and accumulation of sulfur from the two major forms of sulfur pollution (sulfur dioxide and sulfur containing acid rain), by seedlings of corn (*Zea mays* L.).

Plants were exposed to matched treatments containing equivalent µmoles S/treatment in sulfur dioxide or simulated acid rain containing sulfuric acid. Pollution levels were chosen to represent low, medium and high ambient pollutant concentrations (0.13, 1.3 and 130.0 µmoles S/treatment). The uptake and distribution of sulfur by plants was followed by using radioactively labelled sulfur (35-S) in both pollutants. Plants were exposed to the pollutants via a single injection of sulfur dioxide or by rainfall simulators with acid rain treatments.

From the sulfur dioxide concentrations evaluated (0.67; 1.00; 2.60; 6.70; and 16 ppm), maximum absorption occurred at the highest concentration while sulfur was more efficiently absorbed at lower concentrations. Absorption of sulfur by plants exposed to acid rain (pH 5.4; 4.4; 3.4; and 2.6) was higher with high sulfur/low pH treatments. pH *per se*, was not responsible for increased sulfur absorption at low pH treatments. Of the total sulfur associated with the plant following exposure to sulfur dioxide and acid rain, 55% and 97%,respectively was not absorbed, and could be released after one minute of a foliar wash.

Translocation of sulfur occurred throughout the plant within 24 hours, irrespective of the sulfur source. Maximum uptake and accumulation of sulfur occurred in the youngest and more rapidly growing plant parts. Initial uptake of sulfur by the foliage following an acid rain episode was related to the physical orientation of individual plant parts and the incoming rain droplets.

At each equivalent concentration of sulfur, corn seedlings absorbed significantly greater amounts of sulfur from sulfur dioxide than acid rain. Sulfur was more efficiently absorbed by corn seedlings from sulfur dioxide than from acid rain.

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CHAPTER I

Introduction

The sulfur biogeochemical cycle is a fundamental biological cycle of our planet, important to all living processes. Alterations or modifications to this sulfur cycle by anthropogenic activities are known to have direct and far reaching consequences on living components and the interelated carbon cycle (Glass, 1978). Major alterations appear to be now taking place as industrial emissions of sulfur have significantly increased the atmospheric content of sulfur to levels where sulfur can potentially cause adverse effects on the ecosystem and to human health (Berry and Bachmann, 1976; Niagru, 1980). In the Northeast, sulfur content of the atmosphere has been reported to be directly related to local combustion of fuels and transport of gaseous combustion products fom industrialized areas of the Midwest (Brady, 1974; N.A.S., 1978; Interagency Task Force, 1982). High levels of sulfur dioxide, 10-20g per cubic meter per year (N.A.S., 1978), and low pH rain (acid rain), of pH 4.0-4.3 (Godfrey, 1983), have been routinely measured in the Northeast. Future estimates indicate an increase in present atmospheric sulfur levels.

Government policy, socio-economic pressures, and the potential for the relaxation of sulfur dioxide ambient air standards, have lead to the prediction of a probable doubling of future coal use (Books and Hollander, 1979; Glass, 1978; Hibbard, 1979; Rosencranz, 1980). Sulfur dioxide and sulfur containing acid rain are the two major forms of sulfur pollution that would increase (U.S. Senate, 1980). As sulfur pollution is known to be toxic to plants, potential reductions in plant growth and yield may occur due to the occurance of sulfur in the atmosphere. Thus, an understanding of the effects and fate of these pollutants on vegetation becomes very important in order to develop strategies for eliminating or minimizing any adverse consequnces of sulfur pollution.

While much is known about sulfur pollution (i.e. sources, sinks, dispersal and transport in the atmosphere, and specific biochemical, physiological and phytotoxic effects on specific plant species), little is known about the form of atmospheric sulfur that can best be absorbed and neutralized by plants. No study has yet compared the uptake and accumulation of sulfur from the two major forms of sulfur pollution (sulfur dioxide and acid rain) by vegetation. As the eventual form and deposition of sulfur pollution from industrial sources may be modified by technological factors, an understanding of the ultimate fate of sulfur dioxide and acid rain will help determine which type of sulfur pollution can be better neutralized by vegetation (U.S. Senate and House of Rep., 1980; Interagency Task Force, 1982; U.S. House of Rep., 1981; U.S. Senate, 1980).

The research in this report examined and evaluated via a comparative approach, the absorption and distribution of sulfur as sulfur dioxide and sulfur containing acid rain in plants of corn, *Zea mays* L. Corn was selected as the test plant because it is an important economic plant cultivated in Northeastern areas of the United States most severely affected by sulfur pollution. To determine the uptake of sulfur pollution, plants were exposed to matched treatments of sulfur dioxide or acid rain, based on equivalent amounts of sulfur from each of the sources and on concentrations which simulate ambient pollutant conditions of the Northeast.

The proposed study was designed to generate directly comparable data for indicating the form of sulfur pollution that can best be absorbed by the plant, and to offer a new approach to study different forms of air pollutants thru the application of treatments based on equal amounts of the pollutant species where possible. It is anticipated that this data could serve as part of an informational base on atmospheric pollution and aid in management decisions in the control of sulfur emissions.

CHAPTER II

LITERATURE REVIEW

Sources of Sulfur Pollution. Sulfur dioxide is a direct result of the oxidation of fuel containing sulfur while sulfur containing acid rain is a secondary compound formed by the interaction of sulfur dioxide with moisture in the atmosphere (Anon., 1979; Galloway and Whelpdale, 1980; Varshey and Dochinger, 1979). 1980). In the Northeast, sulfuric acid accounts for approximately 60-70 % of the acidity and nitric acid for 20-30 % of the acidity (Babich, 1980; Cogbill and Likens, 1974; Galloway, 1979; Henry, 1980). Acid rain (rainfall with a pH less than 5.6), is also composed of various other cations, anions, and acids.

The atmospheric processes through which sulfur dioxide is transformed into sulfate and sulfuric acid can not yet be described quantitatively (N.A.S., 1978; Ronneau, 1978). The oxidation of sulfur dioxide within power plant plumes has been reported to be both first order and second order kinetic reactions (Forney, 1980). The overall reaction rate probably changes with changes in droplet acidity, and sulfur dioxide concentration (Freiberg, 1975). The oxidation rate would also be affected by relative humidity (Sheffy, 1980), sunlight intensity (Sheffy, 1980), temperature (Freiberg, 1974), the presence of catalysts in water droplets (Overton, 1979), and other gaseous pollutants (Overton, 1979). It has been estimated that between 50-80% of the sulfur dioxide in the atmosphere is converted by oxidation and photochemical reactions into sulfate and acids for recycling as precipitation (Hill, F., 1973; N.A.S., 1978). The rate of conversion from sulfur dioxide to sulfate appears to vary from 0.1 to 30% per hour and the residence time of sulfur compounds is 2-4 days from emission to deposition (N.A.S., 1978). The pollutants may therefore exist alone or in combination in the atmosphere at any given time with the atmospheric concentrations in constant flux.

Atmospheric dispersion and long range transport of sulfur dioxide and sulfate depend upon the topography and meteorological conditions where temperature, turbulence and wind flow patterns play major roles (Fisher, 1978; Hogstrom, 1978; Shreffler, 1978). In the United States, transportation of most sulfur pollution is generally eastwards or northeastwards by the wind (N.A.S., 1978). Sulfur in the atmosphere is then deposited directly as sulfur dioxide or sulfate species on particulate matter on soil and vegetation (dry deposition) while the rest is removed by wet deposition via rain, fog or snow, or becomes part of the the world-wide sulfur background. Sulfur emissions appear to follow a seasonal and diurnal cycle with the summer months having the highest emissions of sulfur.

It appears that with the sulfur dioxide release into the higher sections of the atmosphere via tall smokestacks more sulfur dioxide can be converted to acid rain as the sulfur dioxide is horizontally and vertically distributed (Nriagu, 1978). Oxides of sulfur are known to be transported thousands of miles from the originating source (Lyons, 1978; Rosencranz and Wetstone, 1980; Wetstone, 1980(b)). Thus, the short range solution of providing taller smokstacks for reduced localized pollution appears to have only created increased regional, national, and international sulfur pollution problems (Babich, 1980; U.S. House of Reps., 1980). While indirect evidence all appears to point to anthropogenic activities as the source of the acid rain phenomenon in the United States and Europe, conclusive proof linking emissions of sulfur and other air pollutants to actual acid deposition is still missing.

<u>Vegetative Absorption of Atmospheric Sulfur</u>. Sulfur dioxide can be directly absorbed by vegetation (Cowling, 1973; Hill, 1971; Kellog, 1972; Linzon, 1979) or adsorbed to plant surfaces and soil particles (Heath, 1980; Smith, 1973; Yee, 1975). The removal

of sulfur dioxide by vegetation appears to be influenced by the vegetative canopy, the boundary layer adjacent to the leaf surface, the stomatal opening, the lining of the walls of the mesophyll cells, the sum of the overall atmospheric resistances (wind, and atmospheric stability (Hill,F., 1973, Shieh, 1972) plus time, duration and concentration of exposure (Lauenroth, 1979). As the sulfur species enters the plant, predominantly by diffusing through the stomata (Spedding, 1969; Heath, 1980), and cell walls (Klein, 1978), it is subjected to similiar physical constraints as are other gaseous species entering the leaf (i.e. carbon dioxide). The rate of uptake is dependent on the rate of diffusion, concentration gradient, and diffusion coefficient (Fowler, 1980; Heath, 1980). Deposition velocities have also been shown to depend on leaf age and position on the plant (Bressan _et al_., 1978) as well as such environmental factors as relative humidity, light intensity, time of the day of exposure and status of nitrogen nutrition (Bressan _et_ _al_., 1978; Heath, 1980; Leone and Brennan, 1972; Shieh, 1972). Sulfur species may also enter to a lesser extent through the cuticle and epidermis (Fowler, 1980; Heath, 1980). In an attempt to quantify sinks for sulfur dioxide deposition on wheat, Fowler and Unsworth (1979) found that of the sorbed sulfur dioxide 70% was sorbed via the stomata, almost 30%

by plant cuticles, and only a few percent by the exposed soil. Several studies have estimated the rate of air pollution removal by vegetation (Bennett, 1973; Craker, 1973; Hill, 1971; Rogers, 1977). Hill (1971) reported that sulfur dioxide was absorbed by plant foliage at a rate of 1.7 $\mu l/m^2$-min ppb, and concluded that vegetation may be a significant sink for sulfur dioxide. The amount of absorption of acid rain is still unknown. Recent work has indicated that the concentration of sulfur in the leaves of bush beans exposed to sulfuric acid-simulated acid rain may increase due to the sulfur in the solution (Evans *et al.*, 1981; Hindawi *et al.*, 1980). Leaves of beans kept in contact with solutions of simulated acid rain labelled with $H_2{}^{35}SO_4$ did incorporate the sulfur, with greater incorporation observed at lower pH levels (Evans *et al.*, 1981). Atmospheric sulfur adsorbed by the soil and available for plant uptake is absorbed by the plant roots in the same manner that soil sulfur or sulfur containing fertilizer is absorbed. Uptake of sulfur by plant roots appears to be an active process, one in which a carrier site is most likely utilized, but the entire process is not well understood (Mengel and Kirkby, 1978).

