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ACID PRECIPITATION: A REVIEW

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ABSTRACT

There are two major groups of thought concerning acid precipitation. Group I holds the view that this environmental problem requires legislative attention, that such precipitation results chiefly from the combustion of fossil fuels which releases oxides of N and S into the atmosphere. Once present N and S may undergo transformation to their respective acids and these substances may be transported great distances. Once deposited, these acids cause damage not only to all components of the natural landscape, but also to statues, monuments, buildings and other anthropogenic materials. In addition, this group opines that this phenomenon has persisted since the mid-1950s; that the problem has worsened and the area affected is steadily expanding. Proponents of Group I present data illustrating a mean decline of 0.5 pH units below the norm for rain (pH 5.6) in the regions affected.

The Group II offers several alternative explanations for the reported and sometimes observed phenomena. They suggest that acid conditions noted in water bodies result from drastic changes in land use, that reexamination of historical data reveal these data to be trendless, that local and natural sources of N and S oxides, especially resulting from the combustion of oil, play a major role in the formation of acidic precipitations in the region at risk. Finally, Group II points out that it is difficult to quantitatively attribute the phenomenon of acid rain falling in one place to its origin in another place.

This review discusses meteorological, physical and biological aspects of acid precipitation from the two points of view just presented and emphasizes the known and the unknown in this complicated area of research.

1. INTRODUCTION

Acid precipitation has been associated with industrial emissions since 1661[1,2], when Evelyn and Graunt noted the effect of such emissions on plants and persons. These early observers saw fit to comment on the atmospheric exchange of pollutants between France and England and even proposed a relocatión of industry remote from populated areas. Although it is apparent that Hales[3] and Linne[4] in the Eighteenth Century had some concept of the inorganic composition of polluted air and rain, it was not until Smith's[5] investigation in 1852 that the chemical contents of rain were scrutinized. He is the creator of the term "acid rain"[6]. Smith was cognizant of the

fact that excessively acidic precipitation was affected, if not induced, by coal combustion. In addition, Smith suggested that the major source of sulfate in rain is the oxidation of H_2S in the atmosphere which is derived from organic decomposition. He thought that such decomposition was largely of terrestrial origin. Smith also noted that frequency and quantity of precipitation as well as distance from the sea were factors important in determining the extent of acidity in rain and snow. Furthermore, he was well aware of the damage to buildings and plants incurred by acid precipitation and even noted the atmospheric deposition of various metals in industrial regions. The work of Smith has gone largely unnoticed though he is well known to limnologists[7,8].

Since Smith's investigations, the environmental effects of acid precipitation have been the intellectual concern of many disciplines but chiefly of limnology, soil science and atmospheric chemistry. The relationship between the chemistry of precipitation and that of oligotrophic lakes would not have been apparent to any investigator who did not have a large body of chemical data at his disposal. Clarke[9] was such an investigator and was the first to observe and record the connection between the chemical composition of precipitation and that of dilute lake waters.

Thus, by 1924, it was known, though largely ignored, that the combustion of coal was largely responsible for the excessive acidity of rain and that the chemical composition of such rain contributed to the chemical composition of lake waters. Since this time, many investigations have contributed to the knowledge of the formation and effects of acidic (pH <5.6) precipitation. Limited space requirements of this review are such that a complete historical sequence of all the contributors to the understanding of "acid rain" is not possible and the reader is referred to some excellent reviews[8,10].

The phenomenon of acidic precipitation may, in the United States, be viewed in terms of a controversy. It is the intent of this review to examine the various aspects of this controversy and to point out the results of the most recent investigation and present this information in summary form.

2. The Controversy

There are two major groups of thought concerning acid precipitation: Group I feels that the problem of acid rain requires legislative attention[11] while Group II believes the situation does not merit governmental action[11]. The position of the first group may be outlined as follows[11]:

A. Acid precipitation results largely from the combustion of fossil fuels which releases oxides of N and S into the atmosphere.

B. These oxides undergo transformation in the atmosphere resulting in the formation of HNO_3 and H_2SO_4.

C. These substances may be transported great distances.

D. Once deposited through the vehicle of rain, snow, hail, mist, dew or fog they cause damage to vegetation, soils and rocks, lakes and rivers, aquatic biota, statues, monuments, and buildings.

E. In addition, this situation has accelerated since the mid-1950s. The areas most affected are southern and southwestern Scandinavia, Florida, California and the states surrounding and including the

Adirondack region of the United States, and the region south of the Pre-Cambrian Shield in Canada, mostly Ontario. Furthermore, this group asserts that the problem of acid rain has worsened since the 1950s and that the regions affected have steadily expanded. Proponents of this position present data illustrating a mean decline of 0.5 pH units or greater below the norm for rain (pH = 5.6), in the regions affected.

The second group[11] presents several alternative explanations for the reported and sometimes observed phenomena. Their position is outlined below[11].

A. Acid conditions in lakes, rivers and streams were first noted in southern Sweden and southwestern Norway. The second group suggests that this is the result of drastic changes in land use that have persisted over the past three decades, rather than the deposition of acid materials from the atmosphere. Changes in agricultural practices and forest husbandry have been noted in southern and southwestern Scandinavia, as well as in New England.

B. Several investigators[11] have reexamined the data that are used to substantiate the suggestion that a trend in acid precipitation has persisted since the mid-1950s such that there has been a gradual decline in the pH since that time. These investigators have found such data to be trendless.

C. The assertion that acid precipitation results from long-range transport of pollutants produced by major complexes of industry and power plants has been refuted by the second group. They point out that in the regions at risk there are natural sources as well as local sources of N and S oxides, especially those resulting from the combustion of oil, that probably play a major role in the formation of acidic precipitation. Furthermore, this group feels that distant sources very likely have little responsibility for the production of acid rain.

D. Physio-chemical and meterological events in the atmosphere are so complex that it is difficult to quantitatively attribute the phenomenon of acid rain falling in one place to its origin in another place. Therefore, it is unclear whether the decline of emissions in one region would actually reduce the acidity of rain in another.

