THE POTENTIAL ACIDITY ASSOCIATED WITH DEWS, FROSTS, AND FOGS

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Abstract. Acidity associated with special meteorological events such as dews, frosts, and fogs may cause significant environmental effects ranging from increased leaching of plant metabolites to material corrosion. In addition, dews, frosts and fogs occur with much greater frequencies than rain or snow in most areas. Due to these facts, a theoretical study was conducted to determine the potential acidity associated with these events.

Results from this study showed the potential acidity associated with these events to be significant. Values of fog pH are extremely sparse, but indicate that they are slightly acidic. However, these experiments have probably under-estimated the actual acidic potential of dew and frost. Theoretical calculations indicate that synergistic acidity from dew or frost in combination with dry deposition may result in very strong localized acidities.

1. Introduction and Background

Acid rain has become one of the major environmental concerns of this decade. In the United States, the northeastern section was the area first known to be affected, but now most areas east of the Mississippi River are affected by acid rain. Increased concern over the problem has resulted in recent government action. In his second environmental message to Congress in August 1979, President Carter identified acid rain as one of the most serious environmental problems associated with the continued use of fossil fuels. This was followed by Congressional passage of the 'Acid Precipitation Act of 1980', which was signed into law by the President on June 30, 1980. The Act calls for a comprehensive 10-year program and establishes an Interagency Task Force on Acid Rain to plan and implement the national efforts.

Acid rain is also an international problem; for example, pollutants may originate in one country, with consequent effects felt in another country. This occurs in Sweden, where the existing acid rain is believed to result from the transport of pollutant emissions from Great Britian and central Europe. Also, the Canadian acid rain problem is partially due to transport of pollutants from the United States. On the international scene, a treaty was signed at the Convention of Long-Range Transport held in Geneva during November 13 to 16, 1979, by the 34 member countries of the Economic Commission from Europe (ECE) which includes the western and eastern European countries, the United States, and Canada. The treaty states that 'The parties will endeavor to limit, and as far as possible gradually reduce, and prevent air pollution.' In addition, cooperation between Canada and the U.S. is continuing on the transboundary transport of acid rain components.

A growing body of scientific evidence suggests that acid rain may be responsible for substantial adverse effects on the environment. Such effects include acidification of

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lakes, rivers and groundwaters, with resultant damage to fish and other components of the aquatic ecosystem; acidification and demineralization of soils; possible changes in agricultural and forest crop productivity; deterioration of man-made materials; and degradation of drinking water systems. These effects may be cumulative or may result from short-term peak acidity episodes.

Acid rain originates principally from the release of SO_x and NO_x into the atmosphere from industrial and/or transportation sources. These constituents are transformed into H_2SO_4 and HNO_3 through an oxidation process. These acids or related sulfates and nitrates are transported and eventually removed from the atmosphere and deposited on forests, crops, lakes, etc. Atmospheric scientists are currently studying the transformation, transport and removal processes with the objective of developing models which would ultimately simulate the various processes. It is clear that the acid rain problem is often a regional transport phenomenon. In other words, emissions in a given state or area often appear to cause an increase in the acidity of precipitation someplace downwind.

In 1977, SO_x accounted for 14% (27.4×10^6 tonne) of the total air pollutant emissions in the United States, while NO_x accounted for 12% (23×10^6 tonne) [1]. Although other pollutants also act as precursors to acid rain, it is believed that these two oxides are the major contributors. Currently, SO_x (mainly from industrial sources) is the major contributor to precipitation acidity in the northeastern United States and southeastern Canada. However, NO_x (mainly from transportation sources) is the major contributor to precipitation acidity along portions of the west coast of the United States [2].

Sulfur oxides are primarily emitted from stationary sources such as utility and industrial boilers burning coal as a fuel. However, NO_x are emitted from both stationary and transportation-related sources. Over the next 20 years, emissions of NO_x should increase relative to emissions of SO_x. In other words, sometime during the next decade, NO_x should become more of a contributor to the acid rain problem.

The extent of the current acid rain phenomenon was recently illustrated by Wisniewski and Keitz [3]. Maps of both pH and H^+ deposition in precipitation were developed for the continental United States by analyzing laboratory pH data from 11 precipitation chemistry networks spread throughout the continental United States and southern Canada for the late 1970's time period. Results of this analysis show the severity of acidity in precipitation to be concentrated in the northeastern United States. However, remaining portions of the eastern United States, states along the western coastline, and a pocket in central Colorado are recording acidic precipitation.

Before proceeding, an explanation of the term 'acid rain' is necessary. Acidic materials, derived primarily from SO_x and NO_x, are removed from the atmosphere via both wet and dry processes. The wet removal process includes aerosol and gaseous scavenging by clouds and subsequent precipitation, leading to deposition by rain-out and snow-out. In periods without rain or snow, acidic substances are removed from the atmosphere by four basic 'dry' mechanisms:

- Gravitational settling
- Aerosol impaction on surfaces

- Gaseous adsorption to surfaces
- Gaseous absorption by surfaces.

