SECOND EDITION

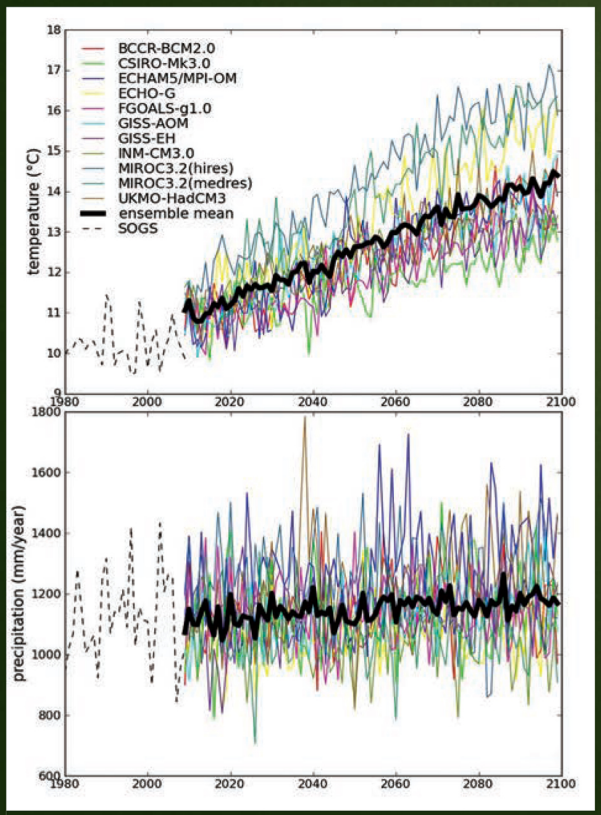
THE HANDBOOK OF NATURAL RESOURCES

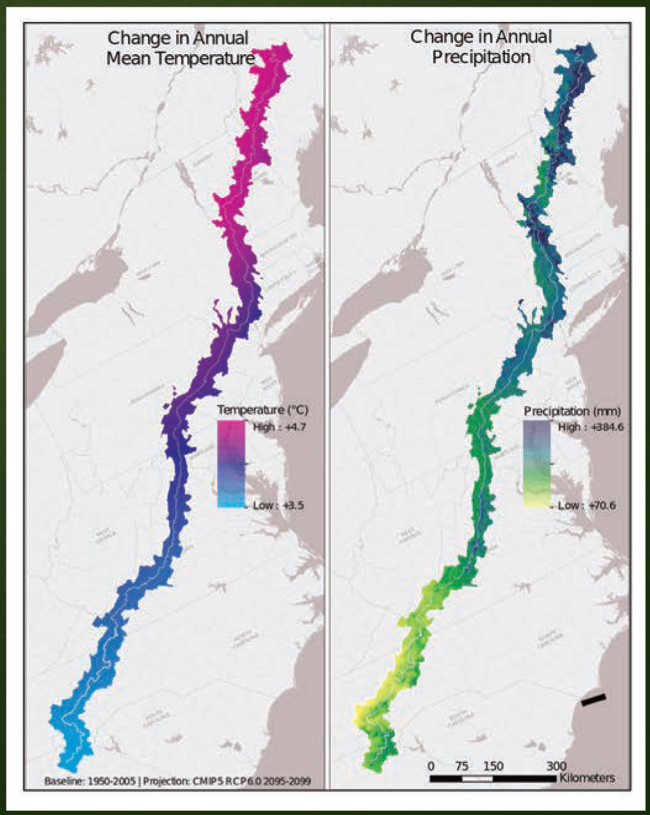
VOLUME VI

Atmosphere and Climate

edited by

Yeqiao Wang





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Atmosphere and Climate

The Handbook of Natural Resources, Second Edition

Series Editor:
Yeqiao Wang

Volume 1
Terrestrial Ecosystems and Biodiversity

Volume 2
Landscape and Land Capacity

Volume 3
Wetlands and Habitats

Volume 4
Fresh Water and Watersheds

Volume 5
Coastal and Marine Environments

Volume 6
Atmosphere and Climate

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Preface

Atmosphere and Climate is the sixth volume of The *Handbook of Natural Resources*. This volume consists of 40 chapters authored by 68 contributors from 7 countries. The contents are organized in three sections: *Atmosphere* (16 chapters); *Weather and Climate* (16 chapters); and *Climate Change* (8 chapters).

Land and atmosphere interactions are driven by continuous exchange of heat, moisture, momentum, and various gases. Land surface heterogeneity leads to spatial variation of land–atmosphere exchanges resulting in various natural phenomena, such as sea breezes, valley winds, and monsoons, at wide ranges of spatial and temporal scales. Human induced land-use and land-cover change from deforestation, agriculture, and urbanization modify such exchanges and affect weather, climate, water, and carbon cycle at multiple scales. Growing demands for food, energy, and natural resources imply that land-use and land-cover change will continue to intensify in the future. Understanding the underlying process of land–atmosphere interactions is critical for predicting the impact of future change on the environment and natural resource base.

Climate change studies reveal the effects of global warming and provide understanding of the changing environment, the impacts and threats caused by changes, and the likely trends in the future for natural resources and associated ecosystems. Adaptive management and mitigation strategies require data and indicators to science-based assessment and effective implementation. This is especially important in view of a changing climate, with direct and indirect consequences on the natural resources.

With the challenges and concerns, the 40 chapters in this volume cover topics in *Atmosphere*, including acid rain and precipitation chemistry, acid rain and nitrogen deposition, air pollutants, albedo, Asian monsoon, atmospheric acid deposition, general atmospheric circulation, atmospheric and oceanic circulation patterns, dew point temperature, fronts, land-atmosphere interactions, ozone and ozone depilation, transpiration and physical evaporation, atmospheric water storage, arctic oscillation, and estimation of Arctic sea-ice shortwave Albedo; in *Weather and Climate*, including agroclimatology, climatology, climate classification, extreme events, moist enthalpy and long-term anomaly trends, trace gas exchange between crops and atmosphere, precipitation, evapotranspiration and soil moisture, drought resistance, drought management, El Niño, La Niña, and the Southern Oscillation, tropical meteorology, ocean-atmosphere interactions, ocean observation and prediction, tropical cyclones, urban heat islands, and wind speed probability distribution; and in *Climate Change*, including climate change, climate change and boreal forests, climate change in coastal marine environment, climate change in polar regions, climate change effects on habitat suitability, climate change and ecosystem dynamics, spatial and temporal variation in global land surface phenology, and in precipitation and temperature.