2.1 Points of Agreement

Despite these opposing, apparently irreconcilable positions, some agreement does exist. The following discussion elucidates some of the areas of agreement between the two groups. The Electric Power Research Institute (EPRI) is supporting large-scale research on the acid rain question. Furthermore, their director of environmental assessment recognizes that[12]:

A. Acid rain below the pH of 5.6 exists.

B. Precipitation that is quite acidic is falling on various landscapes.

C. Such rain brings about ecological damage.

D. Atmospheric emissions from utility plants can play a part in the production of acid rain.

Further, a spokesman for the Central Electricity Generating Board of England[13] observed that industrial air pollutants may travel great distances. In addition, he pointed out that this phenomenon has been shown to occur with natural pollutants.

Even SO_2 has been acknowledged as being transported from power plant emissions[14]. A staff member of the Environmental Assessment Department of EPRI speaking of SO_2 transported from power plant emissions stated that during transport several things happen:

A. SO_2 is diluted by surrounding air.

B. Some SO_2 settles to the ground.

C. Some is oxidized to sulfate compounds.

D. Sulfates are deposited on the ground.

2.2 Points of Disagreement

Basic disagreement[11] prevails concerning historic trends in acid deposition. Available pH data do not support the suggestion that acid deposition has been a serious phenomenon for the past three decades[11]. In addition, coal and oil usage data fail to support the suggestion of an historic trend in acid deposition[11].

There is general agreement that oxides of N and S are transported and undergo transformation to their respective acids. However, there is much disagreement[11] on specific details. For example:

A. Relative rates of transport, transformation and deposition.

B. Difficulty of prediction, i.e., how much of a particular S compound will form, where it will fall, how close or how far and how much of it will remain in the atmosphere.

C. Furthermore, SO_2 may become involved in a variety of pathways. For example:

   1. SO_2 may be converted to H_2SO_4 in the air and then be sorbed by a cloud.

   2. SO_2 may be absorbed as SO_2 by a cloud and then be converted to the corresponding acid.

   3. SO_2 may be deposited as dry deposition, in fog for example, and then converted in the forest canopy.

   4. SO_2 may be deposited on the ground as SO_2.

Recently, Newman[15], an atmospheric chemist, pointed out that since the rate-limiting step for the incorporation of SO_2 into rainwater has not been completely identified for all seasons of the year, reducing the quantity of SO_2 in the air may not bring about a corresponding decline of sulfate in the rainwater. This would be especially true if the rate-limiting step turned out to be a catalyst such as a transition metal or carbon.

In view of these uncertainties, the following section of this discussion will focus on data related to the quantity and distribution of the precursors of acid rain from anthropogenic and natural sources.

3. Sources of SO_x, NO_x, NH_3 and Cl_2 Emissions: Natural and Anthropogenic

3.1 Natural Sources of SO_x

On a global basis, the contribution to the S cycle from natural sources is in excess of that from anthropogenic origins[16]. This is not the case for eastern North America where sulfur budgets show that 90% of all S emissions are man-made[17]. Four percent of the contribution is natural while 6% originates from outside the region[17]. Similar budgets were obtained for Europe[18].

The most important natural source of S originates from the biogenic production of H_2S from ocean shores[16]. Less important sources include organic compounds resulting from bacterial decomposition of organic matter, sulfate reduction in anoxic waters and soils, geothermal and volcanic emissions of H_2S and SO_2 and forest fires[17].

3.2 Natural Sources of NO_x

On a global basis, the contribution to the N cycle from natural sources is thought to be seven times that originating from anthropogenic sources[19]. Tropospheric production of NO_x resulting from lightning discharges may account for as much as 50% of the total atmospheric production of NO_x on a global basis[20]. Major contributors to background NO_x are natural terrestrial sources of NO and NO_2 and the chemical decomposition of nitrates[21]. In eastern North America, however, less than 8% of all NO_x emissions may be attributed to natural sources[22]. In areas where precipitation occurs with a pH of less than 5.6 natural sources of SO_x and NO_x are thought to have only a minimal contribution to the observed acidity.

3.3 Natural Sources of NH_3

It has been suggested[23] that the pH of rainwater may be controlled by the interaction of ammonia (NH_3) and acids (HNO_3, H_2SO_4) and that this neutralization process may take place in the atmosphere[24].

In the presence of water, gaseous NH_3 and SO_2 react to produce ammonium sulfite and ammonium sulfate. This suggests that gaseous NH_3 may neutralize acid rain in the atmosphere[25]. Furthermore, ammonia may not only act to neutralize HNO_3 but it may also react with hydroxyl radicals to form NO_x[20,26].

The major source of ammonia emissions into the atmosphere is through the decomposition of organic matter[27,28]. Volatilization from land and sea, and emissions from forest fires may also be significant[29]. In addition, urea-N may volatilize from feedlots which harbor large amounts of animal urine. The National Research Council[30] has estimated that 50-100% of the urea may be hydrolyzed into ammonia and CO_2.

3.4 Natural Sources of Cl_2

Natural sources of chlorides in the atmosphere originate from salt spray from the sea[31,32], volcanic gases[33], and upper atmospheric reactions[34].

Six percent of the acidity in rainwater is reported to be due to HCl[35]. Various models have been proposed implying the natural production of HCl in the atmosphere. Yue et al.[36] proposed that the formation of HCl in the atmosphere was determined by the interaction of SO_2, ammonia, CO_2, oxygen and H_2SO_4. Salt spray oxidized by ozone and then photochemically hydrolyzed in HCl was another proposed model[37]. This acid was then absorbed by moisture thus producing acid precipitation. Kohler and Bath[38] carried out a mass balance calculation and showed that the sea salt to HCl conversion did not fully account for changes in the Na:Cl ratio found in air. Duce[34] suggested that particulate chloride reacted with NO_2 to produce HCl and Robbins and his co-workers[39] proposed that HCl was produced in the atmosphere as a result of HNO_3 reacting with NaCl.