Gravitational settling is the primary mechanism for removal of large particulates (greater than about 5 μm) such as those from fly ash, entrained soil, and sea-salt particles. For smaller particulates, such as anthropogenic acidic aerosols formed by combustion, the settling velocity is small compared to turbulent velocities in the lower atmosphere. Impaction of the small particles on surfaces accounts for most of their removal from the atmosphere. Gases, such as SO_x and NO_x, are removed from the atmosphere primarily through adsorption to or absorption by natural and man-made surfaces. It is believed that dry deposition is a major contributor to the total deposition of acidic materials from the atmosphere.

In addition to wet and dry events, there is a third group of events which does not fit well into either wet or dry deposition. These 'special' events include dews, frosts, and fogs; their role in acid deposition is twofold. First, they may act to remove acidic substances directly from the atmosphere, thus adding to the total acidic deposition budget. Secondly, and perhaps more important, they may dissolve previously dry-deposited acidic substances on surfaces as shown in Figure 1, leading to potentially severe localized acidic conditions.

While the wet removal processes of rain and snow have been or are currently being intensively investigated, little effort has been made until recently to understand the dry depositional and the special event contribution of acidic components. To date, there have only been a few measurements of the pH and chemical character of special events. Some have found pH values to be close to 5.6, the value expected of water in equilibrium with atmospheric concentrations of CO_2. Others have found the pH values to be generally lower. The terminology 'special acidic events' has occasionally been used as a result of some of these studies. However, it is not necessarily the H^+ concentration of the event which is a major concern, but rather the entire chemistry of the event which is important in order to understand the nature of each of these phenomena.

2. Formation Characteristics of Dews, Frosts, and Fogs

In general, special events (dews, frosts, and fogs) are the result of water vapor condensation (or sublimation) in the layers of the atmosphere closest to the ground. Their relative magnitude compared to rainfall is shown graphically in Figure 2. As shown in this figure, daily dew, frost, and fog deposition is comparable to very light rainfall. Although each specific event does not comprise a great deal of moisture, it is sufficient to cause uniform wetting of natural and man-made surfaces. In some instances, this may be more important than the actual volume of water deposited.

Before proceeding to the discussion of the possible chemical characteristics of special events, it is necessary to gain some understanding of their physical nature. The following subsections briefly discuss the meteorology of special events, including mechanisms of their formation as well as their frequency of occurrence.

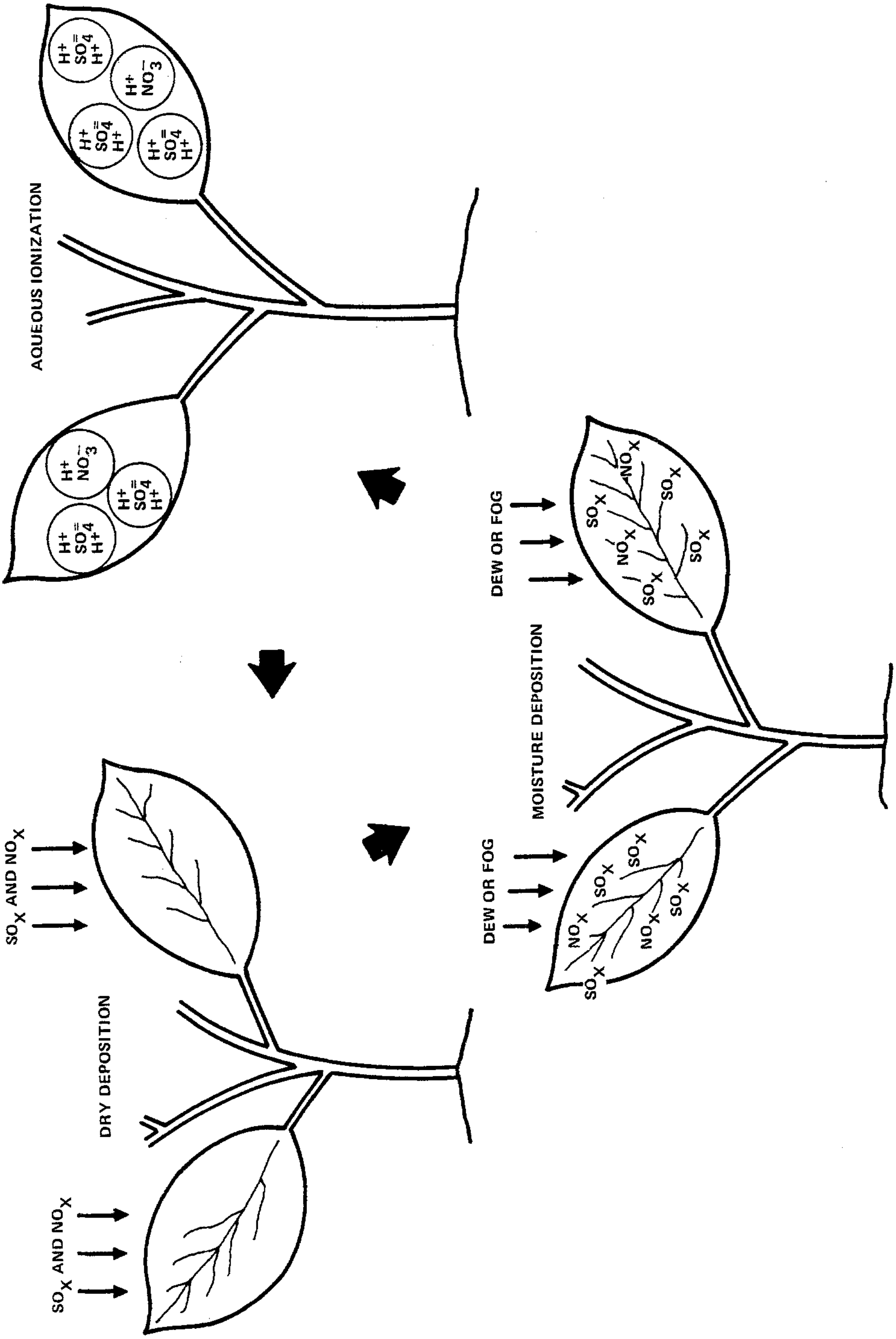
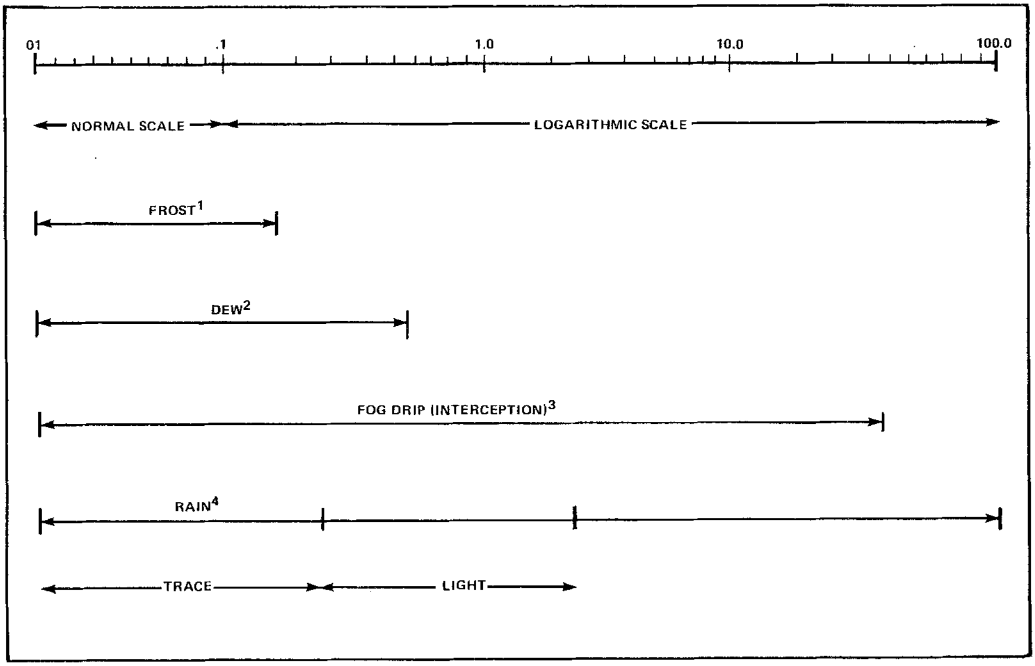


