A

ACID RAIN

Acid rain is one of the major environmental issues confronting industrialized countries, and is a wet form of acid deposition. Acid deposition is composed of sulfuric acid, nitric acid and ammonium, and occurs as wet deposition (rain, snow, sleet, hail), dry deposition (particles, gases and vapor), and cloud or fog deposition. Understanding the nature of acid rain and its impact requires a working knowledge of the concept of acidity and means by which atmospheric processes affect the potential for acid deposition.

Acidity

The acidity of a material is associated with the relative abundance of free hydrogen ions (H^+) when that substance is in a water solution. The pH scale is a logarithmic scale, where a value of 7 indicates neutrality; decreasing values on the scale indicate an increase in acidity and increasing values represent alkalinity. A pH scale with representative examples is shown in Figure 1.

Absolutely pure water (distilled) has a pH of 7, but if it is allowed to react with clean air its pH will decrease to near 5.6. This is a result of the absorption of carbon dioxide in the atmosphere to form weak carbonic acid. Most rainwater will have this pH; acid rain occurs when the pH is less than 5.6. For

this reaction to occur, the atmosphere must be composed of chemicals that provide an acidic source. The atmosphere must also be able to deposit the material at the surface. This deposition is accomplished through the process of atmospheric cleansing.

Atmospheric cleansing

Acid deposition is a result of the "wet deposition" process, which involves the removal of chemicals through precipitation. Impurities in the atmosphere are incorporated in the entire precipitation process, beginning with cloud droplet formation, and are deposited as part of the resulting precipitation. Cleansing can also happen via "dry deposition", which implies that substances in the atmosphere are deposited through gravitational settling. Large particles settle under their own weight; very small particles may be transported far from their source to eventually polymerize until they are large enough to fall under their own weight. These particles generally are returned to earth through the wet deposition process.

Wet and dry depositional processes do not include all aspects of deposition. Other forms include fog droplet interception (especially prevalent in high-altitude forests), dew, frost, and rime icing.

The current distribution of wet-deposition acid in the United States is shown in Figure 2. The eastern part of the country, centered on the northeastern states, clearly has higher acidity than the remainder of the area. In part, this distribution reflects the conditions in the drier west where the chemistry of
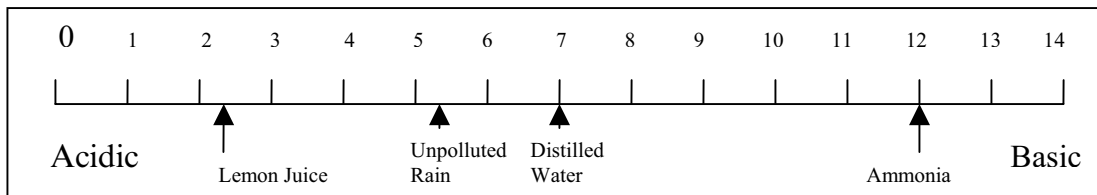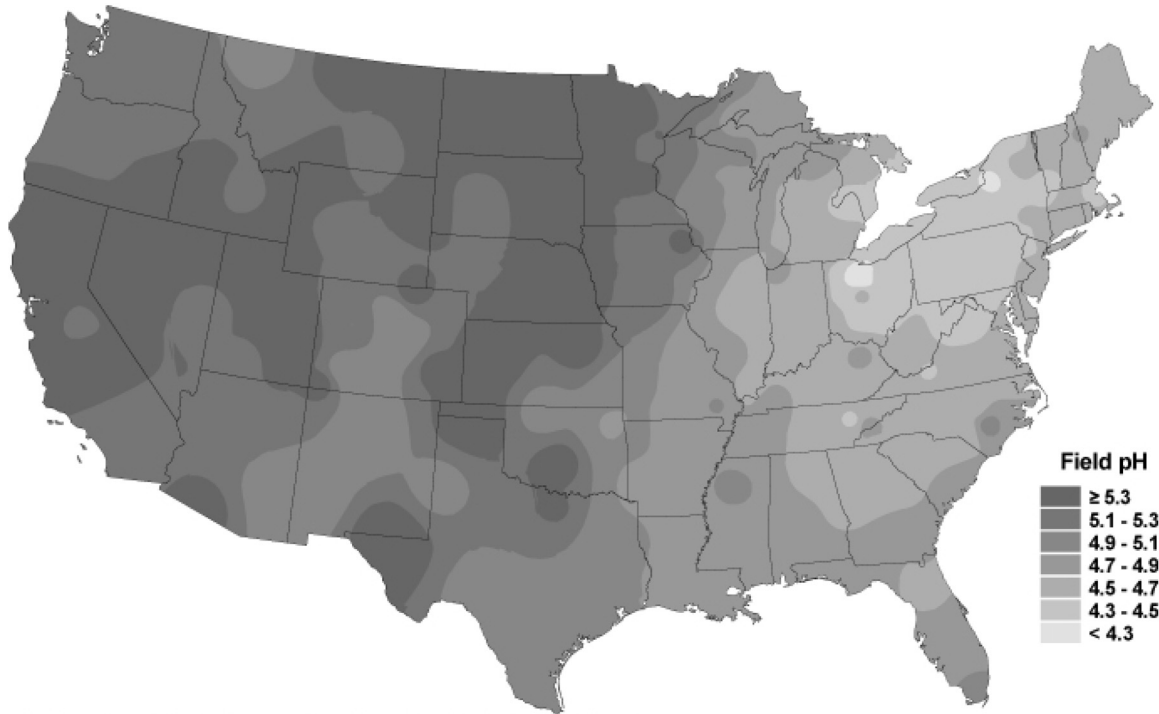

