

## Acid Rain: A Synopsis

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### Introduction

Acid rain is a simple term used to describe both dry and wet forms of acid deposition. These depositions originate from naturally occurring and anthropogenic (man-made) sources. At this point there is a lack of scientific understanding regarding how much man-made pollutants contribute to this complex issue.

Research programs conducted by the federal governments Interagency Task Force on Acid Precipitation are giving us greater understanding of acid rain. This research continues and programs are expanding but acid rain appears to be an issue that will require legislative action before there is full scientific conclusion on cause and effect.

### Historic Note

In 1857 Robert Angus Smith, an English chemist, presented the first detailed analysis documenting polluted precipitation and some of its harmful effects. Twenty years later Smith authored a comprehensive precipitation chemistry study which coined the phrase "Acid Rain."

### Chemistry of Acid Rain

The acidity-alkalinity of a water solution is measured by its pH. The pH scale ranges from 0 (extreme acidity) to 14 (extreme alkalinity) with the value of 7 being neutral. Pure water has a pH of 7 since the dissociation of water molecules into hydrogen (acid) and hydroxyl (alkaline) ions is very small. The scale is logarithmic and each pH unit represents a ten-fold change in the hydrogen/hydroxyl ion concentration.

What is acid rain? Acid rain defined is rain with a pH value lower than 5.6. The reason 5.6 is set as the determining pH is because carbon dioxide in balance with atmospheric moisture creates a carbonic acid solution with this value. Although rain is defined as acid below this level, naturally occurring rain may range down to 4.9 and up to 6.5. These values allow for additional acidity resulting from lightning or alkalinity resulting from atmospheric dust.<sup>2,5</sup> Figure 1 shows the pH scale with a list of values for commonly found substances.

		pH Scale <sup>1,2</sup>	
Extreme Alkalinity	14		
	13	13.0 Lye	
	12	12.0 Household ammonia	
	11		
	10		
	9	8 to 9 Soap	
	8	8.2 Baking soda	
	Neutral (Pure Water)	7	7.4 Human blood
		6	6.4 Milk
		5	5.0 Carrots
	4	4.6 Bananas	
	3	3.0 Apples	
	2	2.2 Vinegar	
	1	1.1 Stomach digestive acids	
Extreme Acidity	0		

FIGURE 1. pH scale with a list of values for commonly found substances.

Rain becomes acidic in several ways. Mainly this occurs from  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{SO}_2$  gases interacting with atmospheric moisture. Carbon dioxide is a naturally occurring gas composing .03 percent of the atmosphere and nitrogen oxides result from lightning and combustion processes. Most sulfur oxides are emitted from fossil fuel combustion at electric generation plants. Figure 2 shows how acids are formed from mixture of these gases with water.

#### Acid Formation

- A.  $\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$   
Carbon Dioxide + Water Yields Hydronium Ion and Bicarbonate
- B.  $2 \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$   
Nitrous Oxide + Oxygen Yields Nitrogen Dioxide  
 $3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO}$   
Nitrogen Dioxide + Water Yields Nitric Acid and Nitrous Oxide  
 $\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$   
Nitric Acid + Water Yields Hydronium Ion and Nitrate
- C.  $\text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_3$   
Sulfur Dioxide + Water Yields Sulfurous Acid  
 $2 \text{H}_2\text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{H}_2\text{SO}_4$   
Sulfurous Acid + Oxygen Yields Sulfuric Acid  
 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$   
Sulfuric Acid + Water Yields Hydronium Ion + Bisulfate

FIGURE 2. Acids formed from mixture of gases with water.

Certain biological filters affect the chemistry of rainwater from its initial point of contact near ground surface to watershed entrance. These filters include: a) the forest canopy, bushes, other plant leaves, and greenery which collect atmospheric dusts and add alkalinity to the water; b) the humus layer from decaying vegetation on the ground which adds acid concentrations; and c) the soil and rock layer containing alkaline minerals providing further alkalinity. These filters have had a constant effect on rainwater chemistry prior to man's influence, therefore any changes to watershed chemistry can be attributed to anthropogenic reasons.