Accumulation, Metabolism and Translocation of Atmospheric Sulfur by Plants. Sulfur, an essential nutrient element for plants, is used for the formation of various amino acids in protein synthesis, for activation of certain proteolytic enzymes, and as a constituent of certain vitamins in plants (Linzon _et_ _al_., 1979; Mengel and Kirkby, 1978). Sulfur is also associated with the protoplasmic structure and with nitrogen fixation as part of the nitrogenase enzyme system (Mengel and Kirkby, 1978).

Once sulfur dioxide is absorbed and is inside the aqueous solution, the sulfur dioxide converts into bisulfite or sulfite ions which can readily be oxidized to sulfate and utilized by the plant cell (Malhotra, 1976). For sulfate to be incorporated into organic compounds, as the sulfur-containing amino acids cysteine, cystine and methionine or proteins, the sulfur must be in a reduced form (Mengel and Kirkby, 1978). Sulfate reduction is thought to occur in the chloroplasts, via the assimilatory sulfate reduction pathway (Schiff and Hodson, 1973), although recent evidence indicates that it may also occur outside the chloroplasts (Stern, 1983). This path is dependent upon photosynthesis and energy as ATP and reductants are required (Mengel and Kirkby, 1978). The reactions of sulfite, it's oxidation products, alterations in cellular pH and disruption of proton gradients in the cell, due to the acidifying nature of these species appear to be responsible for altering cellular components, membranes and metabolic functions such as uncoupling photophosphorylation, that contribute to the phytotoxicity of atmospheric sulfur (Heath, 1980; Malhotra,1976). Sulfur species from absorbed sulfur dioxide for example is reported to inhibit both photosynthetic carbon dioxide fixation and oxygen evolution associated with carbon assimilation, the latter by competiting with phosphate in photosynthetic phosphorylation and limiting ATP synthesis (Cerovic _et al_., 1982; Plesnicar and Kalezic, 1980; Ziegler, 1975).

Sulphate absorbed by the root is mainly translocated in an acropetal direction with basipetal movement of sulfur relatively poor (Mengel and Kirkby, 1978). In contrast, Garsed and Read (1977) report that sulfur absorbed from exposing the foliage to sulfur dioxide can be tranlocated throughout the entire plant.

The comparative characteristics of the absorption of sulfur by different sources (atmospheric versus soil) is not well understood. Garsed and Read (1977) report that incoming sulfur dioxide is metabolized in preference to endogenous sulfur. If this is indeed the case then the 'preference' for metabolizing foliarly absorbed sulfur may be a mechanism by which the plant can regulate and detoxify excessive sulfur. Whether the plant in an atmosphere contaminated with sulfur dioxide selectively stops absorbing soil sulfur or whether it continues absorbing soil sulfur reaching the "mininum" threshold for phytotoxicity earlier is not clear. Coughenour et al. (1980), in their simulation of a grassland sulfur-cycle, proposed that sulfate uptake by the roots is related to the sulfur demand for the whole plant. Use of radioactive sulfur as a tracer of sulfur movement in plants has indicated that plants do not metabolically distinguish or discriminate between sulfur absorbed through roots or through the leaves (Linzon, 1979). Excessive sulfur absorbed by the roots is stored as sulfate-sulfur. As to whether excessive sulfur absorbed from the atmosphere and translocated to the roots is leached or diffused into the root medium is still unclear (Glass, 1978; Jensen, 1975; Taylor, 1975).

Response of Vegetation to Atmospheric Sulfur as SO_2 and Acid Rain. Heath (1980) characterized the initial events of sulfur dioxide injury to plants as alterations in biochemical pathways and/or osmotic imbalances which result in modifications in membrane integrity and inhibitions or declines in plant physiological processes which result in plant stress and injury. Initial cellular injury may include collapse of mesophyll and epidermal cells, distortion of chloroplasts, and changes in cell carbohydrates and proteins (Koziol, 1978; Kozlowski, 1980; Malhotra, 1980; Priebe, 1978). Reports also indicate sulfur dioxide interference in transpiration (Suwannapinunt, 1980), translocation (Noyes, 1980), photosynthetic carbon dioxide fixation (Barton, 1980; Malhotra, 1976; Noyes, 1980; Shimazaki, 1979), chlorophyll content (Suwannapinunt, 1980), mitochondrial ATP production (Malhotra, 1976), energy metabolism (Heath, 1980; Malhotra, 1976) and a variety of enzyme systems (Grill, 1979; Malhotra,1980; Rabe, 1980; Rao, 1983). Silvius *et al*. (1976) reported that the photo-reduction of sulfur dioxide by spinach chloroplasts could result in competitive inhibition of photosynthesis and be responsible for decreased growth and yield of green plants exposed to sublethal levels of sulfur dioxide.

Plants differ significantly in their tolerance or susceptibilty to sulfur dioxide. This difference has been noted between species (Bell and Mudd, 1976; Garsed and Read, 1977; N.A.S., 1978; Roberts, 1976; Winner and Mooney, 1980) and between individual cultivars and individual leaves (Bressan *et al*., 1978; Garsed and Read, 1977; Klein *et al*., 1978; Roberts, 1976). Internal sinks within plants for sulfur may differ for different plants and it is not known whether these sinks are based mainly on physical, chemical, or physiological parameters (Klein et al., 1978).

For an air pollutant to induce a stress or injury on a plant it must first contact a plant surface and remain in contact long enough to either induce a biochemical or physical change with or without being absorbed by the plant. Yet the quantity of sulfur bound (adsorbed) to the leaf surface following exposure to sulfur pollution, and the relationship to absorbed sulfur is largely unknown. Garsed and Read (1977), did indicate that a significant portion of the sulfur may be adsorbed to the leaf surface following a pulse (single injection) of sulfur dioxide. Plants may be able to avoid sulfur dioxide stress by closing the stomates at high sulfur dioxide levels (Noland and Kozlowski, 1979), by storing absorbed sulfur in vacuoles, or as choline sulphate that can be transported throughout the plant (Ziegler, 1975). While the total amount of absorbed sulfur was believed to be directly related to the susceptibilty of a plant, the relative rate of absorption may actually be of greater importance (Bressan _et_ _al_., 1978). Plants naturally detoxify atmospheric sulfur by compartmentalization. As an essential element, sulfur absorbed is metabolically and physiologically used by the plant. Leaves of plants also appear to have the capacity to convert up to ten percent of absorbed sulfur dioxide to hydrogen sulfide, which then is emiited from the plant (Sekiya _et_ _al_., 1982). Hydrogen sulfide emission appears to be a means by which excessive inorganic sulfur anions can leave the plant when hydrogen sulfide acceptors are not available in suffient quantity and may be part of the biochemical basis of resistance to sulfur dioxide (Wilson _et_ _al_., 1978; Sekiya _et_ _al_., 1982).

When a particular soil is limited in sulfur, low concentrations of atmospheric sulfur and nitrogen can be beneficial to meet crop requirements and increase yields of agricultural crops. Cowling _et_ _al_. (1973) reported increased yields of ryegrass grown in sulfur deficient soil from exposure to sulfur dioxide. Sulfur input into the soil from precipitation has also been shown to improve sulfur deficient alfalfa plants which obtained most of the required sulfur from the atmosphere (Hoeff _et_ _al_., 1972). It has also been reported that forests and noncultivated plants obtain sulfur and nitrogen from the atmosphere and which can contribute a significant portion of the total nitrogen and sulfur that enter regional-local ecosystems (Tabatabai, 1981). In studies such as these it appears that when sulfur is limiting to plant growth, inputs of sulfur, from any source, will benefit the plant. A minimum or threshold level below which most plants are not visibly injured by sulfur dioxide exposure, even during chronic exposure has been reported as 0.15 ppm (393 μg per cubic meter) sulfur dioxide (Varshney and Garg, 1979).

Plants can be injured by sulfur dioxide even in the abence of visual symptoms (Heath, 1980; Varshney and Garg, 1979). Where spruce (*Picea abies* L. Karst.) were continually fumigated for 10 weeks with sulfur dioxide at concentrations of 0 to 0.2 ppm, the uptake of carbon dioxide, the width of annual growth rings and the density of late wood were decreased prior to the appearance of visible symptoms (Keller, 1980). Reductions in photosynthesis prior to visible symptoms have also been noted in other species following exposure to sulfur dioxide (Kozlowski, 1980).

Other factors reported to influence sulfur dioxide susceptibility of plants include plant age (Craker and Starbuck, 1973; Varshney and Garg, 1979), exposure period (Costantinidou *et al*., 1976), environmental conditions (Bennett *et al*., 1975; Leone and Brennan, 1972; Peiser and Yang, 1978), and edaphic conditions (N.A.S., 1978). Sulfur dioxide is known to act synergistically with other gaseous air pollutants such as ozone (Menser and Heggestad, 1966; fluorine (Roques *et al*., 1980) and nitrogen dioxide (Bennett *et al*., 1975). Experimental exposure conditions (i.e. concentration of air pollutant, duration of exposure period, species and cultivar selection) have varied greatly among researchers often making direct comparisons difficult. Differences in plant sensitivity are reported for different exposure chambers and measurement techniques (Heck *et* al., 1978; Hill,1971; Hill, 1967; Rogers et al., 1977).

Phytotoxic symptoms (i.e. necrotic lesions) have been reported on many woody species (Cogbill, 1976; Jacobson and Van Leuken, 1977; and Wood and Bormann, 1974), herbaceous species (Evans et al., 1979 Ferrenbaugh, 1976; Hindawi et al. 1980; Lee and Neely, 1980), and lower plants (Sheridan and Rosenstreter, 1973), when exposed to simulated acid rain or mist where the principle acidity source was sulfuric acid. Damage to the foliar epidermis of plant species by acid solutions has been observed (Evans and Curry, 1979; Evans et al., 1977). Acid rain has been reported to adversely affect seed germination and seedling establishment (Varshney and Garg, 1979).