3.5 Anthropogenic Sources of SO_x

The major anthropogenic contributor of SO_x emissions is stationary fuel combustion[40] Fuel combustion accounts for 75% of SO_x emissions[40]. Industrial processes pertaining to primary metals, petroleum, chemical manufacturing and mineral products account for about 18% of the emissions[40]. Transportation and commercial-institutional fuel combustion accounts for the remainder of the contributors to SO_x emissions[40].

3.6 Anthropogenic Sources of NO_x

The major anthropogenic contributor to NO_x emissions is stationary fuel combustion[40]. Forty-seven percent of all man-made NO_x emissions originates from the combustion of gas, oil and coal[40]. Forty-three percent is contributed by transportation via gasoline and diesel fuel combustion[40], the balance originates from industrial processes and commercial-institutional fuel combustion[40].

3.7 Discussion of Anthropogenic Sources of SO_x and NO_x

It is observed that regional (EPA) emissions of NO_x and SO_x are more strongly correlated with population density than are state emissions because utilities in one state often supply electricity to neighboring states[41]. Region V is the most highly populated area and also produces the greatest quantity of SO_x and NO_x emissions[41].

Historical data[40,42] are available from EPA concerning SO_x emissions from 1940-1977. Both SO_x and NO_x emissions reflect a rise in fuel consumption from 1960 to 1970. From 1940 to 1960 only a slight increase in SO_x emissions was noted. The peak in SO_x emissions occurred in 1970. NO_x emissions increased 171% between 1940 and 1960. Again, between 1960 and 1976 there was a 117% increase. NO_x emissions peaked in 1973.

During the late 1970s the ambient air concentrations of SO_x had been reduced to relatively low levels[43]. In fact, by 1980, SO_2 emissions had been reduced by about 17%[44]. Though data for NO_x emissions in urban regions are scant[43] it would be expected that the levels had declined since 1978

since mean annual automobile mileage[45] has decreased as well as the mean fuel consumption per car using the latest available data which are 1982[45].

The amount of SO_x emissions emitted by large boilers depends[46,48] upon the amount of fuel burned, its S content, the type, design and age of the boiler and the method of firing. Nearly all the S compounds in bituminous and anthracite coals are converted to SO_2. Usually about 1-2% SO_x is transformed into SO_3, the amount of formation depending upon combustion conditions, i.e., leaner fuel mixtures increase the rate of transformation[47,48].

Sulfur retention by coals is temperature dependent, the lower the ashing temperature, the higher the quantity of S retained[49]. In some fuels, the elemental composition may exert an effect on S retention. For example, a high Na-lignite may retain more than 60% of the available S in the boiler[50,51]. In the case of low Na-lignites retention of the available S in the boiler ash may not exceed 10%[52,53]. High oxygen content of the combustion chamber increases the emission of primary sulfates from both oil-fired and coal-fired boilers. According to Homolya and Cheney[54] for a given S content, oil-fired units emit more SO_3 than coal fired boilers. In addition, Homolya et al.[55] have noted that compared to pulverized coal, residual oils which contain high quantities of vanadium, discharge greater sulfate emissions on combustion. The combustion of fuel oil requires a higher flame temperature. This requirement intensifies the formation of SO_3, H_2SO_4 and particulate sulfates, while the presence of V stimulates the formation of SO_3 in the combustion process. Emission of SO_3 directly from the combustion process may increase the potential for acid precipitation in areas close to the emission source.

NO_x emissions from coal-fired power plants are excess air and temperature dependent[56]. For a specific furnace temperature, NO_x formation decreases as excess air decreases[56]. A reduction in furnace temperature reduces that NO_x (thermal) that is formed by the reaction of atmospheric oxygen and nitrogen, and has no effect on the fuel NO_x, i.e. that formed by the oxidation of fuel contaminants that contain N[56].

Oil-fired power plants emit less NO_x from tangentially-fired units than all other types[48,57].

3.8 Anthropogenic Sources of NH_3

Anthropogenic sources account for only a small amount of the total ammonia emissions[58]. Eighty percent of the ammonia produced in the U.S. was employed to produce fertilizers[58]. The remaining 20% was utilized in animal feeds, explosives, HNO_3, acrylonitrile and amines[59]. Inefficient handling of fertilizers may result in sizeable ammonia losses to the atmosphere[60]. Ammonia is also a by-product of coke production from coal, ore-refining and fossil fuel combustion[21].

Several authors[61,62] have noted that soil pH may change as a result of nitrogenous fertilizers. Furthermore, subsequent runoff may contribute to the lowering of the pH of receiving aquatic systems. Since fragile aquatic systems located in regions at risk appear to be in forested landscapes, the proposed effect of fertilizer application is not pertinent.

3.9 Anthropogenic Sources of Cl_2

Anthropogenic sources[63,64] of chlorine and chlorides originate in the manufacturing, handling and liquefaction of HCl and Cl_2 gas. Industries involved in the production and use of solvents, pesticides, chlorinated hydrocarbons, plastics and bleaches utilize chlorine. Furthermore, compounds of this halogen are employed in water purification, wastewater treatment, pulp and paper mills, and ferrous and nonferrous metal fluxing[63,64]. Chlorides are also released into the atmosphere as a result of coal combustion[62].

4. Atmospheric Transport, Transformation and Deposition

Anthropogenic sources of oxides of S and N are introduced into the atmosphere at heights ranging from near the ground (car exhaust) to over 1000 ft (tall stacks). As has already been noted natural sources contribute significantly. The fate of these materials is determined by physical processes of dispersion, transport and deposition. Complex chemical transformations take place between the place of emission and the final destination of the pollutant.

Residence time of pollutants in the atmosphere may be short, as when such pollutants become injected during a storm, or long (day or weeks) during drier weather. During the latter case, partially transformed pollutants may be carried for long distances. The ability to predict the fate of these pollutants is a methodology still in the early stages of development.