The chapters provide updated knowledge and information in general environmental and natural science education and serve as a value-added collection of references for scientific research and management practices.

Yeqiao Wang
University of Rhode Island

About The Handbook of Natural Resources

With unprecedented attentions to the changing environment on the planet Earth, one of the central focuses is about the availability and sustainability of natural resources and the native biodiversity. It is critical to gain a full understanding about the consequences of the changing natural resources to the degradation of ecological integrity and the sustainability of life. Natural resources represent such a broad scope of complex and challenging topics.

The *Handbook of Natural Resources, Second Edition (HNR)*, is a restructured and retitled book series based on the 2014 publication of the *Encyclopedia of Natural Resources (ENR)*. The *ENR* was reviewed favorably in February 2015 by CHOICE and commented as *highly recommended for lower-division undergraduates through professionals and practitioners*. This *HNR* is a continuation of the theme reference with restructured sectional design and extended topical coverage. The chapters included in the *HNR* provide authoritative references under the systematic relevance to the subject of the volumes. The case studies presented in the chapters cover diversified examples from local to global scales, and from addressing fundamental science questions to the needs in management practices.

The *Handbook of Natural Resources* consists of six volumes with 241 chapters organized by topical sections as summarized below.

Volume 1. Terrestrial Ecosystems and Biodiversity
Section I. Biodiversity and Conservation (15 Chapters)
Section II. Ecosystem Type, Function and Service (13 Chapters)
Section III. Ecological Processes (12 Chapters)
Section IV. Ecosystem Monitoring (6 Chapters)

Volume 2. Landscape and Land Capacity
Section I. Landscape Composition, Configuration and Change (10 Chapters)
Section II. Genetic Resource and Land Capability (13 Chapters)
Section III. Soil (15 Chapters)
Section IV. Landscape Change and Ecological Security (11 Chapters)

Volume 3. Wetlands and Habitats
Section I. Riparian Zone and Management (13 Chapters)
Section II. Wetland Ecosystem (8 Chapters)
Section III. Wetland Assessment and Monitoring (9 Chapters)

Volume 4. Fresh Water and Watersheds
Section I. Fresh Water and Hydrology (16 Chapters)
Section II. Water Management (16 Chapters)
Section III. Water and Watershed Monitoring (8 Chapters)

Volume 5. Coastal and Marine Environments
Section I. Terrestrial Coastal Environment (14 Chapters)
Section II. Marine Environment (13 Chapters)
Section III. Coastal Change and Monitoring (9 Chapters)

Volume 6. Atmosphere and Climate
Section I. Atmosphere (16 Chapters)
Section II. Weather and Climate (16 Chapters)
Section III. Climate Change (8 Chapters)

With the challenges and uncertainties ahead, I hope that the collective wisdom, the improved science, technology and awareness and willingness of the people could lead us toward the right direction and decision in governance of natural resources and make responsible collaborative efforts in balancing the equilibrium between societal demands and the capacity of natural resources base. I hope that this *HNR* series can help facilitate the understanding about the consequences of changing resource base to the ecological integrity and the sustainability of life on the planet Earth.

Yeqiao Wang
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Acknowledgments

I am honored to have this opportunity and privilege to work on *The Handbook of Natural Resources, Second Edition (HNR)*. It would be impossible to complete such a task without the tremendous amount of support from so many individuals and groups during the process. First and foremost, I thank the 342 contributors from 28 countries around the world, namely, Australia, Austria, Brazil, China, Cameroon, Canada, Czech Republic, Finland, France, Germany, Hungary, India, Israel, Japan, Nepal, New Zealand, Norway, Puerto Rico, Spain, Sweden, Switzerland, Syria, Turkey, Uganda, the United Kingdom, the United States, Uzbekistan, and Venezuela. Their expertise, insights, dedication, hard work, and professionalism ensure the quality of this important publication. I wish to express my gratitude in particular to those contributors who authored chapters for this HNR and those who provided revisions from their original articles published in the *Encyclopedia of Natural Resources*.

The preparation for the development of this HNR started in 2017. I appreciate the visionary initiation of the restructure idea and the guidance throughout the preparation of this HNR from Irma Shagla Britton, Senior Editor for Environmental Sciences and Engineering of the Taylor & Francis Group/CRC Press. I appreciate the professional assistance and support from Claudia Kisielewicz and Rebecca Pringle of the Taylor & Francis Group/CRC Press, which are vital toward the completion of this important reference series.

The inspiration for working on this reference series came from my over 30 years of research and teaching experiences in different stages of my professional career. I am grateful for the opportunities to work with many top-notch scholars, colleagues, staff members, administrators, and enthusiastic students, domestic and international, throughout the time. Many of my former graduate students are among and/or becoming world-class scholars, scientists, educators, resource managers, and administrators, and they are playing leadership roles in scientific exploration and in management practice. I appreciate their dedication toward the advancement of science and technology for governing the precious natural resources. I am thankful for their contributions in HNR chapters.

As always, the most special appreciation is due to my wife and daughters for their love, patience, understanding, and encouragement during the preparation of this publication. I wish my late parents, who were past professors of soil ecology and of climatology from the School of Geographical Sciences, Northeast Normal University, could see this set of publications.

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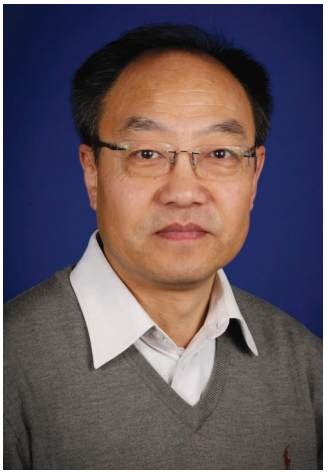
Aims and Scope

Land, water, and air are the most precious natural resources that sustain life and civilization. Maintenance of clean air and water and preservation of land resources and native biological diversity are among the challenges that we are facing for the sustainability and well-being of all on the planet Earth. Natural and anthropogenic forces have affected constantly land, water, and air resources through interactive processes such as shifting climate patterns, disturbing hydrological regimes, and alternating landscape configurations and compositions. Improvements in understanding of the complexity of land, water, and air systems and their interactions with human activities and disturbances represent priorities in scientific research, technology development, education programs, and administrative actions for conservation and management of natural resources.