Major ions influencing rains pH are sulfate  $\text{SO}_4^{--}$ , nitrate  $\text{NO}_3^-$ , chloride  $\text{Cl}^-$ , ammonium  $\text{NH}_4^+$ , calcium  $\text{Ca}^{++}$ , magnesium  $\text{Mg}^{++}$ , and potassium  $\text{K}^+$ . Exactly how much man contributes to excessive acidity through sulfate or nitrate deposition is yet undetermined. It is believed the contributions through power plants, industrial processes, and transportation sources are significant.

#### Affects of Acid Rain

Rain is the natural cleansing agent of the atmosphere. As it forms and falls to the earth it gathers with it various pollutants including those causing acid rain. Ultimately it is the land and watersheds which act as final pollution collectors.

Affects from acid rain are stated to include acidification of lakes resulting in reduced or total loss of fish population, corrosion of buildings and monuments, and reduced seed germination resulting in cuts in crop and timber production. Studies have been conducted showing that a pH of 5 is the level where fish life in general ceases to exist. Acid rain is also able to leach out metals from the soil including aluminum. Once soluble, aluminum can be toxic to aquatic wildlife by clogging the gills of fish and to vegetative species by causing a dehydration condition.

The Congressional Research Service (CRS) has completed a study listing possible effects from the impact of acid rain on aquatic biota. According to CRS; bacteria, algae, vegetative, invertebrate, amphibian, and fish populations shift away from acid sensitive species. More specifically, bacterial decomposition decreases, sensitive fish species die or experience reproductive failure and increases in aluminum make fish

more susceptible to death from exposure to acid conditions.<sup>4</sup> Ironically lakes adversely affected by acid conditions appear crystal clear due to decreases by living biota in them.

One of the major acid rain issues is degradation of the lakes and forests in the Adirondack Park system. This park, largest in America, covers six million acres, and is located in upper New York state. Some high elevation lakes and ponds in this park have acid values less than 5.0 pH<sup>2</sup> and hence do not support most form of fish life. Also, our northern neighbor Canada, is voicing strong concern over acid deposition originating from sources located in the United States but falling on its land and lakes. Recent studies, yet inconclusive, indicate that decline of some forest species from Maine to North Carolina are a result of the acid rain phenomenon.

### **What Should We Achieve with an Acid Rain Regulatory Program**

Rain in the northeastern part of the country has been averaging 4.2 pH. The National Academy of Sciences states that a target level of 4.5 pH is necessary to protect sensitive aquatic ecosystems from acid rain.<sup>6</sup> This pH level allows for natural causes of acidification and gives allowance for the fact that removal of all SO<sub>2</sub> and NO<sub>x</sub> emissions from man-made emission sources would be economically impossible.

The U.S. EPA has estimated that at the start of the 1970's, about 26 million tons of SO<sub>2</sub> and 17 million tons of NO<sub>x</sub> were emitted annually into the atmosphere of the U.S. Of these totals, about 16 million tons of the SO<sub>2</sub> (62 percent) and 5 million tons of the NO<sub>x</sub> (29 percent) were exhausted by fossil fuel burning electric generation plants.<sup>2</sup> In EPA's nationwide emissions report for 1982 power plant SO<sub>2</sub> and NO<sub>x</sub> emissions amounted to 17.5 million tons and 7.5 million tons respectively.<sup>10</sup>

To achieve the necessary reductions of acid rain it is suggested that anywhere from 3 to 12 million tons of SO<sub>2</sub> be removed yearly from power plant exhaust gases. A lesser degree of NO<sub>x</sub> removal is also suggested.

### **Control Methods**

Controlling acid rain means controlling SO<sub>2</sub> and NO<sub>x</sub> emissions. Controlling SO<sub>2</sub> emissions can include the following:

1. Coal washing—Sulfur in coal occurs primarily in two forms, organic and inorganic (pyritic). Organic sulfur, chemically bound to the coal, cannot be removed by physical cleaning. Pyritic sulfur composing up to 45 percent of the sulfur in coal is bound to iron and occurs as a separate particle. Up to 90 percent of the pyritic sulfur can be removed by washing thus yielding reductions of 10 to 40 percent of the total sulfur content.<sup>8</sup>
2. Using low sulfur coal for combustion—Coal generally ranges from 0.5 percent to 5 percent sulfur with western coal having a lower average sulfur content than midwestern coal. By midwestern standards locally mined coal is considered low sulfur when it is 2 percent or less. The lower the coals sulfur content the lower the generated emission level of SO<sub>2</sub>.
3. Exhaust gas scrubbers—Scrubbers are very expensive to install and operate but are effective for controlling SO<sub>2</sub>. All new coal-fired power plants are required to remove 90 percent of the SO<sub>2</sub> gases or control it to a level of 1.2 pounds per million Btu, whichever is stricter. Usually this means scrubber installation.