Meterological effects are also difficult to predict. Generally, during the winter, the winds tend to carry eastern U.S. emissions out to sea while in the summer they are carried northward by the winds. The overall effect is precipitation with a low (<5) average annual pH over eastern North America[65].

Analysis of rainwater from eastern North America suggests that about 62% of the acidity is due to H_2SO_4, 32% to HNO_3 and 6% to HCl[11]. It is believed that the major source of these acids in precipitation is the oxidation end products of SO_x and NO_x. Thus, the rate at which SO_x and NO_x (from their source to their eventual destination) are transformed into their respective acids is a crucial factor in determining not only the pH of precipitation but also the recipient location.

4.1 Chemical Transformation During Transport

Atmospheric sulfur dioxide may be converted to sulfate in two ways[18]. The first type of reaction involves substances that are present in the gas phase. In polluted atmospheres, gaseous sulfur dioxide is oxidized to sulfate after gas-phase collisions with strong oxidizing radicals ($HO^{\cdot}$, $HO_2^{\cdot}$, $CH_3O_2^{\cdot}$)[18]. Photo-oxidation of hydrocarbon-NO_x emissions provides these radicals as intermediate products[18]. The ratio of hydrocarbon to NO_x, solar radiation, temperature, dew point and the concentrations of sulfur dioxide and the oxidizing radicals determine the rate of oxidation[18,66]. When this process is carried out in pure air, the production of sulfate is insignificant[66]. Estimated rates of this reaction in polluted air range from 0.1-10% per hour[18].

The second type of reaction, which is believed to remove 90% of the sulfur dioxide from the atmosphere[67] proceeds in liquid particles or on particle surfaces: (1) when transition metals such as Fe and Mn are present

in high (>10^{-5} M) concentrations in the atmosphere, they may bring about the catalyzed oxidation of SO_2 in solution[68], (2) another mechanism is dependent upon ozone and H_2O_2 sorbed in liquid droplets which are able to promote oxidation of SO_2 at a rate comparable to that of indirect photo-oxidation[18], and (3) a third mechanism has been demonstrated only in the laboratory and is primarily concerned with surface-catalyzed oxidation of SO_2, the surface in this case being carbon or soot[69]. Sulfur dioxide oxidation to sulfate on filters filled with soot does not necessarily relate to such a phenomenon's occurring in the atmosphere. The rates of occurrence of these three mechanisms in the atmosphere are unknown.

The process by which NO and NO_2 are converted to acidic end products are of principal concern in the formation of acid rain and are generally poorly understood[70]. Nitric oxide emissions are partially converted to NO_2 by gas-phase reactions[70]. The rate at which this process proceeds is concentration-dependent[70]. At high concentrations it may proceed at the rate of 8% per minute[70]. In a polluted atmosphere exposed to solar radiation the process may proceed in a matter of seconds, as it is known to do in smog[70]. Involved in this rapid conversion are transient species and other compounds such as CO, hydrocarbons and aldehydes[21]. Diurnal photochemical cycles both produce and destroy ozone[21]. As parts of this set of reactions NO_2 is converted to HNO_3 vapor, and NO and NO_2 may be sorbed onto existing particles[21]. Exact conversion rates are not well known and are thought to vary seasonally[71,72]. It is also thought that N compounds have a greater residence time than SO_x[72].

4.2 Removal of Pollutants by Precipitation

Kladlecek *et al.*[73] recently published a paper on the chemical composition of cumulus clouds. The pH of clouds is more acidic in rural regions than in urban ones. Tanner and his co-workers[74] have also made this observation. Clouds, however, vary between urban and rural regions in the sense that they may differ in size, in altitude, and in formation; therefore, these data are not entirely comparable and should be viewed only as a "rule of thumb". The second point that may be gleaned from their figures is that the total composition of the cumulus cloud needs to be considered; HNO_3 and H_2SO_4 are clearly not the whole story.

The removal of substances from the atmosphere may occur in two steps[75]. The first involves the condensation of water vapor on cloud condensation nuclei. The step is called rainout. Some of these nuclei are thought to be sulfate particles formed by gas-phase collisions with oxidizing radicals ($HO^{\cdot}$, $HO_2^{\cdot}$, $CH_3O_2^{\cdot}$)[75]. At this point the size of droplets begins to increase, and soluble pollutants dissolve, undergo chemical changes, and slowly begin to fall to the ground[75]. The removal of materials below the cloud base through rain is called washout[75]. The presence of NH_3 hastens the absorption of SO_2 and its conversion to sulfate[76]. NO_x undergoes similar processes which bring about its removal from the atmosphere[76].

While the rate of gas-phase oxidation of SO_2 in the atmosphere is primarily controlled by the concentration of $HO^{\cdot}$[77] and to a lesser extent by $HO_2^{\cdot}$ and $CH_3O_2^{\cdot}$, the production of H_2SO_4 within cloud droplets and rain is chiefly governed by H_2O_2[77]. The quantity of H_2O_2 in solution apparently determines the extent of its contribution to the acidity of cloud droplets and rain[77].

4.3 Local Transport and Long Range Transport of Emission Pollutants

It has been asserted that acid rain is primarily the result of long range transport of pollutants that have been emitted from tall stacks belonging to coal-fired utilities [11]. These pollutants are believed to originate from the combustion of large quantities of fossil fuels [11]. Recently, some studies have been published which have presented data that refute the idea that acid rain results primarily from long range transport of pollutants [78].

Esposito et al. [78] have shown that the U.S. regions most at risk consume large quantities of oil. Forty percent of the residual and 36% of the distillate oil burned in the country is consumed in the eight-state region surrounding the Adirondack Mountains. California is the second largest oil consumer and Florida is the third. Moreover, oil fired boilers produce 3-10 times as much sulfate (not SO_2) per unit of S content as do coal-fired units. As mentioned earlier, the presence of V is thought to hasten this process [18]. It may be speculated that local sources may be more important than long range transport.