The chapters of The *Handbook of Natural Resources, Second Edition (HNR),* are authored by world-class scientists and scholars. The theme topics of the chapters reflects the state-of-the-art science and technology, and management practices and understanding. The chapters are written at the level that allows a broad scope of audience to understand. The graphical and photographic support and list of references provide the helpful information for extended understanding.

Public and private libraries, educational and research institutions, scientists, scholars, resource managers, and graduate and undergraduate students will be the primary audience of this set of reference series. The full set of the HNR and individual volumes and chapters can be used as the references in general environmental science and natural science courses at different levels and disciplines, such as biology, geography, Earth system science, environmental and life sciences, ecology, and natural resources science. The chapters can be a value-added collection of references for scientific research and management practices.

Editor



Yeqiao Wang, PhD, is a professor at the Department of Natural Resources Science, College of the Environment and Life Sciences, University of Rhode Island. He earned his BS from the Northeast Normal University in 1982 and his MS degree from the Chinese Academy of Sciences in 1987. He earned the MS and PhD degrees in natural resources management and engineering from the University of Connecticut in 1992 and 1995, respectively. From 1995 to 1999, he held the position of assistant professor in the Department of Geography and the Department of Anthropology, University of Illinois at Chicago. He has been on the faculty of the University of Rhode Island since 1999. Among his awards and recognitions, Dr. Wang was a recipient of the prestigious Presidential Early Career Award for Scientists and Engineers (PECASE) in 2000 by former U.S. President William J. Clinton, for his outstanding research in the area of land cover and land use in the Greater Chicago area in connection with the Chicago Wilderness Program.

Dr. Wang's specialties and research interests are in terrestrial remote sensing and the applications in natural resources analysis and mapping. One of his primary interests is the land change science, which includes performing repeated inventories of landscape dynamics and land-use and land-cover change from space, developing scientific understanding and models necessary to simulate the processes taking place, evaluating consequences of observed and predicted changes, and understanding the consequences of change on environmental goods and services and management of natural resources. His research and scholarships are aimed to provide scientific foundations in understanding of the sustainability, vulnerability and resilience of land and water systems, and the management and governance of their uses. His study areas include various regions in the United States, East and West Africa, and China.

Dr. Wang published over 170 refereed articles, edited *Remote Sensing of Coastal Environments* and *Remote Sensing of Protected Lands*, published by CRC Press in 2009 and 2011, respectively. He served as the editor-in-chief for the *Encyclopedia of Natural Resources* published by CRC Press in 2014, which was the first edition of *The Handbook of Natural Resources*.

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I

Atmosphere

1

Acid Rain and Nitrogen Deposition

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Introduction

Air pollution has occurred naturally since the formation of the Earth's atmosphere; however, the industrial era has resulted in human activities greatly contributing to global atmospheric pollution.[1,2] One of the more highly publicized and controversial aspects of atmospheric pollution is that of acidic deposition. Acidic deposition includes rainfall, acidic fogs, mists, snowmelt, gases, and dry particulate matter.[3] The primary origin of acidic deposition is the emission of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from fossil fuel combustion; electric power generating plants contribute approximately two-thirds of the SO_2 emissions and one-third of the NO_x emissions.[4]

Acidic materials can be transported long distances, some as much as hundreds of kilometers. For example, 30–40% of the S deposition in the northeastern U.S. originates in industrial midwestern U.S. states.[5] After years of debate, U.S. and Canada have agreed to develop strategies that reduce acidic compounds originating from their countries.[5,6] In Europe, the small size of many countries means that emissions in one industrialized area can readily affect forests, lakes, and cities in another country. For example, approximately 17% of the acidic deposition falling on Norway originated in Britain and 20% in Sweden came from eastern Europe.[5]

The U.S. EPA National Acid Precipitation Assessment Program (NAPAP) conducted intensive research during the 1980s and 1990s that resulted in the "Acidic Deposition: State of the Science and Technology" that was mandated by the Acid Precipitation Act of 1980.[6] NAPAP Reports to Congress have been developed in accordance with the 1990 amendment to the 1970 Clean Air Act and present the expected benefits of the Acid Deposition Control Program[6,7] http://www.nnic.noaa.gov/CENR/NAPAP/. Mandates include an annual 10 million ton or approximately 40% reduction in point-source SO_2 emissions below 1980 levels, with national emissions limit caps of 8.95 million tons from electric utility and 5.6 million tons from pointsource industrial emissions. A reduction in NO_x of about 2 million tons from 1980 levels has also been set as a goal; however, while NO_x has been on the decline since 1980,

projections estimate a rise in NO_x emissions after the year 2000. In 1980, the U.S. levels of SO_2 and NO_x emissions were 25.7 and 23.0 million tons, respectively.

Acidic deposition can impact buildings, sculptures, and monuments that are constructed using weatherable materials like limestone, marble, bronze, and galvanized steel,[7,8] http://www.nnic.noaa.gov/CENR/NAPAP/. While acid soil conditions are known to influence the growth of plants, agricultural impacts related to acidic deposition are of less concern due to the buffering capacity of these types of ecosystems.[2,5] When acidic substances are deposited in natural ecosystems, a number of adverse environmental effects are believed to occur, including damage to vegetation, particularly forests, and changes in soil and surface water chemistry.[9,10]