Fig. 1. Representation of Dew – Dry Deposition Interaction.



1. (ANDERSON, 1978)
2. (WALLIN, 1967)
3. (KITTREDGE, 1948, OBERLANDER, 1956)
4. (DUNNE, 1978)

Fig. 2. Ranges of Observed Daily Moisture Deposition (Equivalent Millimeters of Water).

2.1 DEW

Dew is water which has condensed directly onto a surface where the temperature is at or below the ambient dew-point temperature. The dew point is the temperature at which saturation occurs if air is cooled at constant pressure without addition or removal of vapor (i.e. the relative humidity equals 100%). On clear nights, surfaces such as plant foliage or metallic objects cool rapidly by longwave radiation of energy skyward. Light winds also promote cooling by carrying heat away by turbulent transfer [4, 5]. This cooling may result in leaf surface temperatures which are as much as 1.4 °C cooler than the ambient air temperature, actually allowing dew to form when the relative humidity is about 90% in the surrounding air [5]. Metallic surfaces have been observed to collect dew under conditions where the relative humidity was 50% [6]. This indicates that the surface was about 11.0 °C cooler than the air temperature [7].

Dew requires that some type of condensation nuclei, similar to rain and snow, be present in order to form. However, there is no lack of such nuclei on exposed surfaces, and various surface features may also act as nuclei [8]. As a dew deposit grows, it forms numerous lenticular droplets which gradually coalesce into a few large droplets. The process of coalescence tends to sweep any water-soluble matter into the larger droplets, cleansing the areas between droplets [8] and causing contaminants to be accumulated in the dew. Two common acidic contaminants, H_2SO_4 and HNO_3, are both highly soluble in water, and thus easily scavenged by dew. As will be discussed in the following section, this creates the potential for low pH values in dew droplets.

The maximum amount of dew that may form in one night has been theoretically calculated to be about 0.05 ml cm^{-2} or 0.5 mm of equivalent depth over a surface [5]. Other estimates [4, 9] suggest that the maximum may be two to three times as great. Observed amounts reported in the literature range from about 0.1 mm to 0.54 mm [10].

Unfortunately, dew is not a commonly monitored meteorological event in the U.S. As of 1979, only 12 stations in Alabama, Georgia, and Florida routinely monitor dew occurrences [11]. Thus, it is not possible to determine the frequency distribution of dew occurrence in any great detail. However, a few localized studies scattered across the U.S. have been reported in the literature [11, 12, 13, 14, 15, 16, 17]. Results from these studies show that dew occurs in most locations on well over 50% of the days, with the highest frequency of occurrence being in summer. This is to be expected, since absolute humidities are usually highest in summer.