Another approach to the transport controversy has been utilized by Rahn [79-81] who has attempted to "fingerprint" emissions by utilizing element matrix analysis. He has proposed that the elemental concentration of particulate matter in aerosols might reflect the origin of such matter and may even help resolve the question of long range transport contribution in contrast to that of local sources. Thus, aerosols relatively enriched in V might suggest a petroleum contribution, while those high in Mn might reflect coal combustion. As yet, this methodology has not been systematically evaluated for eastern North America. A number of concerns must be alleviated before this approach can become routine. First, the underlying assumption is that particulate matter enriched in V or Mn behave in the same fashion in the atmosphere as those enriched in sulfates and nitrates. Furthermore, Mn is often found enriched in large particles which, due to the nature of their size, are unlikely to contribute to those aerosols typical of long range transport [82]. Coal is deficient in Mn relative to that of soil [82]. Thus, the origin of fine particles enriched in Mn is not certain. Even though Rahn's method includes a correction for the presence of crustal chemical contributions, the source of these fine particles enriched in Mn remains uncertain. Vanadium, on the other hand, is found enriched in fine particles in the eastern United States. Again, the source of such particles is unknown [92]. It should be noted that Se is also released in coal combustion and its behavior is more likely to simulate that of S than Mn [82]. This suggestion, however, has not been systematically pursued. A second concern with Rahn's approach is the inability to separate out air masses of varying chemical composition which originate in the midwest but have received chemical contributions from eastern cities [82].

Although Rahn's approach has not been validated or confirmed for eastern North America [81], it apparently has been successful elsewhere [83,84]. For example, his data suggest that Arctic haze noted in Alaska may originate from possible smelter operations in Eurasia [84].

Still another approach is being used. Dr. L. Newman of the Brookhaven National Laboratory and a group at Argonne National Laboratory are studying the distribution of stable isotopes of S (^{32}S, ^{34}S) and O (^{18}O) in the atmosphere. The pioneer in this approach was M. L. Jensen [85] who studied the $^{32}S/^{34}S$ distribution in the vicinity of Salt Lake City. By using stable isotopes of S, he was able to separate biogenic contributions from anthropogenic ones. During the copper workers strike of July 1971, when a large

scale copper smelter was shut down, he was able to show that the principal source of S in the atmosphere was the Great Salt Lake where bacteriogenic S was released by anaerobic activity in the mud. When the copper smelter was again functioning, the city received twice as much from the smelter as it did from the lake and 15 times as much S as it did from refineries and automobiles.

4.4 Deposition

"Acid rain" refers to precipitation that has a pH less than the norm of 5.6 since unpolluted rain may be similar to distilled water in equilibrium with CO_2 which has a pH of 5.6. The term dry deposition refers to acid deposited in the form of gases, solids, fogs, hazes and mists. The contribution to terrestrial acidity from dry deposition is poorly understood and difficult to measure: however, Galloway and Whelpdale[86] in their proposed S budget for the eastern portion of the United States, employed a greater rate of deposition per square meter of land surface for dry deposition than for rain. In contrast, Kerr[87] in his Adirondack study proposed that dry deposition of SO_x was about 33% of the total deposition.

The quantity of hydrogen ions in fog can be great[88,89]. A study[89] was carried out in southern California which showed fog water to have a greater concentration of $SO_4^=$, NO_3^- and NH_4^+ than observed in water droplets. These authors suggest that their observations result from fog water condensing and evaporating on preexisting aerosols and from scavenging of gas-phase HNO_3.

It is not possible in this review to cover all the pertinent aspects of acid precipitation under the heading of atmospheric sciences. There are many reviews that may be examined for detailed discussions of dry deposition, model approaches to various aspects of transport and deposition, and the variation of N and S oxides in precipitation in relation to the season of the year. The most recent and up-to-date of these reviews is the two volume work edited by Altshuller and Linthurst[90] to which the reader is referred.

5. Environmental Effects of Acid Precipitation

5.1 Acid Precipitation Time Trends

Cogbill and Likens[35] gathered precipitation data from the 1950s and the 1960s and calculated the pH from the ion concentrations. Based on these calculated figures, they constructed maps and estimated long term trends. These long term trends have been widely quoted and republished. Based on these calculated figures, it has been concluded that New England and New York have been suffering from rains of increasing acidity over the past three decades and furthermore that the geographic distribution of these rains is widening.

There has been much criticism of this work. In particular, sampling methods[91] and preservation[91] differed between the 1950s and the early 1970s, and the sampling sites were not similar. Specific faults with the Cogbill and Likens data are listed below[14,91].

1955-56 and 1965-66
10 common sites
4 showed an increase in pH
2 showed a decrease in pH
4 remained the same

1955-56 and 1972-73
2 common sites
1 showed an increase in pH
1 showed a decrease in pH

1965-66 and 1972-73
8 common sites
3 showed an increase in pH
2 showed a decrease in pH
3 showed no change

Therefore, critics feel that the historical aspects of the acid precipitation problem is apocryphal in the states surrounding and including the Adirondacks. It is clear that data such as that shown above are trendless[14]. In addition, a U.S. Geological Survey of the acidity of precipitation and surface waters in New York State from 1965-1978 has failed to show any significant trend in declining pH values for the period studied[92]. These authors also discovered that the sulfate quantity in precipitation declined an average of 1-4% annually, that no trend in nitrate was noted, and that the hydrogen ion concentration failed to correlate with measured trends of sulfate and nitrate. This observation suggests that variable neutralizing factors are at work that have clearly not been identified[92]. This would suggest that the proposal of Cogbill and Likens[35] namely that there is an historical aspect to the acidity of precipitation in New England and New York is unsubstantiated.

Peters et al.[92] have noted that during the period 1965-1978 significant trends in the pH of surface waters in New York State occurred. The effect of precipitation could not be identified because of the contributions from agriculture and industry. Despite this conclusion, these authors point out that a 1-4% annual decline in sulfate concentrations in streams was similar to that noted in precipitation.