Sources and Distribution

Typical sources of acidic deposition include coal- and oil-burning electric power plants, automobiles, and large industrial operations (e.g., smelters). Once S and N gases enter the Earth's atmosphere they react very rapidly with moisture in the air to form sulfuric (H_2SO_4) and nitric (HNO_3) acids.[2,3] The pH of natural rainfall in equilibrium with atmospheric CO_2 is about 5.6; however, the pH of rainfall is less than 4.5 in many industrialized areas. The nature of acidic deposition is controlled largely by the geographic distribution of the sources of SO_2 and NO_x (Figure 1.1). In the midwestern and northeastern U.S., H_2SO_4 is the main source of acidity in precipitation because of the coal-burning electric utilities.[2] In the western U.S., HNO_3 is of more concern because utilities and industry burn coal with low S contents and populated areas are high sources of NO_x.[2]

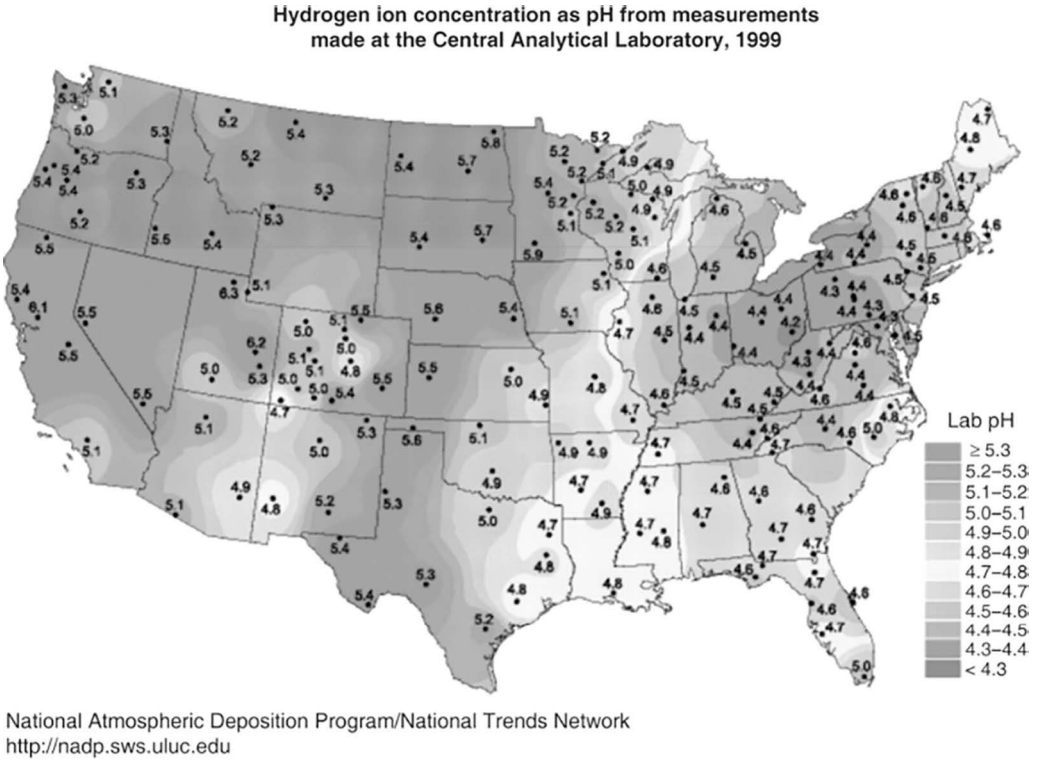

FIGURE 1.1 Acidic deposition across the U.S. during 1999.

Emissions of SO_2 and NO_x increased in the 20th century due to the accelerated industrialization in developed countries and antiquated processing practices in some undeveloped countries. However, there is some uncertainty as to the actual means by which acidic deposition affects our environment,[11,12] http://nadp.sws.uiuc.edu/isopleths/ maps 1999/. Chemical and biological evidence, however, indicates that atmospheric deposition of H_2SO_4 caused some New England lakes to decrease in alkalinity.[13,14] Many scientists are reluctant to over-generalize cause and effect relationships in an extremely complex environmental problem. Although, the National Acid Deposition Assessment Program has concluded there were definite consequences due to acidic deposition that warrant remediation[6,7] http://www.nnic.noaa.gov/CENR/NAPAP/. Since 1995, when the 1990 Clean Air Act Amendment's Title IV reduction in acidic deposition was implemented, SO_2 and NO_x emissions have, respectively, decreased and remained constant during the late 1990s.[4]

Both H_2SO_4 and HNO_3 are important components of acidic deposition, with volatile organic compounds and inorganic carbon also components of acidic deposition-related emissions. Pure water has a pH of 7.0, natural rainfall about 5.6, and severely acidic deposition less than 4.0. Uncontaminated rainwater should be pH 5.6 due to CO_2 chemistry and the formation of carbonic acid. The pH of most soils ranges from 3.0 to 8.0.[2] When acids are added to soils or waters, the decrease in pH that occurs depends greatly on the system's buffering capacity, the ability of a system to maintain its present pH by neutralizing added acidity. Clays, organic matter, oxides of Al and Fe, and Ca and Mg carbonates (limestones) are the components responsible for pH buffering in most soils. Acidic deposition, therefore, will have a greater impact on sandy, low organic matter soils than those higher in clay, organic matter, and carbonates. In fresh waters, the primary buffering mechanism is the reaction of dissolved bicarbonate ions with H^+ according to the following equation:

$$H^+ + HCO_3^- = H_2O + CO_2 \tag{1.1}$$

Human Health Effects

Few direct human health problems have been attributed to acidic deposition. Long-term exposure to acidic deposition precursor pollutants such as ozone (O_3) and NO_x, which are respiratory irritants, can cause pulmonary edema.[5,6] Sulfur dioxide (SO_2) is also a known respiratory irritant, but is generally absorbed high in the respiratory tract. Indirect human health effects due to acidic deposition are more important. Concerns center around contaminated drinking water supplies and consumption of fish that contain potential toxic metal levels. With increasing acidity (e.g., lower pH levels), metals such as mercury, aluminum, cadmium, lead, zinc, and copper become more bioavailable.[2] The greatest human health impact is due to the consumption of fish that bioaccumulate mercury; freshwater pike and trout have been shown to contain the highest average concentrations of mercury.[5,15] Therefore, the most susceptible individuals are those who live in an industrial area, have respiratory problems, drink water from a cistern, and consume a significant amount of freshwater fish.