Plants do differ in their sensitivity to simulated acid rain (Evans et al., 1978; Jacobson and Van Leuken, 1977; Varshney and Garg, 1979). Plants possess characteristics that may exclude precipitation and offer protection against phytotoxicity of acid rain. Mechanisms for plant tolerance to acid rain can be based on Jacobson's (1980), classification of exclusion, neutralization, and metabolic feedback reactions. Exclusion is based on leaf and flower orientation and morphology, chemical composition of cuticle, and protection of reproductive organs and pollination. Neutralization of incoming acidity is based on the buffering capacity of the leaf and presence of salts on the leaf surface to neutralize the acidity. Enzymatic reactions that consume hydrogens ions or yield alkaline products refer to metabolic feedback mechanisms. Foliar injury has not yet been correlated with yield effects (Lee and Neely, 1980), and to date there has not been any legal documented cases of acid rain damage to naturally growing plants or cultivated crops.

Lee and Neely (1980), examining the effects of simulated acid rain on yield and foliar injury for several herbaceous crops, concluded that dicotyledons were more adversely affected than monocotyledons. Among dicotyledons, the yields of root crops were most affected, followed by leaf, cole, and tuber crops. Legumes and forage crops may be more susceptible and grain crops may be more tolerant of acid rain conditions. Hindawi et al. (1980) reported reductions of seed and pod growth of bush beans when exposed to simulated acid rain even though no visible foliar injury was detected. Kratky et al. (1974) found that fruit set was decreased as a result of acid retardation of pollen germination and pollen tube growth.

Evans et al. (1978, 1980) reported that sexual reproduction of bracken fern was decreased significantly in laboratory solutions with acidic pH and by the addition of sulfate. Erosion of epicuticular waxes of plant leaves by sulfuric acid (Shriner, 1976), as well as accelerated foliar leaching of organic and inorganic substances from leaves (Fairfax and Lepp, 1975; Hindawi et al., 1980; Hoffman, 1980; Liken, 1972; Scherbatskoy and Klein, 1983) have been observed from foliage subjected to low pH simulated rain solutions. The rate of leaching appears to be influenced by pH of the solution with the highest rate occurring at the more extreme acidic concentrations (Evans et al., 1981). Few studies have looked at foliar incorporation of sulfur compounds from acid rain by plants following exposure to acid rain, and the contribution of rain on the nutrient composition of plants is unknown (Jacobson, 1980). It is still unclear whether the components in acid rain actually penetrate the foliage directly and contribute to the internal pool of available elements (i.e. sulfur and nitrogen) necessary for plant growth and development or to its potential phytotoxicity.

Foliar injury of agricultural crops and ornamental crops from acid rain could result in a significant reduction of the quality of the harvestable and marketable plant parts if necrotic lesions or any other visual injury occurs. Several studies have indicated that the development of necotic spots following exposure to simulated acid rain on plant leaves (Lee and Neely, 1980; Simon et al., 1983), and flowers (Keever and Jacobson, 1983), and fruit (Forsline _et_ _al_., 1983) can decrease the quality and marketablity of these crops.

It is still unclear whether yields and selected qualitative parameters are affected under natural conditions (either positive or negatively). In some locations, particularly those agricultural and grassland ecosystems that receive little or no fertilizers inputs of nitrogen, sulfur and phosphorus in rain may be benficial to plant growth, irregardless of whether the minerals are absorbed via the foliage or roots. (Tabatabai, 1981).

Soil Absorption of Atmospheric Sulfur. Soils have the ability to absorb large quantities of atmospheric sulfur. Nyborg et al. (1976) reported that certain Canadian soils could absorb as much as 50 kg S/ha/yr. The adsorption process is rapid and near complete sorption generally occurs within 40 minutes after exposure to sulfur dioxide (Yee _et_ _al_., 1975).

The removal of sulfur dioxide by soil is influenced by the soil type (Yee _et_ _al_.,1975), moisture level (Hales and Suter, 1973; Terraglio and Manganelli, 1966), atmospheric conditions, residence time of the sulfur dioxide passing over soil, and the direct exposure of the soil to the atmosphere (Eriksson, 1963; Yee _et_ _al_., 1975). Norton (1976) has theoretically predicted that sulfur dioxide adsorption is influenced by differences in soil acidity. Yee et al. (1975) reported that the sorption capacity of sulfur per unit weight of soil increased with sulfur dioxide concentration and specific surface area of the soil. Organic matter appears to increase sulfur dioxide sorption (Ghiorse and Alexander, 1976). Sulfur dioxide solubility is also affected by the pH of atmospheric moisture. Hales and Sutter (1973) experimentally measured a reduced solubility of sulfur dioxide in water when pH was lowered from 4.0 to 3.0. Soils with higher soil moisture contents sorb greater amounts (up to ten times) of sulfur dioxide than dry soils (Norton, 1976; Terraglio and Manganelli, 1966). Higher temperatures as well as the presence of metals, such as iron and manganese, enchance sorption of sulfur dioxide (Barrie and Georgi, 1976; Johnson and Cole, 1976; Parfitt and Smarti, 1978).

Soil sulfur is generally found in the form of sulfate, present either in the soil solution, adsorbed on soil colloids, or as organically bound sulfur. Sulfate can be directly absorbed by vegetation, leached from the soil, or exchanged onto the soil colloids (Bohn et al., 1979). The movement of sulfate is dependent on soil composition and precipitation patterns. Organic sulfur becomes available to the plant via microbial activity which by the process of mineralization forms hydrogen sulfide which is transformed rapidly under aerobic conditions to sulfate (Mengel and Kirkby, 1978).

Response of Soil to Atmospheric Sulfur as SO_2 and Acid Rain.

Soil acidification, due to organic acidity and chelation (Brady, 1974; Bohn *et al*., 1979), nitrification, mineralization (Brady, 1974; Bohn et al. 1979), and oxidation of parent materials are natural processes. These sources tend to release hydrogen ions in concentrations of up to 1 keq/ha/yr (Bache, 1980), an amount significantly less than the potential contribution by anthropogenic inputs. (Greenfelt *et al*., 1980). Most soils appear to exhibit a certain buffering capacity that permits sorption of atmospheric sulfur by soils without inducing great environmental changes (Brady, 1974; Shriner and Henderson, 1978; Singh *et al*., 1980). However, continuous exposure to atmospheric sulfur could potentially result in increased acidification (Baker *et al*., 1976; McFee *et al*., 1976; Shriner and Henderson, 1978) because the atmospheric sulfur is oxidized to sulfate (Smith *et al*., 1973). Subsequent removal of the sulfates by leaching, immobilization, and plant uptake would make the sorption exchange sites available for additional sorption of sulfur. Mobility of the sulfate is related to sulfate adsorption capacities of individuals soils, which in turn are dependent on the aluminum contents of these soils (Singh et al., 1980).

Soil acidification estimates due to acid rain, range from a one pH unit drop in 10 to 20 years for Canadian prairie soils (Nyborg, 1976) to a 0.6 pH drop over a 100 year period for some typical midwestern forest soils (McFee et al., 1976). Soils respond to an increase in hydrogen ions in the soil solution through changes in properties of particle surfaces and surface adsorption (Bache, 1980; Wiklander, 1980), as well as through changes in the concentration and structure of the aluminum-hydroxide solids and complexes (Bache, 1980; Ulrich, 1980; Van Breemen and Wielemaker, 1974). Acid neutralization is also observed in soils through mineral degradation or transformation (Bohn et al., 1979; Van Breemen and Wielemaker, 1974). Acidification leads to an increased leaching of exchangeable bases, especially calcium and magnesium (Baker et al., 1976; Brady, 1974; Bohn et al., 1979), ultimately increasing the chemical weathering of the soil and the alteration of the clay mineralogy (Bohn et al., 1979; McFee et al., 1976; Norton, 1976). These changes are reflected in elevated levels of extractable hydrogen and aluminum and depressed values for exchangeable cations and cation exchange capacity (McFee et al., 1976).

The effects of acid rain and prolonged exposure to atmospheric sulfur probably most apparent in uncultivated soils (Frink and Voight, 1973) which are slightly acidic, poorly buffered, and free draining with low anion-binding capacity. These soils are commonly found in Northeastern United States and Eastern Canada where the greatest amounts of acid rain are falling (Varshey and Dochinger, 1979). Soils in areas of low-order drainage systems are sensitive to alterations particularly where the bedrock is chemically unreactive such as with granite and acidic metamorphic rocks (Johnson, 1979). Field surveys indicate the greatest damage to aquatic ecosystems has been occurring in these areas of the Northeastern United States (Johnson and Freedman, 1980).

The influence and significance of pH changes in soil systems needs to be viewed within the context of the soil ecosystem in question. Soils which generally would respond most to acidic deposition by a drop in pH, and concurrent mobilization of compounds (i.e. aluminum, iron, manganese) in the soil that could adversely affect the soil, plant and biota are the poorly buffered uncultivated soils. Alterations in the nutrient cycle for these soils could critically alter and damage the capacity for that soil to maintain or support the present biota (productivity of and species composition). Agricultural soils, in contrast, are generally well buffered and subject to large inputs of fertilizers, lime, and a host of additional soil amendments. Thus, agricultural soils would be less influenced by additions of acid rain. Acidity created by adding fertilizer to agricultural soils have been reported to have a greater impact on pH changes and soil chemistry than acid rain. (Tabatabai, 1981; Tamm, 1976). Adverse effects on nitrogen fixation by simulated sulfuric acid rain caused by acidification and lowering of soil pH has been observed (Denison *et al*., 1976; Shriner, 1976).

Effects of Sulfur Dioxide and Acid Rain to Terrestrial Ecosystem.

Any disturbance to a plant ecosystem can be accompanied by a change in growth, development and maturation of that ecosystem. For example, there could be a reduction in plant diversity through the elimination of sensitive species. In forests, this has been observed as an elimination of the upper tree canopy and survival of the lower more resistant shrubs and herbs (Woodwell, 1970). The implications of sulfur pollution changing the composition of plant species within an ecosystem has not been fully explored.

Sulfur dioxide concentrations are presently known to be of sufficient magnitude to act as a major nutrient input and modifier of nutrient cycling in terrestrial ecosystems (Glass, 1978). The effects of acid rain on terrestrial ecosystems,with principal effects on vegetation, have been summarized by Varshney and Dochinger (1979) as changes in the nutrient budgets of forests and agricultural lands, loss of species diversity, and inhibition of soil microorganisms such as nitrogen-fixing bacteria. Other reports have indicated decreased plant yields due to suppressed or inhibitory growth of mycorrhizal fungi (Tamm and Cowling, 1976) and reduced photosynthesis (Varshney and Garg, 1979). Exposure to sources of acidity can result in increased leaching of cations in forest soils (Cole and Johnson, 1977; Overrein, 1972), leaves (Fairfax and Lepp, 1975; Hindawi et al., 1980; Scherbatskoy and Klein, 1983), and bark (Hoffman et al., 1980), plus alter plant responses to pathogens and symbiotic organisms (Denison et al., 1976; Shriner, 1976; Tamm and Cowling, 1976; Varshney and Dochinger, 1979). Plant responses to additional environmental stresses may also be altered after exposure to sulfur pollution. Decourt et al. (1980) found that the development of Beech bark disease was decreased with increased sulfur pollution levels. It has been proposed that additions of sulfite on the foliage may actually inhibit the germination of fungal spores thus offering protection as a fungicide. Pastor and Bockheim (1980) estimated that the forest canopy's leaf and bark surfaces may sorb up to 40% of the incoming acidity due mainly to sulfuric acid.