2.2. Frost

Frost forms under the same general nocturnal conditions as dew with the main difference being the surface temperature. Frost forms on surfaces where temperatures are below 0 °C when water is deposited as a solid directly from the vapor phase, through a process known as sublimation. Anderson [18] observed a maximum frost equivalent to only 0.012 ml cm^{-2} of liquid water, which is comparable to a light dew.

In terms of special acidic events, frost, the solid phase of water, is not very important because ice usually incorporates very little foreign material within its crystalline structure. Frost is an important factor primarily when it melts, forming essentially a light dew which may dissolve water-soluble contaminants on the surface. For this reason, frost-derived water is discussed in the subsequent sections as dew.

During this discussion, frost is defined as the deposition of ice by sublimation. A more common definition, especially in agricultural meteorology, equates frost with the condition that exists with water when the temperature at the earth's surface falls below 0 °C [4]. In this regard, 'freezing' would be a more correct terminology.

Many climatic atlases contain data on mean first and last day of 'frost' in fall and spring, respectively, and mean annual number of days with 'frost'. However, none of these data relate directly to the event of frost accretion.

2.3. Fog

Essentially, fog is a cloud which forms near the surface of the earth. It is comprised of minute water droplets which have condensed from water vapor. The process of condensation is the same as for dew except that it proceeds much further. Whereas dew is formed when surfaces cool below the dew point, fog is formed when an entire layer of the atmosphere cools to the dew point. The cooling necessary for fog formation may occur in various ways and results in different types of fog. The most important types are radiative, advective, frontal, and upslope fogs [19].

During calm conditions, the tiny water droplets which make up fog remain suspended in the air. Coalescence will cause some drops to grow and be deposited by gravitational settling, but the amount of water deposited is probably quite small. However, during windy conditions, relatively large amounts of moisture may be deposited from fog in its interception by plant foliage and other objects, a phenomenon known as fog drip [20]. Frequently occurring advective and upslope fogs carried by high winds result in high moisture deposition on foliage in this area. This type of moisture deposition may also occur in mountainous regions where upslope-forced fog is common. In some cases, the amount of moisture from fog drip exceeds the amount of rainfall and represents a critical source of water for many plant species [20, 21, 22].

Of the special events, fog is the only one which has been monitored widely for a number of years. Knowledge of fog occurrence is vital to aviation operations, thus it is routinely recorded at most airports and first-order weather stations. A number of maps of fog frequency have been generated over the years by various investigators [23, 24, 25, 26]. Not unexpectedly, the regions with highest heavy fog frequencies are the coastal areas and moist Appalachian mountain regions. Frequencies range from about 20 to over 70 days per year. The interior plains have moderate frequencies ranging from about 10 to 20 days annually. The lowest number of heavy fog days occurs in the dry intermontane and southwest desert regions, averaging from less than 5 to about 10 days per year.

However, it should again be emphasized in the above discussion that no estimate of light fogs is available at this time. Light fogs have the potential to create higher acidities, due to the smaller amount of moisture associated with these events (causing a lesser dilution of dry deposited acidic components). Data to generate an estimate of these events are available through the National Weather Service.

2.4. ACIDITY ASSOCIATED WITH SPECIAL EVENTS

Because of the seeming insignificance of micrometeorological events such as fog and dew compared with the larger events of rain and snow, little research has been focused on their chemistry. The results available at present are too few and too sparse to draw definitive conclusions concerning the acidity and chemical character of special events, not to mention the environmental effects from these events. However, available direct and indirect evidence, along with theoretical calculations, may provide a better indication of the potential acidity associated with special events.

3. Observed Acidity in Special Events

Of the special events, the chemistry of fog and fog interception has been the most widely studied:

– Houghton [27] collected 90 samples of coastal and mountain fogs in the northeastern U.S. and found acidity values around 4.5. Those fogs with significant open water trajectories were found to be generally neutral (pH 7.2);

– Anderson [18] investigated pH values of nine radiation fogs in the Catoctin

Mountains of Maryland. He found acidities ranging from pH 4.7 to 5.6, with a mean of about 5.3;

– Mrose [28] collected about 100 samples of various fog types in West Germany and found mean pH ranges from 3.8 to 5.1;

– A number of studies [29, 30, 31, 32] have been performed at Whiteface Mountain in the Adirondack Mountains of New York State. Measured pH values ranged from 2.4 to 6.0 with a mean of about 3.5. The fogs measured are upslope – forced clouds which intercept the mountain [31]. Because these fogs occur with much greater frequency than precipitation, fog drip from vegetative interception is probably a significant contributor to the total acid loading in the region. Recently Falconer and Kadecek [32] expanded the cloud-water chemistry analysis at Whiteface Mountain using ion chromatography and conductivity measurements.