Figure 1 The pH scale denoting examples of some common substances

Figure 2 Distribution of acidity in the United States (National Atmospheric Deposition Program/NTN). Hydrogen ion concentration as pH from measurements made at the field laboratories, 2002

precipitation is altered by alkaline substances contributed to the atmosphere.

Acid rain sources

Acid rain is primarily a result of the release of sulfur oxides (SO_2) and nitrogen oxides (NO_x) into the air by industrial and transportation sources. These oxides are transformed into sulfuric acid and nitric acid through oxidation and hydrolysis. Oxidants play a major role in several of these acid-forming processes. Rates of transformation are controlled by environmental conditions such as temperature, humidity, clouds, sunlight, and the presence of other select chemicals.

Table 1 summarizes all the major chemicals that influence the acidity of rain, with both natural and man-made sources identified. As noted above, man-made sources of SO_2 and NO_x contribute significantly to the development of acid rain. It is important to note that 95% of the elevated levels of NO_x are the result of human activities, including transportation sources (50%), electric utilities (26%), and industrial combustion (14%). The major sources of sulfur dioxide emissions were electric utilities (60%), industrial combustion (17%), and industrial processes (8%), measured in 1997.

Central to this conclusion is the question of a transport mechanism for air pollutants responsible for acid rain and the location of the source to areas that are currently experiencing acid deposition. Given that pollutants can return to earth instantaneously or remain airborne for a week or longer, then atmospheric circulation patterns and prevailing winds are significant.

Examination of continental air currents demonstrates that seven states in the Midwest comprise the dominant source area for sulfur dioxide emissions that travel downwind to the Northeast (Driscoll et al., 2001). These states contributed 41% of the total national emissions of SO_2 in 1997. Furthermore, five of these states accounted for 20% of the total national emissions of NO_x.

Defining the location of actual sources contributing chemicals to acid rain is compounded by both political and economic circumstances. As mentioned above, there has been much controversy over the role of Midwestern industries and power plants using high-sulfur coal, thereby advancing acid rain in the northeastern United States. However, Phase I of the Clean Air Acts Amendment, Title IV (1995) has resulted in lower sulfate concentrations in precipitation in both the Eastern US and along the Ohio River Valley.

In 1980 the US Congress established the National Acid Precipitation Assessment Program to research the effects of acid deposition. Studies identified electric power generation as responsible for two-thirds of SO_2 emissions and one-third of NO_x emissions. Utilizing findings from these studies, Congress created the Acid Rain Program under Title IV (Acid Deposition Control) of the Clean Air Act Amendments (CAAA) of 1995. The Acid Rain Program set a goal of reducing NO_x by two million tons from 1980 levels, and requires a 50% decrease in SO_2 emissions from electric-generating facilities by 2010. By 2001, SO_2 levels have been reduced by 30% in the United States. However, nitrogen oxide emissions were not significantly affected. Research in the northeast United States has shown that acid rain is still a significant issue.