CHAPTER III

MATERIALS AND METHODS

General. Studies on the absorption and neutralization of the pollutants sulfur dioxide and acid rain by plants were conducted by exposing corn seedlings to sulfur dioxide and acid rain. Comparative information on the absorption of both pollutants was obtained by baseing the treatment concentrations of sulfur dioxide and sulfur containing acid rain on equivalent amounts of sulfur.

Plant and Soil Material. Seedlings of corn, *Zea mays* L. cv. Sprite (Harris Seeds, Moreton Farm, Rochester, NY) were used in all studies. Additional cultivars of corn (Muncy Chief Hybrid [GGO MF-7], Hoffman Seed and Grain Co., Muncy, PA; Northrup King Hybrid Seed Corn [PX11-35015], Northrup King Co., Minneapolis, MN; and Quicksilver, Harris Seeds, Moreton Farm, Rochester, NY) were used in experiments to examine whether uptake of sulfur from sulfur dioxide and acid rain was influenced by cultivar. For physiological studies, seeds were imbibed in tap water for 48 h at room temperature and subsequently seeded 1 cm deep in a steam-sterilized soil mix (2 parts Hadley silt loam, 1 part sand, 1 part peat, and 75 g limestone /cubic meter), (Table 1), in

Table 1

Chemical Composition of the Soil Media[1]

pH	6.4
Buffer pH	7.2
Soluble salts	13.0
C.E.C. (meg/100g)	4.6
Nutrient Levels (ppm)	
NH_4N	5.0
NO_3N	120.0
P	3
K	33
Ca	505
Mg	186
Cu	0.3
Fe	8.0
Mn	8.0
Al	53.0

1. Analyzed by the Soil and Plant Testing Laboratory, Coop. Ext. Serv., Sub. Exp. Sta., Waltham, MA

specially constructed columnar acrylic containers (10 cm diameter X 15 cm depth). The containers served as the base portion of the exposure chamber during treatment with pollutants (Figure 1). Corn seedlings used in the studies to assess the differences in the uptake of sulfur by corn cultivars, were seeded directly (1 plant/pot) into plastic pots (7.5 diameter X 7.0 cm depth) containing the soil mix. All plants were grown in a controlled environment room (14 h photoperiods, 65 $\mu Em^{-2}s^{-1}$ photosynthetic active radiation [PAR], 25°C day/ 20°C night temperatures).

Sulfur dioxide and acid rain treatments. Sulfur dioxide and acid rain concentrations were chosen to represent potentially low, medium, and high levels of sulfur pollution. Most studies are based on exposure of plants to a single two hour exposure of 1.3 μmoles sulfur, equivalent to a sulfur dioxide concentration of 6.7 ppm (1.75 x 10^{4} μg sulfur dioxide per cubic meter) or a simulated rain solution of pH 4.4 (Table 2).

Sulfur dioxide (prepared from air dilutions of concentrated sulfur dioxide), was added to the treatment chamber (at concentrations listed in Table 2) using a hypodermic needle and syringe to inject the sulfur dioxide into an inlet port located near the top of the exposure chamber (Figure 1). This was immediately followed by an injection of a fixed amount of

TABLE 2

Basic Treatment Schedule for Sulfur Dioxide and Acid Rain Uptake Studies

I.		SO_2		
Treatment	ppm	µg SO_2/m^3	µmoles SO_2/m^3	µmoles S/treatment
1 (control)	0	0	0	0
2	0.670	$1.75 \times 10^{+3}$	27.4	0.13
3	1.00	$2.62 \times 10^{+3}$	40.90	0.19
4	2.60	$6.81 \times 10^{+3}$	106.33	0.50
5	6.700	$1.75 \times 10^{+4}$	274.0	1.3
6	67.000	$1.75 \times 10^{+5}$	2740.0	13.0

1 Based on the volume of the exposure chamber illustrated in Figure 1.

II.			ACID RAIN		
Treatment	pH	µg SO_4^{-2}/ml	µmoles SO_4/ml	ml/treatment[2]	µmoles S/treatment[3]
1 (control)	5.4	0	0	104	0
2	5.4	0.12	1.25×10^{-3}	104	0.13
3	4.4	1.20	1.25×10^{-2}	104	1.3
4	3.4	12.00	1.25×10^{-1}	104	13.0
5	2.6	120.00	1.25	104	130.0

2 As simulated rain with surface plane of 15.71 cm^2.

3 Calculations are based on the exposure chamber illustrated in Figure 1.

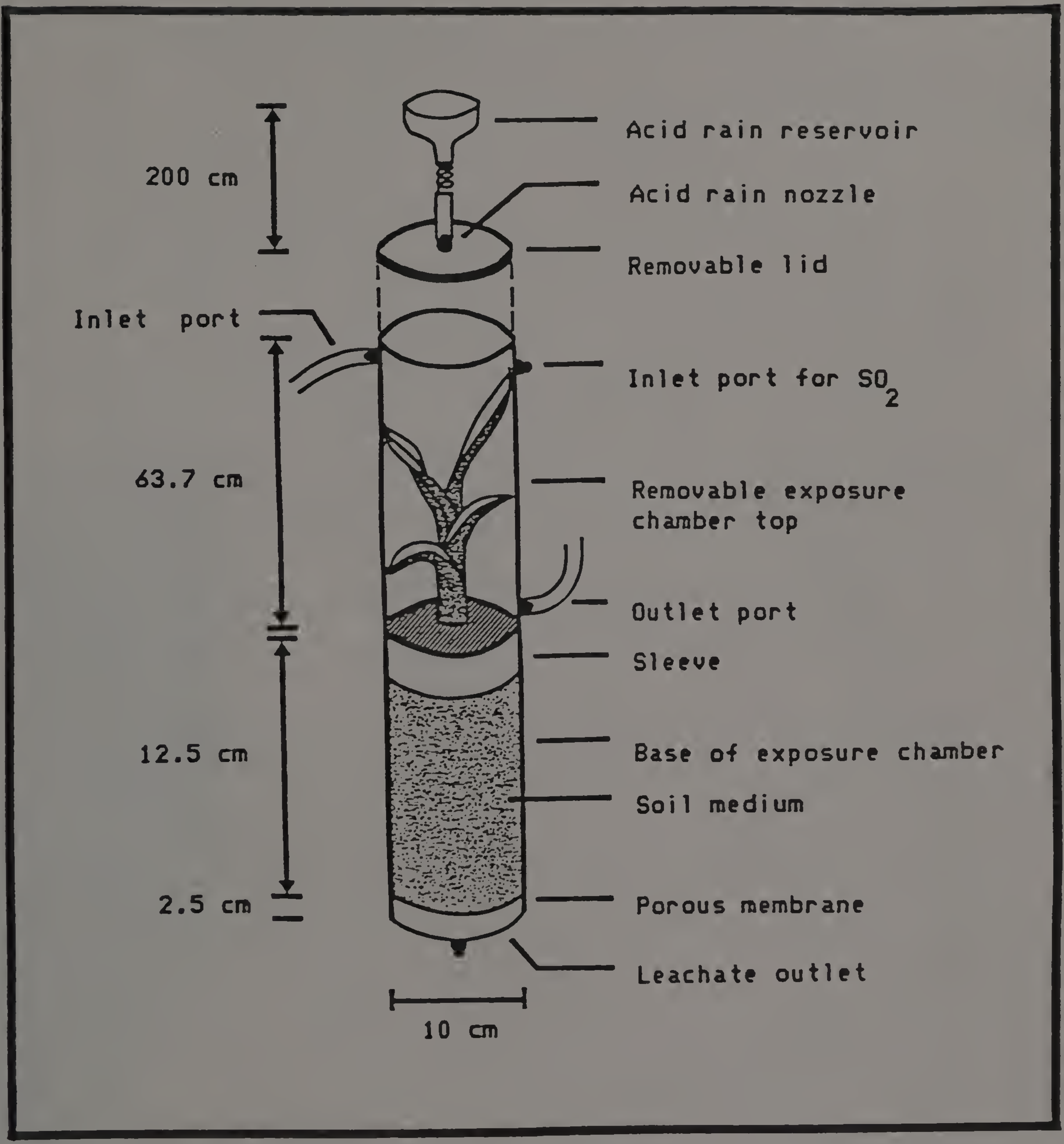

Fig. 1. Sulfur dioxide and acid rain exposure chamber. A sealed air pump was used to continuously circulate air round plant tissue by moving the chamber air from outlet port to inlet port.

radioactively labelled sulfur (^{35}S), (Amersham Radiochemical Corp, Arlington Heights, IL), as sulfur dioxide in order to trace and quantify the uptake of sulfur by the plant.

Simulated acid rain solutions were prepared by the addition of reagent grade salts and sulfuric acid to distlled, deionized water as indicated in Table 3. A fixed amount of radioactively labelled sulfur (^{35}S) in sulfuric acid (New England Nuclear, Boston, MA), was added to pH solutions just prior to treatment with acid rain. The chemical composition of the simulated rain was similiar to natural rainfall composition of the Northeastern United States (Lee and Neely, 1980). All pH measurements were made using a digital expandomatic pH meter (Fischer Accumet pH meter model 620).

Simulated acid rain was applied to the plants via a plastic spray nozzle (No. 78, Melnor Industries, Moonachie, N.J.), located at the top of the exposure chamber (Fig. 1) that produced a constant rate of 11-20 ml/min with an evenly distributed surface plane of droplets near the soil level (Table 4). Simulated rain treatments were continuous until the selected treatment amount had been added. Separatory funnels, suspended from an overhead rack, 2 meters above the chambers, served as the acid rain reservoirs for each of the pH treatments. Flow rates to

Table 3

Composition of Simulated Acid Rain[1]

Component	Concentration[2]
Ca^{+2}	11 µeq/l
Na^{+}	12 µeq/l
K^{+}	2 µeq/l
Mg^{+2}	5 µeq/l
NO_3^{-}	12 µeq/l
Cl^{-}	12 µeq/l
H_2SO_4	as required for appropriate pH and SO_4^{-2}

---

[1] Modified from Lee and Neely (1980).

[2] In distilled, deionized water.