Contrary to the situation with fog, very little research has been performed on the chemistry of dew and frost. A few investigators have suggested that acidic conditions may be present in dew and others have attempted simple measurements of pH:

– Fowler and Unsworth [33] showed that the rate of SO_2 deposition to wheat increased when dew was present, but did not report any pH measurements;

– Brimblecombe and Todd [34] collected dew from meadow grasses in East Anglia, Great Britain, and reported individual droplet pH values between 5 and 7. They also investigated Na and K in dew, and found a ratio of $[K]/[Na] \sim 1$ in dew, as compared with 15 for grass blades and 1/15 for rain. They suggested that dew formed preferentially on deposited aerosols rich in Na and then gained K from the leaf surface. Thus, Brimblecombe and Todd indicate that the potential effects of dew might be through dissolution of previously deposited substances as opposed to initial deposition of substances;

– Anderson [18] investigated the pH of dew at three locations in Maryland using petri dishes containing glass wool as a condensate collector. The petri dishes were set out in the evenings and collected the following mornings. In this manner, contamination by previous deposition on the collecting surface was avoided. A few dozen samples were also collected from the tips of grass leaves. The grass leaves were not precleaned, but were chosen in areas relatively free of wind-blown dust. Of over 100 petri dish samples collected, 77% had pH values between 5.4 and 5.8 and 97% had pH values between 5.2 and 6.1. The grass leaf samples, on the average, were about 0.1 pH unit more acidic than the petri dish samples. The results suggest that contamination may lead to more acidic conditions than would be expected on non-contaminated surfaces. Anderson, in the only study of frost chemistry found in the literature, collected 14 samples of frost at College Park, Maryland, using plexiglas plates. After collection, the frost was warmed to melting and pH values were measured; pH's ranged from 5.4 to 6.1 and were considered to be indistinguishable from those of dew at the same site.

The results from the various studies are summarized in Table I. Because the data are highly localized or extremely sparse, no generalizations should be made. The findings of Falconer and Farrel [29], Falconer and Falconer [31], Falconer and Kadecek [32] and Houghton [22] indicate that fog is an extremely good scavenger of atmospheric

TABLE I

Observed pH ranges for various condensation events

Investigator	Location	Observation period	Event type	pH Range	Mean pH
Houghton (1955)	Brooklin, Maine	Summer, 1954	Fog	3.5 – 6.3	4.7
Houghton (1955)	MT. Washington, New Hampshire	Summer, 1954	Cloud interception	3.0 – 5.9	4.5
Castillo (1979)	Whiteface MTN. New York	1976	Cloud interception		4.9 – 5.4
Falconer &	Whiteface MTN.	Aug. – Sept., 1977	Cloud interception	2.4 – 6.0	3.55
Falconer (1979)	New York	Aug. – Sept., 1979		2.6 – 5.2	3.50
Anderson (1978)	MT. Catoctin, Maryland	1978	Fog	4.7 – 5.6	5.27
Anderson (1978)	Hyattsville, Maryland	1978	Dew	5.0 – 6.2	5.45
Anderson (1978)	Rainbow Lake, Maryland	1978	Dew	5.0 – 5.9	5.5
Anderson (1978)	College Park, Maryland	1978	Dew	5.5 – 5.9	5.65
Anderson (1978)	College Park, Maryland	1978	Frost	5.6 – 6.0	5.7

pollutants, perhaps better than rain or snow. As a result, certain ecosystems which receive a high percentage of their total water budgets as fog drip (such as mountain ecosystems), may also be receiving a correspondingly high input of acidic substances.

The case with dew and frost is more uncertain, due to the lack of data on both the pH and the overall chemistry of these events. Although the measurements of Brimblecombe and Todd [34] and Anderson [18] show dew to be only slightly acidic, these results are probably an underestimate of the actual acid potential of dew. The pH in this case is misleading because it does not indicate the total ion balance in the dew water. Theoretical calculations in this paper indicate that dew-water may, in extreme cases, have pH values as low as 2.0. The following subsection describes the reasoning and calculations leading to this result.

4. Potential Acidity of Special Events

The chemistry of special events is dependent on primarily two factors. The first is the amount and type of material (gases, aerosols) absorbed by dew and fog directly from the atmosphere. The second controlling factor is the presence of substances on the surface of which the moisture is deposited. The source of most of these materials is dry deposition of natural and anthropogenic substances from the atmosphere, which includes soil particles, fly ash, pollen, microbes, trace metals, aerosols, and adsorbed gases [35]. Another anthropogenic material source is the evaporation of contaminated rain drops which adhere to surfaces after a rainfall. Of particular concern here are those substances considered most acidic or acidifying – the various forms of S and N compounds.

To illustrate how the synergism of the previously mentioned pollutants with special events may cause highly acidic conditions on surfaces, two examples are presented. The first is from a paper by Brimblecombe [36], who investigated dew as a sink for SO_2. Although his conclusion was that dew could only absorb a small percentage of the total SO_2 emitted in the United Kingdom, calculations indicated that dew may become very acidic in this process. The pH values calculated for a dewfall of 0.5 mm (heavy) and a SO_2 concentration of 31 $\mu g\ m^{-3}$ were 3.67 and 4.71. The differences in the pH values were due to the use of two different SO_2 depositional velocities, one of which was based on actual measurements of SO_2 deposition to a wheat field [37] and the other on the aqueous diffusion constant for SO_2. The latter depositional velocity assumes that the rate of SO_2 absorption is limited by pH and is governed by the presence of alkaline material in the solution to raise the pH. The study concluded that there must be a source of alkaline material either from particulate matter on the leaf, NH_3 from decaying organic material on the ground, or materials leached from the plant itself, in order to justify the Fowler and Unsworth [37] results, which indicated a high rate of SO_2 absorption.