A long-term urban concern is the possible impact of acidic deposition on surface-derived drinking water. Many municipalities make extensive use of lead and copper piping, which raises the question concerning human health effects related to the slow dissolution of some metals (lead, copper, zinc) from older plumbing materials when exposed to more acidic waters. Although metal toxicities due to acidic deposition impacts on drinking waters are rare, reductions in S and N fine particles based on Clean Air Act Amendments will result in annual public health benefits valued at $50 billion with reduced mortality, hospital admissions and emergency room visits.[16]

Structural Impacts

Different types of materials and cultural resources can be impacted by air pollutants. Although the actual corrosion rates for most metals have decreased since the 1930s, data from three U.S. sites indicate that acidic deposition may account for 31–78% of the dissolution of galvanized steel-and copper,[7,8]

http://www.nnic.noaa.gov/CENR/NAPAP/. In urban or industrial settings, increases in atmospheric acidity can dissolve carbonates (e.g., limestone, marble) in buildings and other structures. Deterioration of stone products by acidic deposition is caused by: 1) erosion and dissolution of materials and surface details; 2) alterations (blackening of stone surfaces); and 3) spalling (cracking and spalling of stone surfaces due to accumulations of alternation crusts.[8] Painted surfaces can be discolored or etched, and there may also be degradation of organic binders in paints.[8]

Ecosystem Impacts

It is important to examine the nature of acidity in soil, vegetation, and aquatic environments. Damage from acidification is often not directly due to the presence of excessive H^+, but is caused by changes in other elements. Examples include increased solubilization of metal ions such as Al^{3+} and some trace elements (e.g., Mn^{2+}, Pb^{2+}) that can be toxic to plants and animals, more rapid losses of basic cations (e.g., Ca^{2+}, Mg^{2+}), and the creation of unfavorable soil and aquatic environments for different fauna and flora.

Soils

Soil acidification is a natural process that occurs when precipitation exceeds evapotranspiration.[2] "Natural" rainfall is acidic (pH of ~ 5.6) and continuously adds a weak acid (H_2CO_3) to soils. This acidification results in a gradual leaching of basic cations (Ca^{2+} and Mg^{2+}) from the uppermost soil horizons, leaving Al^{3+} as the dominant cation that can react with water to produce H^+. Most of the acidity in soils between pH 4.0 and 7.5 is due to the hydrolysis of Al^{3+},[17,18] http://www.epa.gov/airmarkets/acidrain/effects/ index.html. Other acidifying processes include plant and microbial respiration that produces CO_2, mineralization and nitrification of organic N, and the oxidation of FeS_2 in soils disturbed by mining or drainage.[2] In extremely acidic soils (pH < 4.0), strong acids such as H_2SO_4 are a major component.

The degree of accelerated acidification depends both upon the buffering capacity of the soil and the use of the soil. Many of the areas subjected to the greatest amount of acidic deposition are also areas where considerable natural acidification occurs.[19] Forested soils in the northeastern U.S. are developed on highly acidic, sandy parent materials that have undergone tremendous changes in land use in the past 200 years. However, clear-cutting and burning by the first European settlers have been almost completely reversed and many areas are now totally reforested.[5] Soil organic matter that accumulated over time represents a natural source of acidity and buffering. Similarly, greater leaching or depletion of basic cations by plant uptake in increasingly reforested areas balances the significant inputs of these same cations in precipitation.[20,21] Acidic deposition affects forest soils more than agricultural or urban soils because the latter are routinely limed to neutralize acidity. Although it is possible to lime forest soils, which is done frequently in some European countries, the logistics and cost often preclude this except in areas severely impacted by acidic deposition.[5]

Excessively acidic soils are undesirable for several reasons. Direct phytotoxicity from soluble Al^{3+} or Mn^{2+} can occur and seriously injure plant roots, reduce plant growth, and increase plant susceptibility to pathogens.[21] The relationship between Al^{3+} toxicity and soil pH is complicated by the fact that in certain situations organic matter can form complexes with Al^{3+} that reduce its harmful effects on plants.[18] Acid soils are usually less fertile because of a lack of important basic cations such as K^+, Ca^{2+}, and Mg^{2+}. Leguminous plants may fix less N_2 under very acidic conditions due to reduced rhizobial activity and greater soil adsorption of Mo by clays and Al and Fe oxides.[2] Mineralization of N, P, and S can also be reduced because of the lower metabolic activity of bacteria. Many plants and microorganisms have adapted to very acidic conditions (e.g., pH < 5.0). Examples include ornamentals such as azaleas and rhododendrons and food crops such as cassava, tea, blueberries, and potatoes[5,22] In fact, considerable efforts in plant breeding and biotechnology are directed towards developing Al-and Mn-tolerant plants that can survive in highly acidic soils.

Agricultural Ecosystems

Acidic deposition contains N and S that are important plant nutrients. Therefore, foliar applications of acidic deposition at critical growth stages can be beneficial to plant development and reproduction. Generally, controlled experiments require the simulated acid rain to be pH 3.5 or less in order to produce injury to certain plants.[22] The amount of acidity needed to damage some plants is 100 times greater than natural rainfall. Crops that respond negatively in simulated acid rain studies include garden beets, broccoli, carrots, mustard greens, radishes, and pinto beans, with different effects for some cultivars. Positive responses to acid rain have been identified with alfalfa, tomato, green pepper, strawberry, corn, lettuce, and some pasture grass crops.

Agricultural lands are maintained at pH levels that are optimal for crop production. In most cases the ideal pH is around pH 6.0–7.0; however, pH levels of organic soils are usually maintained at closer to pH 5.0. Because agricultural soils are generally well buffered, the amount of acidity derived from atmospheric inputs is not sufficient to significantly alter the overall soil pH.[2] Nitrogen and S soil inputs from acidic deposition are beneficial, and with the reduction in S atmospheric levels mandated by 1990 amendments to the Clean Air Act, the S fertilizer market has grown. The amount of N added to agricultural ecosystems as acidic deposition is rather insignificant in relation to the 100–300kg N/ha/yr required of most agricultural crops.