TABLE 4

Comparison of Natural Rainfall and Rainfall Simulator[1]

Source of rain	Mean volume of rain in container subsections (cc)[2]	Measured C.V. of rainfall (%)
Natural	2.81 ± 0.1	20
Simulated	2.81 ± 0.3	42

[1] Measured at the soil surface.
[2] Adjusted for 104 cc/treatment.

the spray nozzles were controlled by gravity. To minimize the effects of nozzle to nozzle variation, the nozzles were cleaned, rotated, and calibrated between treatments.

Control plants, exposed to only ambient air (no addition of sulfur dioxide) or simulated rain of pH 5.4 were used in all sulfur dioxide and acid rain experiments, respectively. Treatment effects from the addition of sulfur dioxide or acid rain were determined by a comparison of treated plants to controls.

Exposure chambers and general treatment techniques. Plants were exposed to sulfur treatments at the four open leaf stage (2-3 weeks following seeding) (Fig. 2 and 3). During the treatment period, exposure chambers were connected onto the plant containers and secured with a nylon sleeve that was adjusted over the base and top (Figure 1). High vacuum grease (Dow Corning Corp., Midland Michigan) was applied between the nylon sleeve and containers to prevent air exchange between the chamber and the ambient atmosphere. Plants were acclimated to the treatment conditions for 45 minutes prior to the addition of sulfur dioxide or acid rain. In order to reduce boundary layer resistance, and to provide greater uniformity of pollutant concentration in the exposure chamber, tygon tubing and a varistaltic pump (Manostat) were used to continuously circulate (0.6 lpm) polluted air around

Fig. 2. Photograph of corn seedlings in exposure chambers during treatment with sulfur dioxide.

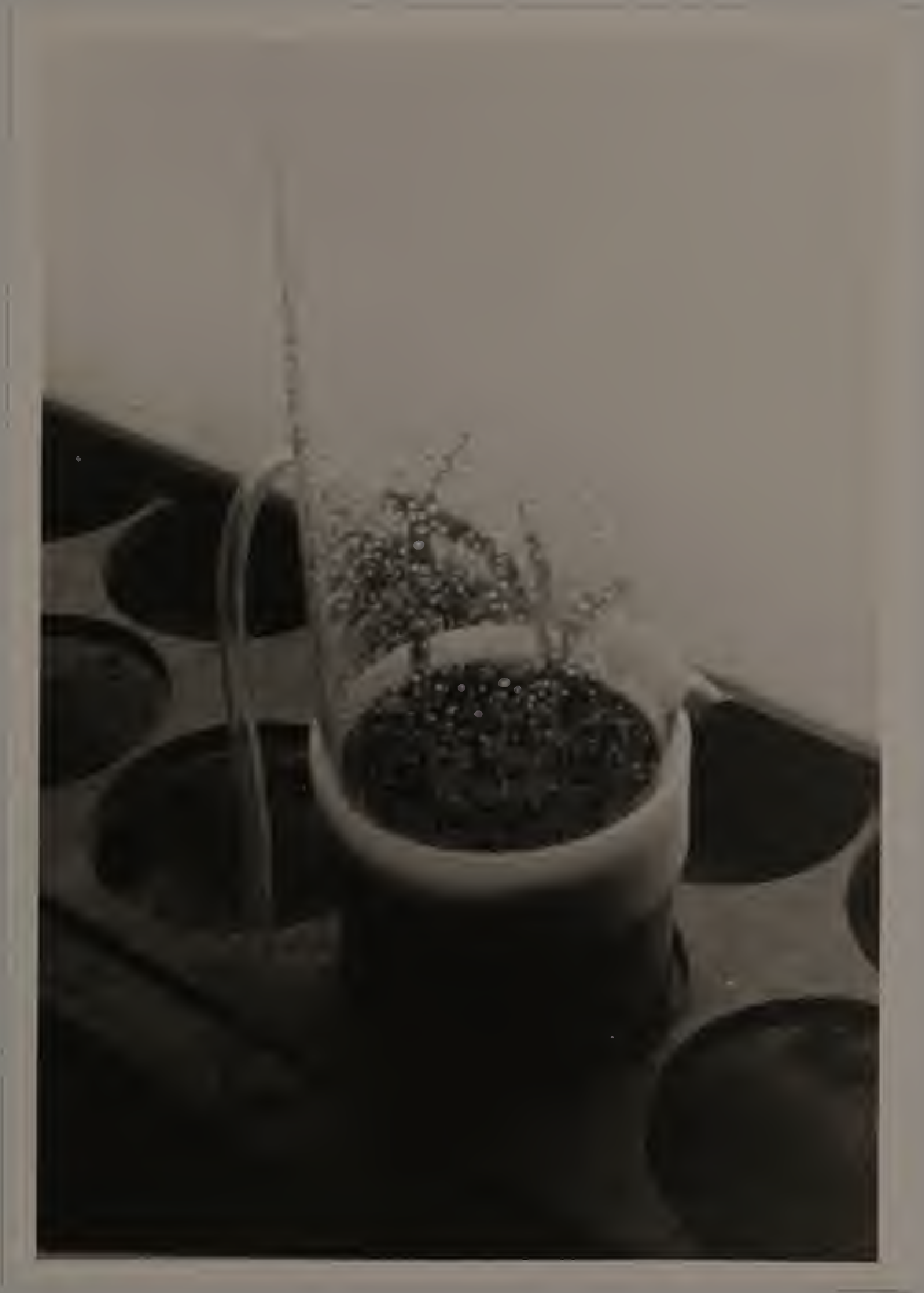

Fig. 3. Photograph of corn seedlings in exposure chamber during treatment with acid rain.

plant tissue by moving the enclosed chamber air from an inlet port at the top of the exposure chamber above plant foliage to an outlet port located near the soil line below plant foliage (Fig. 1). At the termination of the treatment period, exposure chambers were disconnected from the plant containers and the plants sampled or returned to the growth environment.

Plant analysis. Plants were analyzed for the presence of absorbed and adsorbed sulfur at a preselected period of time following treatment with sulfur dioxide or acid rain. For all foliar analyses, the above ground portion of the plant (1 cm above the soil line) or specific leaf blades were carefully inverted, submerged into a test tube containing 20.0 cc of distilled water, and gently rotated/shaken for 20 seconds to release all easily removable sulfur from the foliar surface. The sulfur that was removed from this foliar wash was considered to come from adsorbed sulfur. Sulfur physically present on the foliar surface (as in water droplets) but not adsorbed onto the foliar surface was included in the collection from plants subjected to acid rain. The rate of absorption and desorption or detoxification of sulfur via foliar washing was determined by submerging plants into test tubes containing 20 cc distilled, deionized water and attaching the tubes to a wrist-action shaker (200 oscillations/minute) for a period of 2h. Samples (0.5 cc) were periodically withdrawn from the solution and assayed for sulfur. At the termination of the washing the entire plant was digested and assayed for radioactivity. To avoid contamination from cut surface exudation, the cut portion of the unopenned whorled leaf sheaths or leaf blade was not submerged into the water solution. Fresh water solutions and clean test tubes were used for each sample. Following the foliar wash, the foliage was gently blotted dry on absorbant tissue (Kimwipes, Kimberly-Clark Corp.) and for most studies, one or two sets of 10 leaf discs were sampled from the most recently mature leaf blade with a cork borer (size 1). Initial studies with sulfur dioxide indicated that this leaf blade absorbed sulfur more than or equal to the other leaf blades and were without any visual signs of senescence. Leaf discs were taken from a distal area of the leaf that was wide enough to avoid sampling the midvein. Leaf discs were taken in the same location for all plants because in preliminary studies this site absorbed more sulfur than other areas on the leaf . Leaf discs were immediately weighed and placed in 1.0 dram (15 x 45 mm) scintillation vials containing 5.0 cc of aquassure liquid scintillation cocktail (New England Nuclear, Boston, Ma). Vials were hand shaken for 15 seconds to ensure contact and digestion of plant material in the scintillation fluid with the release of absorbed sulfur. To reduce quenching, vials with plant material and scintillation fluid were exposed to ambient light for several days to lower the chlorophyll content (Lee, 1980). A liquid scintillation counter (Mark 1, Model 6860, Nuclear-Chicago Corp. and Searle and Co.), was used for determining the radioactive sulfur content. Total sulfur content of tissue was calculated using the ratio of radioactive to non-radioactive sulfur established at the beginning of the treatment. When the entire leaf and/or vegetative portion of the plant was sampled, the fresh weight and total leaf area, measured with a leaf area meter (LiCor model LI3000) were determined. Leaves and vegetative portions were sectioned into small pieces (1.0 cm^2 or less) and digested with aquassure for 72 hours to release absorbed sulfur into the solution. Radioactive sulfur was determined on 0.5 cc aliquots of the digested solution.

Uptake of sulfur by plants. Absorption of sulfur from sulfur dioxide and acid rain by plants was determined using the techniques described above. For each treatment, 1 or 2 plants per replication were exposed to sulfur dioxide or acid rain at one of the treatment concentrations for 2 h (Table 1). Following each treatment, plants were examined for visual injury and the leaves, separated into expanding, mature, and senescing leaves. An assessment of both the quantity and rate of foliar absorbed sulfur and the rate at which the roots could absorb and translocate the sulfur to the foliage was determined by separate exposure of foliage and soil to acid rain. Rain solutions were applied to the soil by adding the equivalent volume of rain onto the soil surface directly, rather than treating the top of the plant as previously described. The rate at which sulfur could be assimilated via the roots and translocated through the plant from the soil mix was determined by analyzing the foliar tissue for the presence of sulfur at selected periods of time following exposure of soil to sulfur pollution. Adsorbed sulfur quantified from the foliar wash solution and the absorbed sulfur in the foliage were compared and used to also estimate both the rate of sulfur uptake and the percent of sulfur that could be desorbed from the leaves.

Cultivar response. Cultivar differences in the absorption of sulfur from sulfur dioxide and acid rain were tested on four corn cultivars. Seedlings were grown and treated with sulfur dioxide (6.7 ppm) and acid rain (pH 4.4) as previously described.

Differences in leaf anatomy and moisture content of the leaf between corn cultivars were accounted for by taking two sets of 10 leaf discs from the most recently mature leaf blade of each plant. Each set was sampled in the same area but on only one side of the midvein in the location and manner described above. One set of leaf discs was used for sulfur analysis and the second set of leaf discs were air dried and weighed with the dry weights used in calculating the sulfur content.

Comparative uptake of sulfur from sulfur dioxide and acid rain. The comparative uptake of sulfur from sulfur dioxide and acid rain was calculated from treatments using equivalent concentrations of sulfur (1.3 µmoles S/treatment) as sulfur dioxide or acid rain. Distribution patterns of sulfur within the plants were expressed as the percentage of total radioactivity (representing total sulfur) present. Comparison on the total amount of absorbed sulfur by the plant was calculated as the total µgrams of absorbed sulfur per gram of sampled plant tissue. Direct comparisons on the total amount of sulfur absorbed, rate of absorption, and distribution/accumulation patterns were constructed from the above collected data.