The second example presents a theoretical discussion based on assumptions of the occurrence of dry deposition of $SO_4^=$ and deposition of moisture as dew to form localized acids as illustrated in Figure 1. Although this discussion will concentrate on dew interaction, the same discussion might also apply to deposition of fog moisture and frost melt. The $SO_4^=$ anion was chosen because more is known about its dry deposition velocities and also because it is the predominant anion in both wet and dry deposition in the northeastern U.S. The only cation chosen was H^+, in order to simplify the theoretical calculations. It is understood that in real world situations other cations and anions, both acidic and basic, interact in a synergistic fashion.

The calculations in this study were initiated by approximating ambient $SO_4^=$ concentrations of 1.0 $\mu g\ m^{-3}$ and 9.0 $\mu g\ m^{-3}$, the latter of which is near the mean of EPA's data from the National Air Surveillance Networks for the years 1971–1976 [38]. Estimated dry deposition velocities for $SO_4^=$ were also used. Shieh *et al.* [39] compiled a guide for estimating dry deposition velocities for SO_2 and $SO_4^=$ over the eastern United States. The velocities vary according to season and land use, both of which affect the surface characteristics and stability classifications. Values were found to vary between 0.1 and 1.3 cm s^{-1}, with very few values greater than 0.9 cm s^{-1}. Typical values appear to be about 0.7 cm s^{-1} for SO_2 and 0.8 cm s^{-1} for $SO_4^=$. A minimum value for $SO_4^=$ deposition velocities of 0.1 cm s^{-1} and a maximum value of 0.9 cm s^{-1} were chosen for this analysis. The two low values for $SO_4^=$ concentration and depositional velocity and the two high values were then combined using the following formula to give a low and high depositional flux (micrograms of $SO_4^=$ per square centimeter per day):
Formula

$$D_s = [SO_4^=]_{\text{air}} \times V_s \times C$$

where

D_s = depositional flux of $SO_4^=$ ($\mu g\ cm^{-2}\ day^{-1}$) to surface ;

$[SO_4^=]_{\text{air}}$ = ambient atmospheric $SO_4^=$ concentration ($g\ m^{-3}$) ;

V_s = depositional velocity for $SO_4^{=}$ (cm s^{-1}) ;

C = conversion factor (m^3 s cm^{-3} day) = 0.0864 .

Values used in calculations

$[SO_4^{=}]_{air}$ = 9.0 μg m^{-3} (high value) ;

1.0 μg m^{-3} (low value) ;

V_s = 0.9 cm s^{-1} (high value) ;

0.1 cm s^{-1} (low value) .

Results

D_s = 0.70 μg cm^{-2} day^{-1} (high value) ;

$D_s = 8.6 \times 10^{-3}$ μg cm^{-2} day^{-1} (low value) .

Combining the resultant estimates of total dry $SO_4^{=}$ daily deposition with hypothetical heavy (0.5 mm) and light (0.1 mm) dewfalls generates a concentration of $SO_4^{=}$ in equivalents per liter. The formula being:

$$\mathrm{pH} = -\log[\mathrm{H}^+] = -\log \frac{2 \times D_s \times T \times K}{W \times E}$$

where

pH = pH value in dew ;

$[H^+]$ = H^+ concentration from H_2SO_4 (assumed to be double the $SO_4^{=}$ concentration (μeq l^{-1})) ;

D_s = depositional flux of $SO_4^{=}$ to surface (μg cm^{-2} day^{-1}) ;

T = time of previous dry deposition (days) ;

W = volume of dew deposited (ml cm^{-2}) ;

E = conversion factor = 48×10^6 μg eq^{-1} for $SO_4^{=}$;

K = conversion factor (ml l^{-1}) = 1000 .

Values used in calculations

D_s = 0.70 μg cm^{-2} day^{-1} (high) ;

8.6×10^{-3} μg cm^{-2} day^{-1} (low) ;

T = 0.5 to 5 days ;