Table 1 Chemicals that influence the acidity of rainfall

Ions in deposition	Source	Type	Significance
Sulfate (SO_4)	Swamps	Natural	
	Volcanoes	Natural	Minor
	Oceans	Natural	
	Power plants	Human activities	
	Industrial processes	Human activities	Major
	Smelters	Human activities	
Nitrate (NO_3)	Lightning	Natural	
	Soil biologic activity	Natural	Minor
	Industrial processes	Human activities	
	Transportation	Human activities	Major
Chloride (Cl)	Oceans	Natural	Minor
	Land surface	Natural	
	Industrial processes	Human activities	Minor
	Road salt	Human activities	
Ammonium (NH_4)	Biologic processes	Natural	
	Animals	Natural	Moderate
	Industrial processes	Human activities	
	Agriculture	Human activities	Minor
Calcium (Ca)	Land surface	Natural	Moderate
	Industrial processes	Human activities	Minor
	Agriculture	Human activities	
Sodium (Na)	Oceans	Natural	
	Land surface	Natural	Minor
	Road salt	Human activities	Minor
Magnesium (Mg)	Industrial processes	Human activities	
Potassium (K)	Land surface	Natural	Minor
	Agriculture	Human activities	

Effects of acid rain

In the 1960s and 1970s researchers in Scandinavia and the United States found that there was an increase in acidity and decrease in fish population in certain lakes and streams. Although acid rain can degrade water quality by lowering pH levels, the relationship is much more complex. Surrounding soils and vegetation contribute chemical ions that also modify acidity. Acid rain can also decrease the acid-neutralizing capacity and increase the aluminum concentrations of surface water.

Acid rain is also thought to have a detrimental effect on forests. Trees may be injured by the direct action of acid on leaves or needles, or by changes in soil chemistry caused by the acid solution. By the early 1980s 20–25% of European forests were classified as moderately or severely damaged by acid rain. The decline of red spruce and sugar maple trees in the northeast United States has been occurring for the past four decades and has been linked to acid rain. Agricultural productivity may also be adversely impacted by acid rain.

Scientists have determined that, in soils impacted by acid rain, nutrients such as potassium, magnesium, and calcium are displaced by excess hydrogen ions, and that plant growth is retarded. Aluminum may also be released by excess hydrogen. Aluminum can be toxic to plants and, when released, can compromise the plant's ability to absorb water and nutrients. Acid rain also increases the accumulation of sulfur and nitrogen in the soil.

Buildings and monuments are also impacted by acid rain. Chemical reactions resulting from both wet and dry deposition have been recognized as a cause of extensive damage to historical buildings. Monuments such as the Acropolis in Athens and Jefferson Memorial in Washington DC show signs of damage from acid rain. Marble and limestone are susceptible due to the acids attacking the calcium carbonate in these materials. In addition to stone structures, acid rain also damages other building materials, particularly iron, steel, zinc, paint, and wood, and can cause the lifetimes of these structures to be shortened noticeably.

The chemicals comprising acid rain can also have an impact on human health, among other things. EPA has associated NO_x with photochemical smog, respiratory illness, ecosystem changes, visibility impairment, acidification of fresh-water bodies, eutrophication of estuarine and coastal waters, and increasing levels of toxins harmful to fish and other aquatic life. Likewise, high levels of SO_2 concentrations have been associated with increased respiratory difficulties.

The future

There are still many unanswered questions concerning acid rain. If acid rain proves to be as destructive as suggested by many writers, then it is certainly one of the major environmental concerns that must be dealt with in the near future.

Climatology will play an integral role in deriving many of the answers. Of importance is the transport of pollutants in the atmosphere, a problem that is associated with both meso- and macro-circulation patterns; a complete understanding of the

chemistry involved in the wet deposition process; and comprehension of dry deposition processes. Additionally, politics, both national and international, will also play a role.

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Cross-references

Aerosols
Air Pollution
Climatology Atmospheric Nuclei and Dust
Climatic Hazards
Precipitation
Wind, Principles.

ADIABATIC PHENOMENA

An adiabatic process is one in which the system being considered does not exchange heat with its environment. The most common atmospheric adiabatic phenomena are those involving the change of air temperature due to change of pressure. If an air mass has its pressure decreased, it will expand and do mechanical work on the surrounding air. If no heat is taken from the surroundings, the energy required to do work is taken from the heat energy of the air mass, resulting in a temperature decrease. When pressure is increased, the work done on the air mass appears as heat, causing its temperature to rise.

The rates of adiabatic heating and cooling in the atmosphere are described as lapse rates and are expressed as the change of temperature with height. The adiabatic lapse rate for dry air is very nearly 1°C per 100 m. If condensation occurs in the air parcel, latent heat is released, thereby modifying the rate of temperature change. This retarded rate is called the pseudo-adiabatic lapse rate; it is not a constant for its value depends on the temperature at which the process takes place and the amount of water vapor in the air mass. However, for general descriptive purposes it is assumed as 0.5°C per 100 m.