Statistical analysis. Experiments were selectively short term, replicated a minimum of four times, with one or two plants per replication. Standard errors of the mean were utilized to indicate variation within and between treatments.

CHAPTER IV

RESULTS

Corn seedlings exposed to sulfur dioxide and acid rain served as sinks for atmospheric sulfur. Plants subjected to sulfur dioxide or acid rain absorbed approximately 45% and 3%, respectively of the total applied sulfur at the termination of 2 hour exposure period (Figs. 4 and 5). All nonabsorbed sulfur (adsorbed sulfur and sulfur physically adjacent as in water droplets or in contact with but not adsorbed onto the foliar surface), associated with the plant tissue, following the 2 hour exposure period, was rapidly removed with a foliar wash. Approximately 55% and 97%, of the total sulfur associated with the plant tissue following exposure to sulfur dioxide and acid rain, respectively, was adsorbed. Most adsorbed sulfur was removed after one minute of the two hour foliar wash.

The absorption of sulfur by corn was influenced by the concentration of sulfur dioxide (Table 5). As the concentrations of sulfur dioxide increased, the amount of sulfur absorbed by the plant increased. The largest amount of sulfur was absorbed at the highest sulfur dioxide concentration (16 ppm) to which the plants were exposed. A comparison of the uptake ratio of

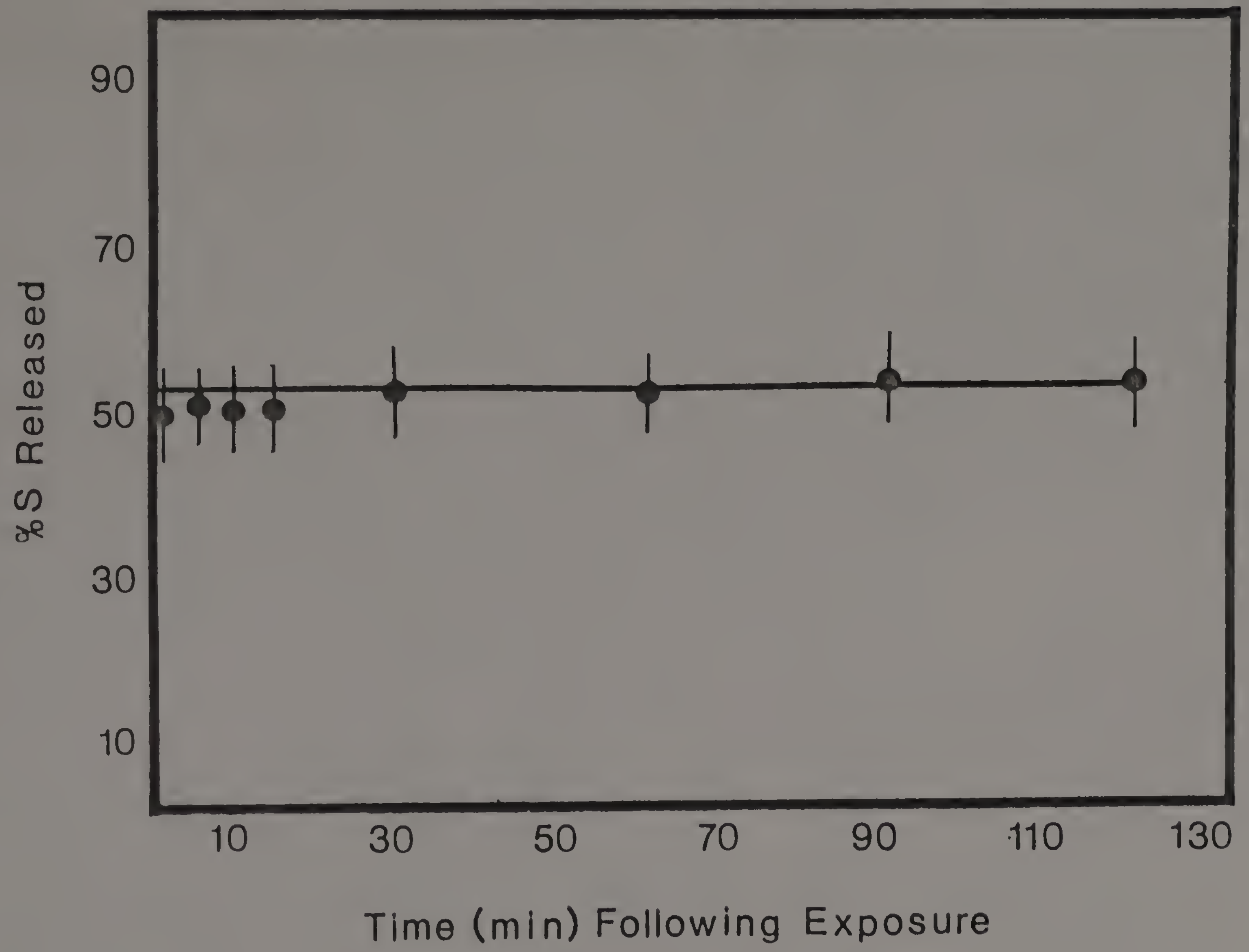

Fig. 4. Release of adsorbed sulfur by corn seedlings following exposure to sulfur dioxide (1.3 μmoles S·2h).

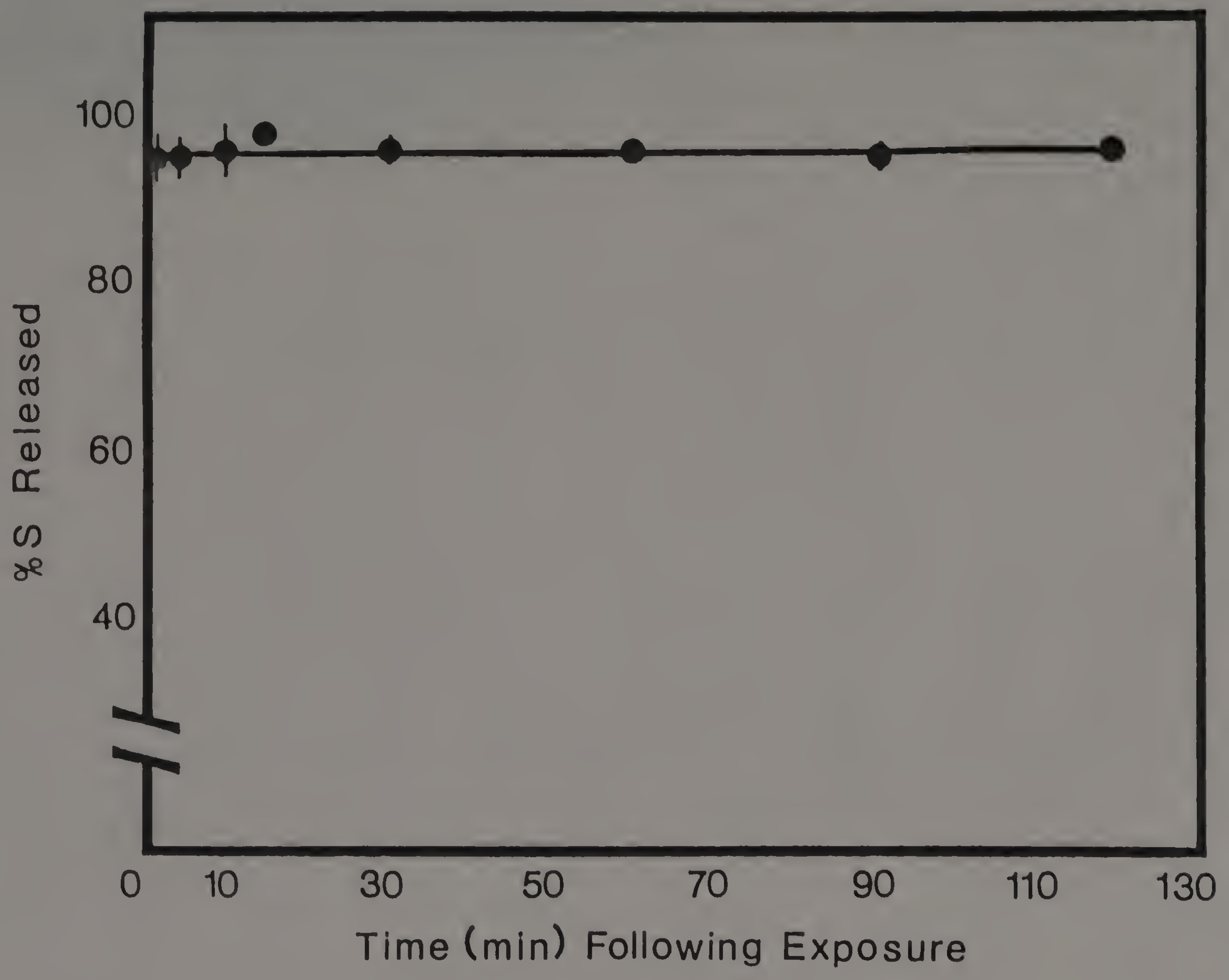

Fig. 5. Release of adsorbed sulfur by corn seedlings following exposure to acid rain (1.3 µmoles S·2h).

TABLE 5

Sulfur Dioxide Concentration and Foliar Uptake of Sulfur by Corn Seedlings

SO_2 (ppm)	µmoles S/trt	µmoles absorbed S/g FWt.	$S_{absorbed}$: S_{trt}
0.67	0.13	0.098	0.75
1.00	0.19	0.174	0.92
2.60	0.50	0.426	0.85
6.70	1.30	0.895	0.69
16.00	13.00	5.743	0.44

[1] SO_2 exposure period=2 h.

absorbed sulfur to the total sulfur applied as sulfur dioxide however, indicated the corn seedlings were less effective in absorbing sulfur at the highest concentration of sulfur dioxide as compared with lower concentrations of sulfur dioxide tested. Most of the sulfur dioxide was absorbed in the first 5 minutes of a two hour exposure period with no significant increase in the absorption of sulfur by corn occurring at later time periods (Table 6).

The concentration of sulfur in acid rain influenced the measured amounts of sulfur absorbed by plant tissue. Plants absorbed more sulfur when exposed to higher sulfur/lower pH treatments compared with lower sulfur/higher pH levels (Table 7). A comparison of the uptake ratio of absorbed sulfur to total applied sulfur indicated that corn seedlings were equally effective in absorbing sulfur at all concentrations of sulfur and pH levels tested.

The uptake of sulfur by corn following exposure to sulfur dioxide (Table 8), indicated that all plant parts, were capable of absorbing sulfur. The most absorption of sulfur occured in the more actively growing and expanding leaves, followed by mature leaves, older and/or senescing leaves, and stalk, respectively.