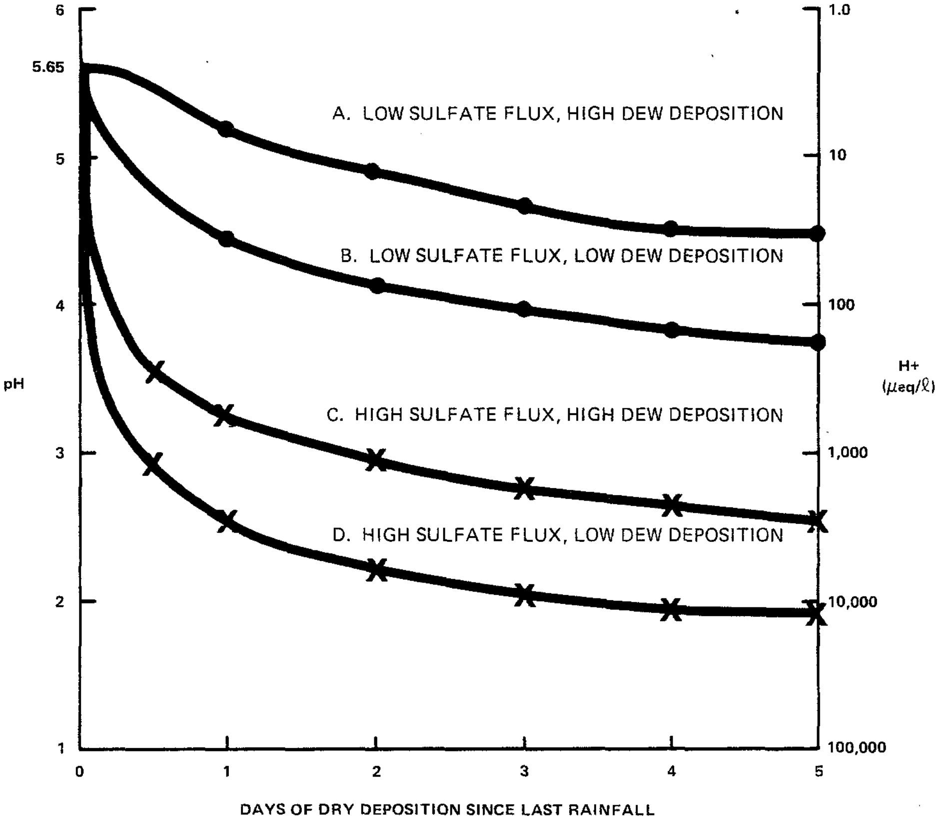
W = 0.05 ml cm^{-2} (high) ;

0.01 ml cm^{-2} (low) .

Inherent in this computation and analysis are the following simplications and assumptions:

– Deposition of $SO_4^=$ and dew is spatially uniform on the surface of interest, even though this probably does not occur in reality [35]. However, the process of coalescence of the dew tends to sweep any water soluble material into the resultant drops. Thus, this assumption appears to be reasonable;

– Once the $SO_4^=$ is deposited on the surface, it remains there. This is not always the case, but work by Lindbert *et al.* [35] has shown *net* downward $SO_4^=$ fluxes to leaves



VALUES USED FOR GENERATING CURVES:

CURVE	AMBIENT $SO_4^=$ CONCENTRATION	$SO_4^=$ DEPOSITIONAL VELOCITY	$SO_4^=$ DEPOSITIONAL FLUX (per day)	DEWFALL
A	1.0 µg/m^3	0.1 cm/s	8.64x10^{-3}µg/cm^2	0.5mm
B	1.0 µg/m^3	0.1 cm/s	8.64x10^{-3}µg/cm^2	0.1mm
C	8.9 µg/m^3	0.9 cm/s	0.70 µg/cm^2	0.5mm
D	8.9 µg/m^3	0.9 cm/s	0.70 µg/cm^2	0.1mm

Fig. 3. Potential Synergistic Acidity from Dew and Previous Dry Deposition. (The same Calculations could be Modified Accordingly to Obtain Frosts and Fog Acidities.).

of about 0.3 μg cm^{-1} day^{-1}. This value is within the range of depositional fluxes being used;

– The contribution to overall pH by HCO_3^- is very small for pH's from 5.5 to 5.0 and negligible below pH 5.0. For example, at pH 5.0, only 3.8% of the total inorganic C species exist as HCO_3^-, with 96.2% in the form of free CO_2. Galloway *et al.* [40] state that carbonic acid does not influence free acidity in precipitation samples with pH less than 5.0;

– Finally, as previously mentioned, the cation associated with the $SO_4^=$ is assumed to be totally H^+, forming H_2SO_4. This is a 'worst case' assumption, used to investigate the *potential* acidity of dew. Surprisingly, if one assumes that the solution is partially neutralized, the effect on the pH is not as profound as one would think.

The results of the computations are presented graphically in Figure 3. From the graph, a potential for extremely low pH values in dew is shown. In the worst case, shown in curve D, pH values are less than 3.0 following only one-half day of dry deposition. Analysis of the results reveals that the major influence on potential dew-water acidity is the initial rate of dry acidic material deposition. After the first day of deposition, the number of days of additional deposition has much less influence on the pH. For example, curve D shows dew pH to decrease from the CO_2 equilibrium pH of 5.6 to 2.5 after the initial day of deposition. Thereafter, the pH declines at a much slower rate per additional day of dry deposition, due to the logarithmic nature of the pH scale. This implies that brief periods of elevated dry acid deposition episodes may have a marked effect on the synergistic dew-dry deposition acidity. The amount of dew deposition has a somewhat lesser influence, causing only about a 0.7 pH unit variation between high and low dewfalls.

One influence to be considered in the previous analysis is the role of neutralizing agents such as carbonates, NH_3 and other alkaline substances. In the 'real world', the substances collected on plant and material surfaces from dry deposition are undoubtedly a combination of sulfate and nitrate salts as well as H_2SO_4 and HNO_3 aerosols. The influence they have on the dew-dry deposition solution needs exploration.

5. Impacts from Special Acidic Events

Dew, frost, and fog mainly affect surfaces. Dew and frost form directly on surfaces and fog is deposited by gravitational settling and impaction. With some exceptions, special events deposit only small amounts of moisture onto surfaces, yet the effects from this deposition in combination with dry acidic deposition (as suggested above) may be significant. Direct and indirect evidence of effects from these events are discussed below.