The usefulness of the adiabatic approximation has led to the development of special thermodynamic diagrams that enable the results of adiabatic processes to be determined graphically.

These charts are characterized by having two thermodynamic variables as coordinates and the values of various others represented by isopleths. Well-known examples of these "adiabatic diagrams" are the Tephigram, Stuve diagram, and Skew-T diagram.

Large-scale atmospheric motions are approximately adiabatic, and clouds and snow or rain associated with them are primarily adiabatic phenomena in that they result from cooling air associated with decreasing pressure of upward air motion. Simpler adiabatic phenomena occur on a smaller scale. A common example is that of rising "bubbles" of air on a warm day, leading to cumulus cloud forms. The growth of such cumulus clouds into thunderclouds is more complex but still a largely adiabatic phenomenon.

An example of the reverse effect, heating due to an increase in pressure, is the warm Foehn or Chinook wind that results from the descent of air from higher levels.

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Boundary Layer Climatology
Cloud Climatology
Lapse Rate
Local Winds

AEROSOLS

Aerosols are technically defined as a relatively stable dispersion of solid or liquid particles in a gas. However, in common usage in the atmospheric sciences the term refers to the particles themselves. Aerosols are involved in a number of important atmospheric processes. These include atmospheric electricity; visibility; cloud and precipitation formation, including acidity of the precipitation; atmospheric biogeochemical cycles; and the radiative properties of the atmosphere. In all of these processes the size distribution of the aerosols is particularly important, as is their chemical composition.

Atmospheric aerosols are generated by a number of natural processes and as a result of human activities. Aerosols may be classified as "primary" or "secondary", depending on their production process. Primary aerosols are particles that are injected into the air directly, often by some mechanical process such as wind erosion of land surfaces (mineral aerosol), or wave breaking (sea salt aerosol). Secondary aerosols result from gas-to-particle conversion processes within the atmosphere that generate new particles. Table 1 presents the estimated source strengths for different types of primary and secondary aerosols. In terms of mass, sea salt and mineral aerosols (or dust) dominate the primary aerosols and also total global aerosol production. Industrial dust, various combustion

Table 1 Sources and radiative forcing of aerosols[a]

Aerosol type	Source strength (Tg y/year)	Anthropogenic fraction (%)	Fine fraction (%)	Global mean direct radiative forcing[b] (W m^{-2})
Primary				
Sea salt	3300	0	<1	—
Mineral dust	2200	~50	20	−0.60 to + 0.40
Biomass burning	60	>90	~100	−0.20
Fossil fuel burning	35	100	~100	−0.10 or + 0.20[c]
Biogenic	55	0	small	—
Industrial dust	100	100	~100	—
Total Primary	*~5800*	*~20*	*~10*	
Secondary				
Sulfate	200	~60	~100	−0.40
Nitrate	18	~80	~100	—
Organic compounds	17	~4	~100	—
Total Secondary	*~235*	*~60*	*~100*	
Global total	*~6000*	*~25*	*~15*	

[a] Numbers are derived from Houghton et al. (2001); 1 Tg = 1 × 10^{12} g.

[b] Values have uncertainties of a factor of 2 to 3. The global mean total *indirect* aerosol radiative forcing is estimated at 0 to −2.0 W m^{-2}.

[c] Organic carbon is −0.10 and black carbon is +0.20.

processes and direct injection of particles from vegetation are also significant primary aerosol sources. The most significant secondary aerosols include sulfate, nitrate and organic particles, all resulting from the reaction of gaseous precursors in the atmosphere.

Table 1 also provides information on the size of the particles from each of these sources. Typically aerosols are categorized according to size as "coarse (generally greater than ~1 μm radius) and "fine" (generally less than ~1 μm radius). Essentially all of the aerosol mass for secondary aerosols is in the fine category, whereas most of the mass of the primary aerosols is in the "coarse" category. The "fine" particles in turn have two components: the nuclei mode, from about 0.005 to 0.1 μm radius; and the accumulation mode, from about 0.1 to 1.0 μm radius. Particles in the nuclei mode are formed from the nucleation of atmospheric gases. The accumulation mode particles result from the coagulation of nuclei mode particles as well as from some condensation of gases onto existing particle surfaces.