The accumulation of absorbed sulfur from acid rain indicated that by 2 hours following a 5 minute rain episode, sulfur was

TABLE 6

Exposure Period and Foliar Uptake of Sulfur from Sulfur Dioxide by Corn[1]

Exposure Period (m)	μ moles S absorbed / g FWt.
5	0.589
15	0.385
30	0.563
60	0.354
120	0.462
180	0.633

[1] SO_2 concentration= 6.7 ppm.

TABLE 7

pH and Foliar Uptake of Sulfur from Acid Rain by Corn[1]

pH	µmoles S/trt	µmoles absorbed S/g FWt	$S_{absorbed}$: S_{trt}
5.4	0.13	0.001	0.0077
4.4	1.3	0.007	0.0054
3.4	13.00	0.085	0.0065
2.6	130.00	1.166	0.0090

[1] Rainfall treatment of 104 cc analyzed 2 h following exposure.

TABLE 8

Distribution of Sulfur in Corn Following Exposure to Sulfur Dioxide[1]

Plant part		(% Absorbed S)
Leaf blade	1[2]	16 ± 2
	2	22 ± 1
	3	26 ± 3
	4	32 ± 2
Stalk		4 ± 1

[1] Sulfur dioxide = 6.7 ppm 2h.

[2] Leaf blades 1 to 4; oldest to youngest, respectively.

absorbed by the foliage and by the roots (Tables 9 and 10). The uptake and distribution patterns of sulfur by the plant from acid rain were different for plants where either the foliage and roots or where only the roots were subjected to a rain episode. In treatments where both the plant and soil were exposed to acid rain, a higher percentage of sulfur was absorbed by the whorled leaf sheaths as compared to treatments in which only the soil was exposed to acid rain. A portion of the sulfur initially absorbed by the rapidly growing parts of the plant (most recently mature leaf blades and whorled leaf sheaths) was redistributed to the older plant parts within 24 hours due to translocation of sulfur throughout the plant. The oldest leaf blade, absorbed sulfur via the foliage and accumulated a greater percentage (13%) of the absorbed sulfur in the plant from foliar applied acid rain, than the same leaf in plants where only the roots were exposed to acid rain. Where only the soil was exposed to acid rain, both the two oldest leaf blades contained no measurable sulfur after 2 hours. The majority of absorbed sulfur from acid rain treatments was accumulated by the rapidly growing parts of the plant (Tables 9 and 10). This occurred when either the foliage and soil, or when only the soil was exposed to sulfur-containing acid rain.

TABLE 9

Distribution of Sulfur in Corn Following Exposure of Foliage and Soil to Sulfur-containing Acid Rain[1]

	Time (h)[3]			
Plant part	2	24	48	72
	(% Absorbed S)			
Leaf blade 1[2]	5	1	4	17
2	0	2	4	5
3	10	15	15	14
4	40	59	46	39
Stalk	45	23	31	25

[1] Rain of pH 4.4 (104 cc). Plant material remained in treatment chamber for 2 h.

[2] Leaf blades 1 to 4; oldest to youngest, respectively.

[3] Time following rain treatment.

TABLE 10

Distribution of Sulfur in Corn Following Exposure to Sulfur-containing Acid Rain Applied to Only the Soil[1]

Plant Part		Time (h)[3]			
		2	24	48	72
Leaf blade	1[2]	0	2	4	4
	2	0	4	8	7
	3	21	12	22	21
	4	51	48	40	45
Stalk		28	34	26	23

[1] Rain of pH 4.4 (104 cc) applied to the soil surface. Plant material remained in treatment chamber for 2 h.

[2] Leaf blades 1 to 4; oldest to youngest, respectively.

[3] Time following rain treatment.

TABLE 11

Uptake of Sulfur Dioxide by Corn Cultivars[1]

Cultivar	μmoles absorbed sulfur/g D.Wt.
Muncy Chief GGOMF-7	4.35
Northrup King PX11-3015	5.96
Quicksilver	3.21
Sprite	7.35

[1] Sulfur dioxide = 6.7 ppm·2h.

TABLE 12

Uptake of Sulfur Containing Acid Rain by Corn Cultivars[1]

Cultivar	μmoles absorbed sulfur/g D.Wt.
Muncy Chief GGOMF-7	0.04
Northrup King PX11-3015	0.13
Quicksilver	0.18
Sprite	0.02

[1] Rain of pH 4.4 (104 cc). Plant material remained in treatment chamber for 2 h.

Uptake of sulfur over time periods longer than 2 hours indicated a continual increase in the sulfur content of foliar tissue due to increased amounts of absorbed sulfur, from acid rain treatments by way of the foliage and roots over a 72 hour time period (Fig. 6). Simultaneously over the same time period, a decreasing amount of adsorbed sulfur remained associated with the leaf surface (Fig. 7).

Plants exposed to equivalent concentrations of sulfur (µmoles S/treatment), from sulfur dioxide and acid rain absorbed significantly greater amounts of sulfur from sulfur dioxide at each of the pollutant concentrations tested (Table 13). A comparison of absorbed sulfur to total applied sulfur indicated the corn seedlings were more effective in absorbing sulfur from sulfur dioxide than acid rain at each concentration tested (Table 14).

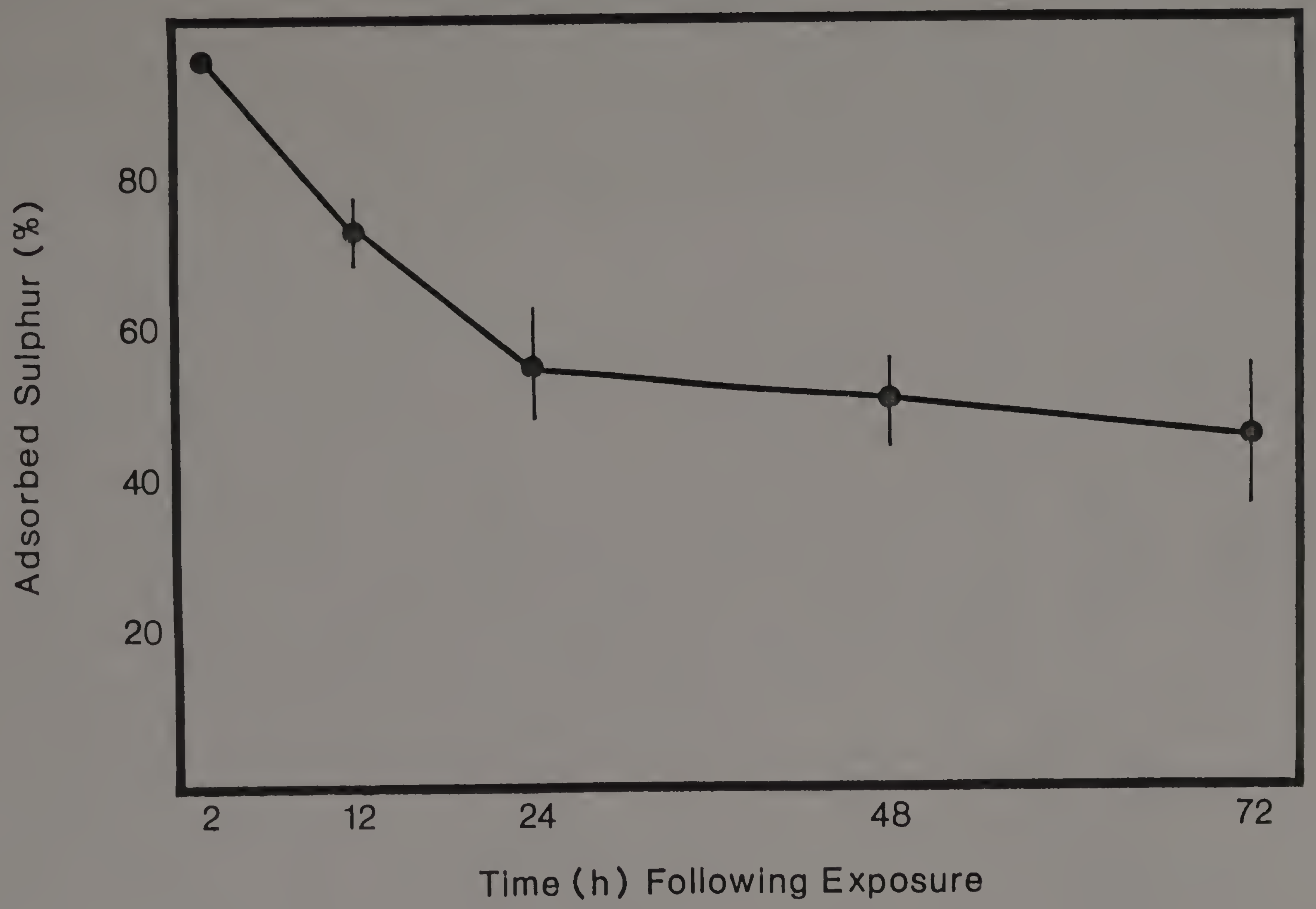

Fig. 6. Absorption of sulfur by corn seedlings from sulfur containing acid rain. Plants were treated with 104 cc of pH 4.4 (1.3 µmoles S).