Pfeiffer and Festa[93] have recently examined surface waters in New York State utilizing a Hellige comparitor, the same colorimetric method utilized in the 1930s. Examining the same group of lakes, they concluded that a general deterioration of both pH and general water quality had occurred during the 40-year period between studies.

Kramer and Tessier[94] published a reassessment of historical pH and alkalinity data. They pointed out that studies such as those of Pfeiffer and Festa[93] should be viewed with the following in mind:

1. Type of sample container must be considered since those employed prior to 1960 could have contributed alkalinity to the sample.

2. Color comparator data, with suitable corrections appears to provide the most reliable data.

Clarke[95] has pointed out that color comparator methods are subject to error due to natural color of waters, to turbidity and, to the weak buffer correction. It is not known whether such considerations were made in the study of Pfeiffer and Festa[83].

Recently, there have been a number of authors [96-100] who have suggested that the acidification of surface waters may in part be the result of major changes in land-use. Further, they have suggested that many of the regions presently at risk have undergone such land-use changes since the turn of this century. It has also been pointed out[96] that soils of the Adirondack

Mountains, New England, southern Scandinavia, and eastern Canada have soils with pH values lower than 4, which is lower than the pH of the rain these areas are presently receiving.

Munger and Eisenreich[100] have published an extensive review on precipitation chemistry. One of their major conclusions has been that precipitation acidity is largely controlled by land-use patterns in a given region and is most pronounced where emissions of N and S oxides of anthropogenic origin are greatest and soil buffering capacity is lowest. Thus, it must be considered that the observed excessive acidification of surface waters in sensitive regions of the world is in part the result of changes in land-uses which have occurred during this century.

Acid precipitation time trends, as reflected by the pH of surface waters, are well-documented in Northern Europe[101]. The work of Wright and his associates[102] clearly demonstrates a decline between 1950 and 1970 in the pH of surface waters in southern Norway. The question of changes in land-use and concomitant increases in the acidity of runoff passing to lakes and streams is discussed by Overrein et al.[101] though the contribution from agriculture is still largely unquantified.

5.2 Areas affected by Acid Precipitation

The chemical composition of a lake is determined by the action of three significant processes: precipitation, watershed drainage, and the anaerobic condition of the mud. Estimating the H^+ contribution to the deeper waters from anaerobic mud is difficult. This creates complications in determining the amount of lime sufficient to raise the pH of a lake.

The granitic regions of the world[35,102-106] have lakes which are particularly at risk. These areas are formed from bedrock that weathers slowly. Such places support soft water lakes which were initially weakly acidic and now are poorly buffered and contain water impoverished in ionic composition. In North America the regions most at risk are: New England[35,106]; eastern Canada[103]; the region south of the Pre-Cambrian Shield, specifically Ontario; the West Coast extending from British Columbia south including Washington, Oregon, all but the northern tip of Idaho and much of eastern California[78]; the western slope of the Rockies in Colorado, and a narrow strip extending south of Pennsylvania forming an arc in a south westerly direction including the Blue Ridge mountains and extending across northern Georgia and Alabama.

There are regions in Maine[107] where the bedrock is granite, the mean pH of the precipitation is 4.3 and the lakes are alkaline. The drainage basins feeding the lakes contain limestone till and marine clay. Thus, the materials received by the lakes from the drainage basin have been heavily buffered and such lakes are not at risk. Soft water lakes in Florida[108], specifically the Trail Ridge Lakes with their low buffering capacity, which received acid precipitation showed a decline in pH since the early 1960s. In contrast, soft water lakes in Highland County, Florida[108] where precipitation is not acidic, have exhibited no such trend in declining pH during the past two decades[108].

The regions in the Old World most at risk are in southern Scandinavia[101,102,105]. These areas are all located in granite bedrock and are soft water lakes that have been receiving acid precipitation thought to be produced by the heavily industrialized areas of continental Europe.

Well buffered lakes with neutral to alkaline pH ranges have maintained their H^+ concentration at stable levels for the past century, but the sulfate content of the surface water has increased several fold[109,110]. Such lakes are found in the calcareous regions of the world. As noted above, if alkaline clays are part of the drainage basin, their buffering capacity protects the receiving lake from the effects of acid precipitation. The Western sections of the United States, the plains and the desert, and most of the mountainous regions do not suffer from acid precipitation apparently due to the observed presence of alkaline particles in the local precipitation[111].

5.3 Effects of Acidic Precipitation on Aquatic Systems

Soft water lakes are usually formed by drainage from acidic igneous rocks. Their naturally occurring biota differs from hard water lakes which are formed by drainage from calcareous deposits and contain high amounts of alkaline earth[13]. Hardness is usually associated with alkalinity which increases the capacity of the water to neutralize or buffer the incoming acidity.

The natural range of pH in lakes of the world is from 1.7 in Miyagi, Japan, a volcanic lake containing 474 ppm $SO_4^=$ to 12 in Lake Nakuru, an alkaline lake in Kenya[7]. The acidic lake supports sulfur bacteria. The alkaline lake harbors algae which are eaten by birds. Both are fishless.

The natural pH range of bodies of water that support fish is 9.0 to 6.5[111]. Above and below this range most fish fail to survive[111]. Impaired body salt regulation is the principal cause of fish death in acid rivers and lakes[111]. Na and Cl ions in blood plasma show consistently lower concentrations under acid stress[111,112]. Secondary effects include reduced K concentrations in muscle tissue[111,112].

Al is leached from soils receiving acid precipitation[113]. An Al buffer system replaces the biocarbonate system when lakes have a pH less than 5[113]. The Al toxicity (0.2 ppm and up) depends on water pH and is maximum around 5[113]. Toxic effects are absent at pH 6[113]. Al toxicity in acid water affects the gills by physically clogging them; thus, initiating mucous development which disturbs ion exchange and brings about a depletion of the body salt content[113].