Controlling NO<sub>x</sub> can be through use of low NO<sub>x</sub> burners in power plants and industrial boilers, and through vehicle emission reductions which are now occurring from currently implemented programs.

Liming lakes has also been suggested as a control supplement and is reasonably cost-effective for regulating the pH of lakes.

### Control Proposals

Several legislative bills have been submitted for action on acid rain. The legislation ranges from a) reductions of 3 million tons of SO<sub>2</sub> from a 10-state area, b) 10 million tons of SO<sub>2</sub> from 31 states east of and touching the Mississippi with additional reductions of NO<sub>x</sub>, and c) 12 million tons of SO<sub>2</sub> from the 48 contiguous states with additional NO<sub>x</sub> reductions. Who funds the equipment needed to yield these reductions range from each state paying for its required equipment and associated reduction to a national tax on most forms of electric generation applied where needed for the program.

### Expense

SO<sub>2</sub> reductions are occurring as New Source Performance Standards for power plants take effect. NO<sub>x</sub> reductions are occurring from NSPS also, and as emission reductions from the newer auto fleet are realized. These reductions however are not happening quickly enough to abate the acid rain problem. Current lack of an effective plan for acid rain is due to: a) the lack of conclusive knowledge about environmental effects coupled with; b) the great expense involved to retrofit controls onto existing utility boilers.

To gain scientific understanding of this issue federal expenditures for acid rain research in fiscal year 1985 will double to \$55.5 million from the 1984 level. The Environmental Protection Agency will receive the bulk of this with a 124 percent funding increase to \$34.3 million.

Regarding expense of a control program the State of Indiana is used as an example for a cost estimate. In 1982 Indiana's total SO<sub>2</sub> emissions from stationary sources amounted to 1,694,000 tons with about 88 percent or 1,490,000 tons coming from power plants.<sup>3</sup> From an EPA survey of all coal burning public utilities in Indiana it was determined that retrofitting scrubbers to control SO<sub>2</sub> emissions would cost 1.85 billion dollars. Operation and maintenance costs for these would amount to another 355 million dollars yearly.<sup>9</sup> With this data an estimated expenditure of \$1,241 per ton of emissions would be required to retrofit scrubbers with an additional expenditure of \$238 per ton for yearly operation and maintenance.

To conform with acid rain control strategy, Robert McKnight, Chief Environmental Engineer at Indianapolis Power and Light, states local utilities electric rates could be up to 31 percent higher from the costs of controlling SO<sub>2</sub> emissions. This figure applies to legislation such as the Stafford bill which requires each state to pay for their own contributing share of emissions.<sup>7</sup> Another study conducted by the Congressional Office of Technology Assessment estimates utility rate increases ranging from 5 to 19 percent as applied to various utilities in affected states. Other studies show as low as a 2 percent increase in rates to customers based on a national tax to fund this program.

It should be understood that implementation of necessary acid rain control legislation for environmental protection could result in associated social problems in the form of: a) displacing jobs in the coal mining industry; and b) increased utility expenses to be shared by the poor and elderly. To minimize social disruption reasonable legislation must also account for job displacement protection and provide assistance to those less fortunate and unable to burden the extra expense of control. If these problems are dealt with fairly, society will surely gain from the benefits of protecting our buildings, monuments, lakes, forests, and aquatic wildlife.

### Conclusion

Our environment has improved since the institution of federal, state, and local

environmental management programs, however, some problems remain. Acid rain is one of these. Environmentalists, industry, and the public all agree a solution is necessary. Perspectives on the solution vary widely but the differences are healthy for from these varied views a balanced effective management program will develop. For now acid rain is long from solved but as research continues and comprehensive management programs evolve our society will come to benefit from protection against acid rain.

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