Forest Ecosystems

Perhaps the most publicized issue related to acidic deposition has been widespread forest decline. For example, in Europe estimates suggest that as much as 35% of all forests have been affected.[23] Similarly, in the U.S. many important forest ranges such as the Adirondacks of New York, the Green Mountains of Vermont, and the Great Smoky Mountains in North Carolina have experienced sustained decreases in tree growth for several decades.[6] Conclusive evidence that forest decline or dieback is caused solely be acidic deposition is lacking and complicated by interactions with other environmental or biotic factors. However, NAPAP research[6] has confirmed that acidic deposition has contributed to a decline in high-elevation red spruce in the northeastern U.S. In addition, nitrogen saturation of forest ecosystems from atmospheric N deposition is believed to result in increased plant growth, which in turn increases water and nutrient use followed by deficiencies that can cause chlorosis and premature needle-drop as well as increased leaching of base cations from the soil.[24]

Acidic deposition on leaves may enter directly through plant stomates.[1,22] If the deposition is sufficiently acidic (pH ~ 3.0), damage can also occur to the waxy cuticle, increasing the potential for direct injury of exposed leaf mesophyll cells. Foliar lesions are one of the most common symptoms. Gaseous compounds such as SO_2 and SO_3 present in acidic mists or fogs can also enter leaves through the stomata, form H_2SO_4 upon reaction with H_2O in the cytoplasm, and disrupt many metabolic processes. Leaf and needle necrosis occurs when plants are exposed to high levels of SO_2 gas, possibly due to collapsed epidermal cells, eroded cuticles, loss of chloroplast integrity and decreased chlorophyll content, loosening of fibers in cell walls and reduced cell membrane integrity, and changes in osmotic potential that cause a decrease in cell turgor.

Root diseases may also increase in excessively acidic soils. In addition to the damages caused by exposure to H_2SO_4 and HNO_3, roots can be directly injured or their growth rates impaired by increased concentrations of soluble Al^{3+} and Mn^{2+} in the rhizosphere[2,25] http://nadp.sws.uiuc.edu. Changes in the amount and composition of these exudates can then alter the activity and population diversity of soilborne pathogens. The general tendency associated with increased root exudation is an enhancement in microbial populations due to an additional supply of carbon (energy). Chronic acidification can also alter nutrient availability and uptake patterns.[8,22]

Long-term studies in New England suggest acidic deposition has caused significant plant and soil leaching of base cations,[1,21] resulting in decreased growth of red spruce trees in the White Mountains.[6]

With reduction in about 80% of the airborne base cations, mainly Ca^{2+} but also Mg^{2+}, from 1950 levels, researchers suggest forest growth has slowed because soils are not capable of weathering at a rate that can replenish essential nutrients. In Germany, acidic deposition was implicated in the loss of soil Mg^{2+} as an accompanying cation associated with the downward leaching of SO_4^{2-}, which ultimately resulted in forest decline.[2] Several European countries have used helicopters to fertilize and lime forests.

Aquatic Ecosystems

Ecological damage to aquatic systems has occurred from acidic deposition. As with forests, a number of interrelated factors associated with acidic deposition are responsible for undesirable changes. Acidification of aquatic ecosystems is not new. Studies of lake sediments suggest that increased acidification began in the mid-1800s, although the process has clearly accelerated since the 1940s.[15] Current studies indicate there is significant S mineralization in forest soils impacted by acidic deposition and that the SO_4^{2-} levels in adjacent streams remain high, even though there has been a decrease in the amount of atmospheric-S deposition.[24]

Geology, soil properties, and land use are the main determinants of the effect of acidic deposition on aquatic chemistry and biota. Lakes and streams located in areas with calcareous geology resist acidification more than those in granitic and gneiss materials.[16] Soils developed from calcareous parent materials are generally deeper and more buffered than thin, acidic soils common to granitic areas.[2] Land management decisions also affect freshwater acidity. Forested watersheds tend to contribute more acidity than those dominated by meadows, pastures, and agronomic ecosystems.[8,14,20] Trees and other vegetation in forests are known to "scavenge" acidic compounds in fogs, mists, and atmospheric particulates. These acidic compounds are later deposited in forest soils when rainfall leaches forest vegetation surfaces. Rainfall below forest canopies (e.g., throughfall) is usually more acidic than ambient precipitation. Silvicultural operations that disturb soils in forests can increase acidity by stimulating the oxidization of organic N and S, and reduced S compounds such as FeS_2.[2]

A number of ecological problems arise when aquatic ecosystems are acidified below pH 5.0, and particularly below pH 4.0. Decreases in biodiversity and primary productivity of phytoplankton, zooplankton, and benthic invertebrates commonly occur.[15,16] Decreased rates of biological decomposition of organic matter have occasionally been reported, which can then lead to a reduced supply of nutrients.[20] Microbial communities may also change, with fungi predominating over bacteria. Proposed mechanisms to explain these ecological changes center around physiological stresses caused by exposure of biota to higher concentrations of Al^{3+}, Mn^{2+}, and H^+ and lower amounts of available Ca^{2+}.[15] One specific mechanism suggested involves the disruption of ion uptake and the ability of aquatic plants to regulate Na^+, K^+, and Ca^{2+} export and import from cells.

Acidic deposition is associated with declining aquatic vertebrate populations in acidified lakes and, under conditions of extreme acidity, of fish kills. In general, if the water pH remains above 5.0, few problems are observed; from pH 4.0 to 5.0 many fish are affected, and below pH 3.5 few fish can survive.[23] The major cause of fish kill is due to the direct toxic effect of Al^{3+}, which interferes with the role Ca^{2+} plays in maintaining gill permeability and respiration. Calcium has been shown to mitigate the effects of Al^{3+}, but in many acidic lakes the Ca^{2+} levels are inadequate to overcome Al^{3+} toxicity. Low pH values also disrupt the Na^+ status of blood plasma in fish. Under very acidic conditions, H^+ influx into gill membrane cells both stimulates excessive efflux of Na^+ and reduces influx of Na^+ into the cells. Excessive loss of Na^+ can cause mortality. Other indirect effects include reduced rates of reproduction, high rates of mortality early in life or in reproductive phases of adults, and migration of adults away from acidic areas.[16] Amphibians are affected in much the same manner as fish, although they are somewhat less sensitive to Al^{3+} toxicity. Birds and small mammals often have lower populations and lower reproductive rates in areas adjacent to acidified aquatic ecosystems. This may be due to a shortage of food due to smaller fish and insect populations or to physiological stresses caused by consuming organisms with high Al^{3+} concentrations.