A variety of studies[114,115] have revealed high Hg concentrations in acid water bodies. These are often an order of magnitude above that acceptable in drinking water supplies. Mercury has been leached out of the drainage basin receiving acid precipitation.

Aquatic systems that have undergone pH declines suffer severe reduction in the number of living species indigenous to a normal water supply. For example, acidification of lakes reduces microbiological activity[116-118]. This results in reduced rates of decomposition and permits organic matter to accumulate. Acidification of lakes also reduces the number of zooplankton[119], phytoplankton[120], aquatic insects[121], benthic crustaceans and molluscs[122], and it fosters the growth of acidophilic plants which tend to clog waterways. Generally, acidification of lakes creates havoc in the ecosystem by destroying the food supply both of fish and of the smaller organisms.

The effects of increased acidification of surface waters on macrophytes has not been well documented; however dominant species appear to be similar in most lakes with a pH of 7.5[123]. Although it might be expected that

dominant macrophyte species may be replaced by Sphagnum which has been noted in some Swedish lakes[124], this has not been observed in oligotrophic lakes in North America[123].

The most pronounced evidence for the influence of acidic precipitation on aquatic biota has been the adverse effects on fish populations. Regions, where historical records are available are southern Norway[125], the lakes of the La Cloche Mountains in Ontario[126], and some lakes in the Adirondack Mountains[127]. It is important to realize that lakes now void of fish need not have lost their fish populations due to increased acidity of their waters. In addition, fishless lakes may always have been void of fish. Historic trend data for the lakes of the Adirondack Mountains are scant and their fishless state can generally not be specifically related to the results of lowered pH.

5.4 Effects of Acidic Precipitation on Terrestrial Systems

5.4.1 Soils

Some investigators[128-130] have stated that the effect of acid precipitation on soils is minimal compared to that of the influence of agricultural practices. Generally, soils that receive various types of nutrient application as a result of agricultural practices are protected from the effects of acidic precipitation[131]. Naturally acid soils are common in regions of high rainfall. Acidic precipitation obviously contributes to this process, though presently the effect is thought to be minimal[131]. Soils that are poorly buffered have probably been acid for some time and such soils are not likely to be damaged by excessively acidic precipitation.

Many years ago it was common to hear farmers comment that farmland in the proximity of urban centers received precipitation beneficial to plants. This fact has been documented since the middle of the last century[132]. It has been presumed that HNO_3 is rapidly utilized by plants but since S deficiencies are rare, the benefits of H_2SO_4 to plant growth are probably slight. It is well known that repeated but small applications of nutrients to leaves has a stimulating and positive effect on yield[133].

Long term effects of acid deposition on soils would be expected to bring about a modified cation exchange capacity by replacing Ca^{++} with H^{+} on available exchange spots in organic matter and clay. Long term effects could also include a removal of necessary plant nutrients which could result in impoverished yields[134]. Clearly, calcareous soils, clays with a pH greater than 6, and cultivated soils are not at risk. Noncalcareous clays and sandy soils with poor buffering capacities are at risk. Slow but continuous removal of Al from a soil profile cannot be beneficial and if the pH of the soil is less than 5, Al availability could conceivably reach toxic levels and be detrimental to forest productivity[135,136]. Of course, this increase in Al availability in soils sensitive to acidic precipitation has great effect on aquatic systems, in particular to fish, as well as on terrestrial plants. Presently the Al phenomenon may be viewed as the single most important known effect of acidic deposition on soils.

Finally, it has been shown[137] that some soil bacteria are sensitive to acidic precipitation; however, field data to support this observation are not extensive.

5.4.2 Vegetation

A variety of chemical species adheres to foliage from the atmosphere through both wet and dry deposition. Sulfates, nitrates and other water soluble components of rain may be utilized by plants through contact with leaf surfaces. Laboratory experiments have provided results that suggest massive damage to certain crops (truck crops, oak, birch and pine)[138-140].

Although there is a lack of published information on the effect of acidic precipitation on herbicides, it has been noted[141,142] that a decline in the pH of rain enhances foliar absorption and increases foliar injury of compounds such as dinitrophenol and phenoxyacetic acid. In addition, alkaline pesticides will be more readily sorbed by soils that have received acidic precipitation. This may decrease the biological activity as well as the compound's mobility[143,144]. Such a series of events would necessitate higher applications of pesticides to achieve the same results. Any changes brought about in the soil microbial populations by "acid rain" will naturally affect the extent of degradation. Chemical degradation will also be changed by acidic precipitation. For example, Edwards[145] noted that malathion and parathion persist longer in acid soils than in neutral soils while atrazine[146] and simazine[146] degrade more rapidly in acidic environments.

According to McLaughlin and his co-workers[147] there is no evidence that acidic precipitation is limiting forest growth in either Europe or the United States. The dieback and decline of the North American spruce [Picea abies] is well documented[148]. This decline is most pronounced at higher elevations in soils that are largely composed of organic matter. The possible release of Al from clay resulting from excessive acidic precipitation, possibly creating a root environment too high in Al, would be difficult to identify as due to Al complexation by the organic matter[149]. Both Johnson et al.[150] and Lord[151] have pointed out that Ca:Al ratios increase with increasing elevation in spruce roots at Camels Hump, Vermont, and that the observed tree mortality is not likely to be due to Al toxicity. Red spruce decline [Picea rubens] has also been noted[152]. It has occurred among trees subject to highly acidic cloud moisture and much research is in progress in high-elevation forests in northern New England[147] in order to isolate the cause of red spruce mortality.

According to Irving[153], available experimental results show that the effect of acid precipitation on domestic crops is minimal though he hastens to point out that the effect has not been scientifically scrutinized for all crops.

5.5 The Effects of Acidic Precipitation on Man-Made Objects

Yocom and Baer[154] have reviewed the literature on the effects of acidic deposition on man-made materials. They conclude that there is little doubt that acidic deposition hastens the deterioration of man-made objects beyond that which could be attributed to natural environmental phenomena. Due to the variety of materials that compose man-made objects, the extend of damage resulting from acidic deposition is difficult to assess. Yocum and Baer[154] point out that further research is required to identify specific deposition processes and the extent of damage created. These authors point out that protective and preventive measures need to be developed in order to preserve the artifacts of human culture.