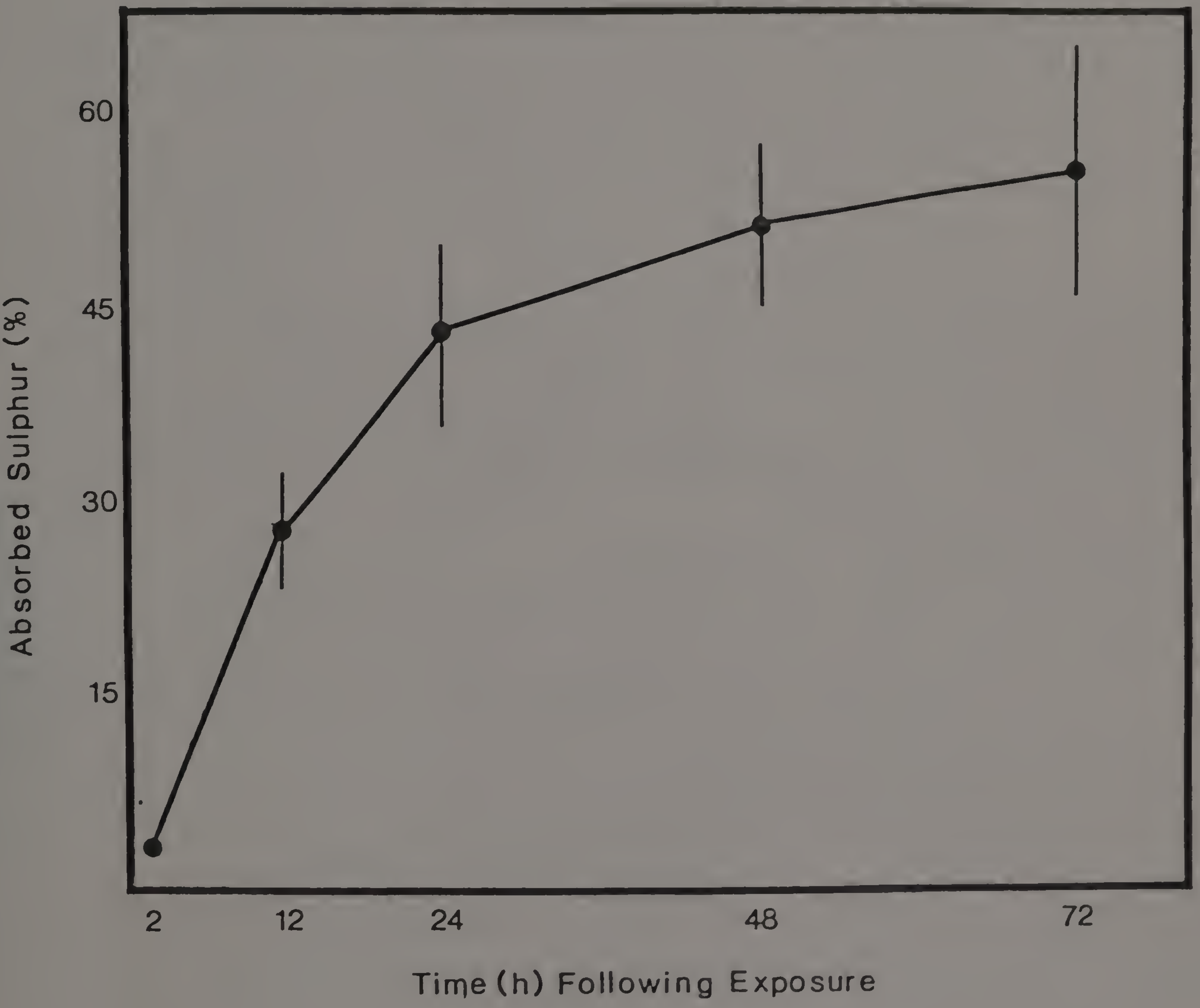

Fig. 7. Adsorption of sulfur by corn seedlings from sulfur containing acid rain. Plants were treated with 104 cc of pH 4.4 (1.3 µmoles S).

TABLE 13

Comparative Uptake of Sulfur by Corn Seedlings from Sulfur Dioxide and Acid Rain[1]

μmoles S/trt	Acid Rain	SO_2
	μmoles absorbed S/gFWt.	
0.13	0.001	0.098
1.30	0.007	0.895
13.00	0.085	5.743

[1] Measured 2 h following treatment

TABLE 14

Comparative Uptake of Sulfur by Corn Seedlings Exposed to Sulfur Dioxide and Acid Rain[1]

μmoles S/trt	Acid Rain	SO_2
	Sulfur absorbed/sulfur applied	
0.13	0.0077	0.75
1.30	0.0054	0.69
13.00	0.0065	0.44

[1] Measured 2 h following treatment

CHAPTER V

DISCUSSION

Corn seedlings absorbed sulfur from sulfur dioxide and sulfur containing acid rain. The absorption and distribution characteristics of sulfur by corn were found to differ between the two sulfur pollutant forms. Approximately, 45% of the sulfur in sulfur dioxide that contacted the foliar surface was immediately absorbed (within the first five minutes), while 55% was adsorbed. This agrees with Garsed and Read (1977), who reported that a large amount (50%) of the sulfur in sulfur dioxide was adsorbed onto the foliage of Phaseolus vulgaris. In contrast, Garland and Branson (1977) reported that little sulfur could be removed by foliar washing of exposed pine shoots to sulfur dioxide. The relative differences in the amount of adsorbed sulfur by pine and beans may be due to differential absorption rates between the tested plants, with a greater percentage of sulfur being more rapidly absorbed by the pine shoots. Alternatively, there could be differences in either the presence or lack of irreversibly adsorbed sulfur by the different plants.

Following an episode of acid rain, corn seedlings absorbed only 3% of the total sulfur associated with the plant tissue, while 97% of the sulfur was adsorbed. The large difference between the amount absorbed and adsorbed 2 hours following treatment may be due in part to the presence of nonadsorbed rain droplets physically associated with the foliage, but not necessarily adsorbed onto the the foliar surface, that was collected with the sulfur during the foliar wash. Presently, it is difficult to compare these results with others, as no other studies on the vegetative effects of acid rain have yet attempted to document the foliar incorporation of acid rain components into vegetation. Evans et al. (1979) reported that sulfur was directly absorbed into the foliage when buffered solutions containing sulfur were kept physically on the leaf surface to ensure continuous contact and promote uptake. However, the incorporation of sulfur in that study was not from actual nor simulated rain episodes, but from solutions containing sulfuric acid that remained in contact with a leaf for 30 minutes.

The large difference in the percentage of sulfur initially absorbed and adsorbed by corn seedlings exposed to sulfur dioxide or acid rain may be explained via a recognition of the pollutants characteristics. Sulfur dioxide is a highly reactive compound, known to react rapidly upon contact with almost all surfaces, including those of the plant, soil and chamber walls (Cox and

Penkett, 1972). The residence time of sulfur dioxide in an enclosed container/system, as the exposure chambers used in this study, is only dependent upon the time period required for the sulfur gas to diffuse to the nearest surface (Cox and Penkett, 1972). No significant differences in the absorption of sulfur were detectable after the initial five minutes (Table 6), and it is assumed that only traces of the pollutant sulfur remained after this time period.

At equivalent sulfur concentrations, sulfur dioxide is absorbed by corn seedlings at a much greater rate than acid rain. Due to the diffusion rate of sulfur dioxide, it would contact a larger surface area of the foliage from which it could be absorbed as compared with acid rain, which is limited to contacting specific areas of the foliage. The extent of acid rain deposition on the foliage is influenced by the physical constraints of raindrops and the physical area occupied by the plant foliage (i.e. covering of lower leaf blades by higher leaf blades) as the rain falls upon and through a vegetative canopy. Absorption of sulfur from sulfur dioxide, in contrast to acid rain, may also be enhanced due to a more rapid rate by which the gaseous sulfur dioxide can enter the leaf via the stomata.

Any consideration on the uptake of sulfur from sulfur dioxide and acid rain, must recognize that a large portion of the sulfur contacting plant surfaces is not absorbed, even after 72 hours following an acid rain episode (Fig. 6). A significant portion of the sulfur pollutant is washed off the foliar surface to the soil whereupon the sulfur may become available to the plant via soil mediated reactions, adsorbed onto soil colloids or leached out of the root zone. Apparently, natural rain or irrigation can wash off up to 55 and 95% of the sorbed (absorbed and adsorbed) sulfur from sulfur dioxide and acid rain, minimizing potential phytotoxic effects from acute doses of atmospheric sulfur.

Maximum absorption of sulfur from sulfur dioxide occurred at the highest sulfur dioxide concentrations. As more sulfur or sulfur dioxide is available to react with the plants, a greater amount is absorbed. However, corn seedlings more efficiently absorb sulfur at the lower concentrations (Table 5). Although the exact reason in this study is unknown, two possible explanations may be suggested. A low concentration of sulfur dioxide may induce stomatal openning, resulting in an increased uptake of sulfur dioxide through stomatal openning. Conversely, a high concentration of sulfur dioxide (16 ppm) may induce partial stomatal closure, resulting in a decreased uptake of sulfur dioxide by the plant leaf blades. Sulfur dioxide has been previously reported to cause both of these types of responses by plants (Heath, 1980; N.A.S., 1978; Rao et al., 1983; Varshney and Garg, 1979).

Similiar to the uptake of sulfur dioxide by plants, absorption of sulfur into plants is higher with high sulfur/low pH acid rain. This appears to occur because more sulfur is available to the plants (Table 7). The pH *per se*, does not appear responsible for increased sulfur absorption at low pH treatments. This differs from reports by Garsed (1981) and Evans et al. (1979), indicating that pH was important in sulfur uptake by *Pinus sylvestris* and *Phaseolus vulgaris*, respectively. Difference in results are probably due to the use of actual rain simulators in this study where little of the acid rain is initially absorbed and direct pH effects are of no consequence. In the other studies, the plant material was kept in treatment solutions.

While the uptake pattern of sulfur by corn seedlings exposed to sulfur dioxide and acid rain differs as to the initial location of maximum uptake, it appears that within 24 hours, translocation of sulfur occurs throughout the plant. Sulfur accumulated from sulfur dioxide is distributed initially throughout all open leaf blades with maximum uptake by the youngest and rapidly growing leaf blades. The whorled unopenned leaf sheaths absorbed the least sulfur dioxide when compared to the leaf blades. This may have occurred in part because less sulfur dioxide was physically present in the lower plant canopy, being absorbed first by the upper and open leaf blades (the first plant surfaces with which sulfur dioxide would contact and react as it circulated from the top to the bottom of the exposure chamber before recycling).

The uptake pattern of sulfur by corn seedlings exposed to acid rain appears to reflect where raindrops from the acid rain actually contact and remain on the plant. The whorled leaf sheath, absorbed higher levels of sulfur than the other foliage parts sampled, because the rain solution was physically held within this area, allowing greater contact and subsequent absorption of sulfur, between the sulfur containing acid rain and the plant. The initial high amount of sulfur absorbed in the youngest expanding leaves is also a reflection of greater initial contact with the rain more than other leaf blades. The youngest leaf blade (leaf blade 4) was physically oriented to recieve more contact with the rain in comparison to the leaf blades. Thus, the foliar orientation, plant stage of growth as well as rainfall treatment itself all probably influence the initial sulfur uptake patterns in a plant. Yet, 24 hours after exposure, all the sulfur becomes distributed throughout the entire plant. Whether the sulfur is foliar or root absorbed from acid rain, maximum accumulation occurs in the more rapidly growing plant parts which would have the greatest demand for sulfur (Mengel and Kirkby, 1978). This was also true with sulfur accumulation by corn seedlings exposed to sulfur dioxide.

At equivalent concentrations of sulfur, both sulfur dioxide and acid rain can be compared to determine which pollutant is more effectively neutralized or absorbed by corn (Tables 13 and 14). In these studies, at each concentration, it is apparent that corn seedlings absorb significantly greater amounts of sulfur from sulfur dioxide than acid rain. Additionally, corn seedlings more effectively absorb sulfur from sulfur dioxide than from acid rain. Thus, although both pollutants can be neutralized by corn, sulfur dioxide can best be absorbed by the plant.

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