Reducing Acidic Deposition Effects

Damage caused by acidic deposition will be difficult and extremely expensive to correct, which will depend on our ability to reduce S and N emissions. For example, society may have to burn less fossil fuel, use cleaner energy sources and/or design more efficient "scrubbers" to reduce S and N gas entering our atmosphere. Despite the firm conviction of most nations to reduce acidic deposition, it appears that the staggering costs of such actions will delay implementation of this approach for many years. The 1990 amendments to the Clean Air Act are expected to reduce acid-producing air pollutants from electric power plants. The 1990 amendments established emission allowances based on a utilities' historical fuel use and SO_2 emissions, with each allowance representing 1 ton of SO_2 that can be bought, sold or banked for future use,[4,6,7] http://www.nnic.noaa.gov/CENR/ NAPAP/. Short-term remedial actions for acidic deposition are available and have been successful in some ecosystems. Liming of lakes and some forests (also fertilization with trace elements and Mg^{2+}) has been practiced in European counties for over 50 years.[16,23] Hundreds of Swedish and Norwegian lakes have been successfully limed in the past 25 years. Lakes with short mean residence times for water retention may need annual or biannual liming; others may need to be limed every 5–10 years. Because vegetation in some forested ecosystems has adapted to acidic soils, liming (or over-liming) may result in an unpredictable and undesirable redistribution of plant species.

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2

Acid Rain and Precipitation Chemistry

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Introduction

Whereas an aqueous solution is acidic if its pH value is less than 7.0, acid rain refers to rainwater with pH less than 5.6. This is because, even without the presence of man-made pollutants, natural rainwater is already acidic as CO_2 in the atmosphere reacts with water to produce carbonic acid:

$$CO_2 + H_2O(1) \Leftrightarrow H_2CO_3(1) \tag{2.1}$$

The pH value of this solution is around 5.6. Even though the carbonic acid in rain is fairly dilute, it is sufficient to dissolve minerals in the Earth's crust, making them available to plant and animal life, yet not acidic enough to cause damage. Other atmospheric substances from volcanic eruptions, forest fires, and similar natural phenomena also contribute to the natural sources of acidity in rain. Still, even with the enormous amounts of acids created annually by nature, normal rainfall is able to assimilate them to the point where they cause little, if any, known damage.

However, large-scale human industrial activities have the potential of throwing off this acid balance, and converting natural and mildly acidic rain into precipitation with stronger acidity and far-reaching environmental effects. This is the root of the acid rain problem, which is not only of national but also international concern. This problem may have existed for more than 300 years starting at the time when the industrial revolution demanded a large scale burning of coal in which sulfur was a natural contaminant. Several English scholars, such as Robert Boyle in the 17th century and Robert A. Smith of the 19th century, wrote about the acids in air and rain; though there was a lack of appreciation of the magnitude of the problem at that time. Individual studies of the acid rain phenomenon in North America started in the 1920s, but true appreciation of the problem came only in the 1970s.

To address this problem, the U.S. Congress established the National Acid Precipitation Assessment Program (NAPAP) to study the causes and impacts of the acid deposition. This research established that acid rain does cause broad environmental and health effects; the pollution causing acid deposition can travel hundreds of miles, and electric power generation is mainly responsible for SO_2 (~65%) and

NO_x emissions (~30%). Subsequently, Congress created the Acid Rain Program under Title IV (Acid Deposition Control) of the 1990 Clean Air Act Amendments. Electric utilities are required to reduce their emissions of SO_2 and NO_x significantly. It was expected that by 2010 they would lower their emissions by 8.5 million tons compared to their 1980 levels. They also need to reduce their NO_x emissions by 2 million tons each year compared to the levels before the Clean Air Act Amendments.

However, it may not be adequate to solve the acid emission merely at the national level. With increasing industrialization of the Third World countries in the twenty-first century, one can expect great increase of the atmospheric loading of SO_2 and NO_x because many of these countries will burn fossil fuels to satisfy their energy needs. Clearly, some form of international agreements need to be forged to prevent serious environmental degradation due to acid rain.

The Chemistry of Acid Rain

Sulfuric acid (H_2SO_4) and nitric acid (HNO_3) are the two main acid species in the rain. The partitioning of acids in rain may be different in different places. In the United States, the partitioning is H_2SO_4 (~65%), HNO_3 (~30%), and others (~5%). While there are many possible chemicals that may serve as the precursors of acid rain, the two main substances are SO_2 and NO_x (and NO_x consists of NO and NO_2), and both are released to the atmosphere via the industrial combustion process. While power generation is the predominant source of these precursors, industrial boilers and automobiles also contribute substantially. When these precursors enter the cloud and precipitation systems, acid rain occurs. Figure 2.1 shows a schematic of the acid rain formation process.

Once airborne, these chemicals can be involved in milliards of chemicals reactions. The main paths that lead to acid rain formation are described as follows.

Sulfuric Acid

SO_2 is believed to be the main precursor for the formation of sulfuric acid drops. Its main source in the atmosphere is the combustion of fossil fuels. This is because sulfur is a natural contaminant in coal (especially the low grade ones) and oil. The following reactions are thought to occur when SO_2 is absorbed by a water drop (see e.g., Pruppacher and Klett,[1] Seinfeld and Pandis[2]):

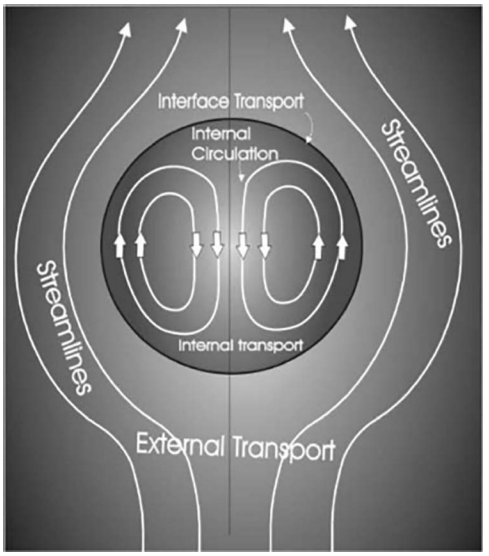

FIGURE 2.1 A schematic of the acid rain formation process.

$$SO_2(g) + H_2O(1) \Leftrightarrow SO_2 \bullet H_2O(1) \tag{2.2}$$

$$SO_2 \bullet H_2O \Leftrightarrow H^+ + HSO_3^- \tag{2.3}$$

$$HSO_3^- \Leftrightarrow H^+ + HSO_3^{-2} \tag{2.4}$$

$$SO_3^{-2} \overset{\text{oxidation}}{\rightarrow} SO_4^{-2} \tag{2.5}$$

The oxidant of the last step can be H_2O_2, O_3, OH, and others. There are still controversies about the identity of the oxidants.