5.6 The Effect of Acidic Precipitation on Human Health

At this writing, no adverse human health effects have been documented as a result of metal mobilization by acidic deposition[155]. It is reasonable to suppose that soils receiving precipitation of low hydrogen ion concentrations would, over time, undergo leaching of their metallic compounds. Such an event could conceivably produce fish with excessive quantities of elements such as Hg, Pb, Cd and Al in their tissues and produce acidic water supplies with unacceptable concentrations of heavy metals. The amount of Hg in fish, for example is affected by the species, the age of the fish, the amount of Hg in the surface sediments and water, the pH of the water, the degree of microbial activity in the surface sediments, the salinity of the water, the concentration of dissolved organics and the amount of dissolved oxygen in the water[156]. Thus, though elevated Hg concentrations in fish may be correlated with low pH, these other factors must also be considered and the Hg content of fish cannot be attributed soley to acidic deposition[155]. High Hg levels have been found in brook trout caught in lakes of low pH as well as those of high pH[157]. In the United States the possible association of high Hg content of fish in relation to waters of low pH has not been documented[155].

Data on the effect of acidic deposition on drinking water quality are scant[155]. Very acid water supplies carried through copper plumbing could conceivably add unacceptable Cu quantities to drinking water. This possibility has as yet not been documented in the scientific literature. Along the same line of thought, exposed soldered connections leached with water low in pH could release Cd, Sb, Sn, and Pb into drinking water. This possibility has also not been noted in the scientific literature.

Generally speaking, no adverse effects on human health, specifically attributed to acidic deposition, have been identified at this time.

6. Current and Proposed Research

6.1 Ameliorative Approach

A. One approach to the management of acid deposition is to lime the affected region. Liming of acid lakes has been carried out in southern Scandinavia since 1975[158]. Long term effects, of course, are as yet unknown. Short term effects include[158] alkalinity and pH increases; a decline in concentration of Al, Zn and Mn; restoration of fish populations, and a return of expected diversity of planktonic species. The cost of liming is estimated at \$75 ha^{-1}[159]. Logistic problems arise when remote and nearly inaccessible areas require liming, and naturally the cost of the operation increases.

B. In the mid-1950s collectors were placed in smoke stacks to remove particulate matter. This had the beneficial effect of reducing particulate materials in the air, but also had the apparently detrimental effect of removing neutralizing particulates that reduced the formation of the precursors of acid rain. Particles produced as a result of combustion by the cement industry, for example, have a neutralizing effect on the formation of acid precipitation. It might be useful, therefore, to relax particulate regulation of certain kinds of industry and to encourage the development of controlled, selected particulate emissions.

C. Fostering the development of practical use of solar energy and safe uses of nuclear energy would do much to control the formation of acid precipitation.

6.2 On-Going Research

The outline presented below represents types of research that are in progress:

A. Development of models that more accurately predict where acid precipitation forms, how far it will travel and where it will fall.

B. Meterological research involving the movement of air masses and their chemical composition.

C. Research in atmospheric chemistry that involves the fingerprinting of emissions through the analysis of accompanying minor elements, or isotope tracking; confirmation of mechanisms for the incorporation of SO_2 into rain water; discovery of what substances behave as catalysts for the oxidation of SO_x; investigation of the formation of dry deposition and its contribution to the S cycle and finally the effect of natural sources.

D. Research in ecology to further understand the effect of acid precipitation on soil profiles; the effect of acid precipitation on forests, and finally the long term effect of liming lakes and landscapes.

6.3 Proposed Research

It is the opinion of many[160] that fossil fuels will be in short supply within another century. Technology needs to be developed to handle other kinds of materials to keep civilization functioning. The best of such substances is hydrogen. Research should be encouraged to develop procedures for the production, safe handling, and use of hydrogen.

7. Conclusions

The conclusions of this review may be expressed in terms of a controversy between the two major groups of thought concerning acidic deposition. Important consideration are as follows:

A. Acid precipitation is a problem and does exhibit pH levels below the expected norm (pH 5.6).

B. Historic trends of progressive decline in the pH of deposition are well documented in northern Europe.

C. Historic trends of progressive decline in the pH of precipitation are poorly documented in the United States for New England. The Trial Ridge Lakes clearly have suffered a decline in their surface waters in the past two decades.

D. Acidic deposition (wet or dry) is probably due to the combustion of fossil fuels, though the confounding effects of drastic changes in land-use patterns cannot be ignored.

E. Local sources in those New World regions at risk probably are more important in the formation and production of acidic precipitation than long range transport.

F. Ecological damage to most aquatic biota is apparent in lakes where surface waters have declined below pH 5.

G. Possible terrestrial damage has not been well-documented, and though dieback in northern U.S. forests has been observed, acid precipitation has not been conclusively identified as the major culprit.

H. Acidic precipitation has hastened the deterioration of man-made objects, but the mechanisms are poorly understood. More research is needed in the area of preservation, prevention, and protection of man-made materials.

I. Adverse human health effects have not been identified, and any health effects that are likely to occur are of a secondary nature.

J. More research is required into the long term effects of the liming of lakes.

K. More research is needed in the discipline of atmospheric chemistry, in particular in the area of identifying sources of emissions at distances remote from their origin; in confirmation of the mechanisms responsible for the incorporation of SO_x into rain water and for the oxidation of SO_x, and in detailed investigations into the formation and effect of various types of dry deposition.

L. Greater study is needed to discover the causes of tree mortality in the northeastern United States.

M. Finally, it is unlikely that the effects of acid precipitation will be alleviated by the regulation of SO_x emissions until the phenomenon of acid precipitation falling in one locale may be clearly attributed to an origin in another locale.

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