The "fine" and "coarse" aerosols not only have very different sources, they are transformed differently, they have different chemical composition and optical properties, and they are removed from the atmosphere by different processes. For example, size has a significant impact on the atmospheric lifetimes of "coarse" and "fine" aerosols. The nuclei mode fraction of the "fine" aerosols has relatively short lifetimes (roughly hours or less) within that size range due to their rapid growth via coagulation with themselves or other particles into the larger accumulation mode aerosols. Accumulation mode aerosols can have atmospheric lifetimes of days to a week or more and can thus be transported great distances in the atmosphere. The primary removal mechanism for the accumulation mode aerosols is by precipitation. The "coarse" aerosols generally have atmospheric lifetimes of from hours to a day or two, with the lifetime decreasing as the particle size increases. Direct dry deposition is important for the coarse aerosol, and this becomes increasingly important as the particle size increases. Even "coarse" aerosols can be transported great distances, however. There have been numerous occasions when mineral dust from the Chinese deserts has been transported in the atmosphere to the east across the Pacific Ocean and North America to the Atlantic Ocean. Similarly, mineral dust from the Sahara Desert in Africa is often carried west across the tropical North Atlantic Ocean and Caribbean Sea to the eastern Pacific Ocean. Similar trans-oceanic transport of pollution-derived aerosols has also been observed on numerous occasions. Atmospheric sea salt aerosols from oceanic regions are also often observed in mid-continent locations.

The data in Table 1 indicate that about 20% of the primary aerosols and 60% of the secondary aerosols are derived from human-related, or anthropogenic, sources. This is particularly important for sulfate aerosols, which are often primarily responsible for visibility degradation and precipitation acidity in urban and near-urban regions. The predominant sources for the gaseous precursors for the secondary sulfate aerosols are industrial emissions and the combustion of fossil fuels. Similarly, fossil fuel combustion is the major source for the gaseous precursors of nitrate aerosols. Contrary to earlier estimates, anthropogenic sources do not appear to be a significant source of organic aerosols.

Table 2 provides information on typical number and mass concentrations of aerosols in different regions. In urban areas particle number concentrations of millions per cubic centimeter are common, whereas in the remote marine atmosphere concentrations can be less than 100 particles per cubic centimeter.

Table 2 Typical properties of aerosols in different regions*

Region	Total number (cm^{-3})	Mass	
		< 1 μm (μg m^{-3})	1–10 μm (μg m^{-3})
Urban (pollution)	1×10^5–4×10^6	30–150	70–150
Rural	2×10^3–1×10^4	3–8	5–30
Remote continental	1×10^2–1×10^4	0.5–3	1.5–7
Remote marine	1×10^2–4×10^2	1–4	10–35

* Derived from Seinfeld and Pandis (1998).

In urban areas the mass concentrations can range up to several hundred micrograms per cubic meter, whereas under some conditions in remote continental regions the mass concentrations can be as low as one microgram per cubic meter or less. In areas near major dust storms concentrations of 1 gram per cubic meter or more have been observed.

Aerosols have both a direct and an indirect role in the radiative forcing of climate. The direct forcing results because they can absorb and scatter both infrared and solar radiation in the atmosphere. Indirect forcing occurs because aerosols can affect and change the processes that control cloud and precipitation formation, which in turn can affect the radiative properties of the atmosphere. There has been strong interest in aerosol forcing. This is because the forcing is negative for most aerosol types, rather than the positive forcing associated with the major radiatively active trace gases, such as carbon dioxide, methane, nitrous oxide, halocarbons and tropospheric ozone. Once again, size distribution and chemical composition are critical factors in the efficiency of aerosols in affecting these forcings. While significant progress has been made in recent years in determining the importance of aerosols of various types in radiative forcing, the uncertainties are still quite large. The most recent Intergovernmental Panel on Climate Change (IPCC, Houghton et al., 2001) report has developed new estimates of aerosol forcing, and some of their results are shown in Table 1. Note that the numbers given represent the mean direct radiative forcing for the aerosols described (except for mineral dust, where only a range was given), but the uncertainties in these estimates range from a factor of 2 to 3. Aerosol types where the evidence shows negative forcing include sulfate aerosols, organic carbon aerosols, and aerosols from biomass burning. The sign of the net forcing for mineral aerosols is still uncertain. Black carbon aerosols appear to cause a positive forcing. Note also that the indirect forcing is estimated to be from 0 to $-2.0\,\mathrm{W\,m^{-2}}$. The values for aerosol forcing in Table 1 can be compared with the best estimate for carbon dioxide forcing of $+1.46\,\mathrm{W\,m^{-2}}$.

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