Note that the equilibrium of the above reaction system is controlled by the pH values of the drop, and the presence of ammonia is often considered together with these reactions since it affects the pH of the drop. A detailed discussion of these reactions and their rates is given in Chapter 17 of Pruppacher and Klett.[1]

Nitric Acid

The main ingredients for the formation of nitric acid are NO and NO_2 (and are often combined into one category, NO_x). It is commonly thought that the main path of nitric acid found in clouds and raindrops is the formation of gas phase, HNO_3, followed by its uptake by liquid water. Although there are reactions of NO_x with liquid water that can lead to nitric acid, they are thought to be unimportant due to their slow reaction rates.

The main reaction for HNO_3 formation is

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{2.6}$$

where M can be any neutral molecule. NO can be converted to NO_2 by the following reaction:

$$2NO + O_2 \rightarrow 2NO_2 \tag{2.7}$$

Drop-Scale Transport Processes of Acid Rain

The chemical reactions described earlier must be considered together with the transport processes to obtain a quantitative picture of acid rain formation. This is especially true for SO_2 because absorption and reactions occur simultaneously. The convective transport influences the concentrations of different species and hence the reaction rates. Figure 2.2 illustrates these processes schematically. These include the following.

External Transport

This refers to the transport of SO_2 gas toward the surface of the drop. It is a convective diffusion process (both convective transport and diffusional transport occur) and is influenced by the flow fields created by the falling drop and atmospheric conditions (pressure and temperature).

Interfacial Transport

Once SO_2 is adsorbed on the surface of the drop, it must be transferred into the interior for further reactions to occur. The time for establishing phase equilibrium is controlled by Henry's law constant and mass accommodation coefficient of SO_2.

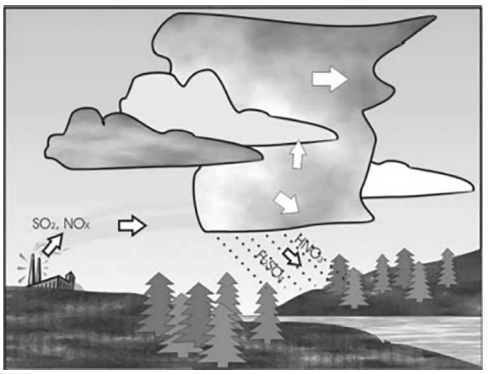

FIGURE 2.2 A schematic of the drop-scale transport process of sulfur species involved in the acid rain.

Internal Transport

In the interior of the drop, reactions[2] occur. At the same time, these species are transported by both diffusion and internal circulation. The latter is caused by the motion of the liquid drop in a viscous medium and can influence the production rates of these species (see Pruppacher and Klett[1]).

Environmental Factors Influencing the Acid Rain Formation and Impacts

Like many environmental hazards, the acid rain process is not driven by a few well-controlled physical and chemical processes, but involves complicated interactions between the chemicals and the environments they exist in. While the main ingredients of acid rain come from industrial activities, many other factors may influence the formation of acid rain and its impacts. The following are some of the most important.

Meteorological Factors

Acid rain occurs in the atmosphere and hence is greatly influenced by meteorological factors such as wind direction and speed, amount and frequency of precipitation, pressure patterns, and temperature. For example, in drier climates, such as the western United States, wind-blown alkaline dust is abundant and tends to neutralize the acidity in the rain. This is the *buffering effect* of the dust. In humid climates, like the Eastern Seaboard, less dust is in the air, and precipitation tends to be more acidic.

Seasonality may also influence acid precipitation. For example, while it is true that rain may be more acidic in summer (because of higher demands for energy and hence more fossil fuel used), the snow in winter can also pick up a substantial amount of acids. These snow-borne acids can accumulate throughout winter (if the weather is cold enough) and then are released in large doses during the spring thaw. These large doses of acid may have more significant effects during fish spawning or seed germination than the same doses at some less critical time.

Topography and Geology

The topography and geology of an area have marked influence on acid rain effects. Research from the U.S. EPA pointed out that areas most sensitive to acid precipitation are those with hard, crystalline bedrock and very thin surface soils. Here, in the absence of buffering properties of soil, acid rains will have direct access to surface waters and their delicate ecosystem. Areas with steep topography, such as

mountainous areas, generally have thin surface soils and hence are very vulnerable to acid rain. In contrast, a thick soil mantle or one with high buffering capacity, such as most flatlands, helps keep acid rain damage down.

The location of water bodies is also important. Headwater lakes and streams are especially vulnerable to acidification. Lake depth, the ratio of water-shed area to lake area, and the residence time in lakes all play a part in determining the consequent threat posed by acids. The transport mode of the acid (rains or runoff) also influences the effects.

Biota

Acid rain may fall on trees causing damages. The kinds of trees and plants in an area, their heights, and whether they are deciduous or evergreen may all play a part in the potential effects of acid rain. Without a dense leaf canopy, more acid may reach the Earth to impact on soil and water chemistries. Stresses on the plants will also affect the balance of local ecosystem. Additionally, the rate at which different types of plants carry on their normal life processes influences an area's ratio of precipitation to evaporation. In locales with high evaporation rates, acids will concentrate on leaf surfaces. Another factor is that leaf litter decomposition may add to the acidity of the soil due to normal biological actions.

References

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