5.1. EFFECTS ON VEGETATION

Special acidic events may cause enhanced cation leaching from foliar surfaces of plants. It is known that acid rain has the ability to leach cations from foliar surfaces [41], and acid dew and fog may also have similar effects. Good and Tukey [42] found that most types of plants are subject to losses of many metabolites and minerals by leaching when exposed to artificial acid mist. Mecklenburg and Tukey [43] discovered that large quantities of nutrients are lost during dew formation. They also found that the volume of a leaching solution had no significant effect on the amount of nutrient loss.

Fairfax and Lepp [41] demonstrated that increases in H^+ concentration of the leaching solution lead to increased losses of cations from leaves of *Nicotiana*. This is consistent with the findings of Mecklenburg *et al.* [44] and led them to suggest that leaf surface wetting and H^+ concentration are the most important factors in regulating foliar nutrient losses.

Although this evidence is by no means definitive, it does suggest that acid dew and fog may be a significant mechanism for foliar cation leaching. The magnitude of this leaching and the effects on plant productivity and development is unknown. Special acidic events may also have other effects on vegetation such as causing foliar necrosis, which has been documented for simulated acid rain [45], but this too is an area where much research is necessary.

5.2. EFFECTS ON MATERIALS

In general, two types of degradation are enhanced by special acidic events: direct chemical attack and electrochemical corrosion. Direct chemical attack occurs when the acid dew or fog reacts with a particular material to cause deterioration. This occurs, for example, when H_2SO_4 in a condensate reacts with the $CaCO_3$ in a building stone to produce $CaSO_4$. The $CaSO_4$ is easily washed away, thus leading to deterioration of the stonework [46]. Electrochemical corrosion may occur when a metallic structure contacts an electrolytically conducting medium. The onset of corrosion is dependent on the formation of a galvanic cell in which one or more sites on the structure act as a cathode, accepting electrons, and others act as anodes, donating electrons. In donating electrons, metals at anodic sites become ionized and the ions migrate into the surrounding electrolytic solution. Thus there is a loss of metal – i.e. corrosion. Where the metallic structure consists of more than one type of metal, one becomes the anode and the other a cathode. On singular metallic surfaces the formation of anodes and cathodes results from various local chemical and physical inhomogeneities [46]. Special events may provide the electrolytic solution which facilitates these reactions. Even a salt solution such as $(NH_4)_2SO_4$ is corrosive in this regard [47].

Evidence of the effects of special acidic events is presented in a number of studies. One of the first to recognize the role of dew in atmospheric corrosion was Anderson [48]. He suggested that the corrosion of Zn was dependent on the frequency of rain and dew, the acidity of condensate on the surface, and the drying rate of the condensate. He postulated that an acidic dewfall would result in the dissolution of Zn, eventually raising the pH to a point where a basic salt would precipitate from solution, forming a film which further acidic moisture must dissolve before attack of the Zn could continue. It is conceivable that acidic rain might easily wash this film away, thus 'cleansing' the surface for further attack.

Dunbar [49] also conducted field studies on Zn corrosion from 1931 to 1957. One of the conclusions of these studies was that condensate formation on the test samples increased corrosion. It was also suggested that drought conditions may cause high accumulations of dry acidic contaminants on surfaces between rainfalls, thus enhancing corrosion when combined with dew.

Studies on materials other than Zn have also illustrated impacts from special acidic events. Fassina [50] performed a study of deterioration of stonework in Venice and concluded that acid aerosols, combined with dew or fog condensate, cause deterioration in calcite-based stone. He found that deterioration resulted from the formation of $CaSO_4$, which caused deterioration of the stonework for two reasons: (1) the fact that $CaSO_4$ is a somewhat soluble salt and is easily eroded by rain; and (2) the fact that $CaSO_4$ crystallizes with a higher volume than $CaCO_2$, thus subjecting the stone to mechanical stresses, leading to cracking or further degradation upon recrystalization.

Sulfuric acid in fog and dew has also been suggested as the cause of deterioration of stain glass windows in Europe [51]. These windows are low in soda content and are especially sensitive to acid attack.

Finally, a unique material problem which is associated with special events plagues power companies [46]. When particulate matter accumulates on high-voltage transmission line insulators, followed by conditions of high humidity, fog or rain, a phenomena known as insulator flashover may occur. The deposited moisture in combination with the dry material acts as a conductor. To prevent flashover, insulators must be cleaned periodically with very high pressure water.

Conclusion

The potential acidity associated with special events appears to be significant. Values of fog pH have been observed to be below 3.0. Data on dew and frost pH are extremely sparse, but indicate that they are also somewhat acidic. Observed pH values range from 5.0 to 6.0; however these values may underestimate the actual acidic potential of dew and frost. Theoretical calculations indicate that synergistic acidity from dew combined with previous acidic dry deposition, may result in pH values of less than 2.0 in some cases. Neutralization effects from alkaline dry deposition, leaching of plant metabolites, or surface reactions could act to raise the pH almost immediately upon formation of the acid solution. However, neutralization in the latter two ways would result in damage to the plant or material surface in question. Review of the literature indicates that special events may cause increased leaching of plant metabolites and material corrosion.

Hard evidence on both the chemistry and effects of special events is still lacking. However, theoretical calculations strongly suggest that potential acidity from these events should be further investigated, especially in light of the fact that special events occur with frequencies much greater than rain or snow in most areas.

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