CHEMICAL COMPOSITION OF ACID PRECIPITATION IN CENTRAL TEXAS

HAL B. H. COOPER, Jr., Ph.D., Assistant Professor, University of Texas at Austin, Department of Civil Engineering, Environmental Health Engineering, Austin, Texas 78712; JERRY M. DEMO, B.S., Permits Engineer, Texas Air Control Board, 8520 Shoal Creek Blvd., Austin, Texas 78758; and JOSE A. LOPEZ, B.S., Research Assistant, University of Texas at Austin, Department of Civil Engineering, Environmental Health Engineering, Austin, Texas 78712.

ABSTRACT

Studies were undertaken to determine factors affecting composition of acidic precipitation formation in the Austin area of Central Texas. The study was initiated to determine background levels of acid and alkalinity producing constituents in an area with elevated natural dust levels from nearby limestone rock formations. Results showed normal rainfall pH values of 6.5 to 6.6 in the area, with extreme variations from 5.8 to 7.3. Significant calcium levels of 1 to 4 mg per liter were observed from probably natural origin which appeared to have a buffering effect on acidity. Significant sulfate and nitrate ion concentrations occurred during the early stages of rainfall where rainfall pH was dependent on calcium-sulfate ratio.

INTRODUCTION

The increasingly serious problems of availability of domestic petroleum energy resources is causing increasing interest in coal burning for electric power generation. It is estimated that the coal-fired generating capacity in the United States will increase from 166,000 megawatts in 1973 to over 400,000 megawatts by 1990. Coal fired generating capacity in the State of Texas is expected to increase from 1,100 megawatts to almost 17,000 megawatts by the year 1990. Major increases in oil-fired electric generating capacities in Texas are expected to occur from 900 megawatts in 1973 to above 24,000 megawatts by 1990 by replacement of natural gas as a boiler fuel.

The burning of coal and oil as boiler fuels for electric power generation and industrial process heating will result in major increases of sulfur oxides and nitrogen oxides emissions to the atmosphere. Sulfur oxides emissions on a worldwide basis are expected to increase from 47 million tons in 1968 to 94 million tons by 1980. Sulfur oxides emissions in the United States are projected to increase from 33 million tons in 1968 to 50 million tons by 1980, and nitrogen oxides emissions are projected to increase from the present 20 million to 30 million tons per year. The burning of coal and oil for electric power generation in Texas is expected to increase sulfur oxides emissions by more than one million tons per year by 1990.

The selective application of particulate controls on electric power plants in the eastern United States burning high sulfur coals has occurred simultaneously with the construction of tall stacks for dispersion of sulfur dioxide in ambient air without attempting to reduce the quantities emitted to the atmosphere. The result has been to minimize the ambient sulfur dioxide concentrations immediately downwind of these power plants but also to create the less obvious but insidious problem of acid rainfall formation at remote locations many miles away. This acid rainfall can create hazards in terms of forestry, agriculture, materials, aquatic life and humans through potential adverse effects.

BACKGROUND

The problem of acid rainfall formation appears to be associated with the presence of sulfur oxides and nitrogen oxides emitted to the atmosphere from combustion of fossil fuels. Acid rainfall was reported to be a problem in the city of Leeds, England by Crowther and Rustan (1911) who measured rain acidity levels equivalent to pH 3.2. Rainfall acidity values in some areas of Sweden and Norway have been reported from pH 3 to 5, with increasing acidity levels observed beginning in the early 1950's by Barrett and Brodin (1955).

Recent studies by Likens and Bormann (1972) (1974) indicate increasing rainfall acidity values in the northeastern United States over the past 20 years as compared to the rest of the country. Average rainfall pH's of 3 to 4 have been observed at several locations in the states of New York and New Hampshire, with extreme values measured as low as 2.1 in 1964 by Fisher et al. (1968). Rainfall acidity values were observed to increase beginning about 1950 even though total sulfur levels in the rainfall began to decrease, ostensibly because of the selective implementation of emission controls for alkaline particulate fly ash without simultaneous controls on acidic sulfur and nitrogen oxides on combustion sources.

Previous studies of rainfall acidity in a nonindustrialized area of northern Florida along the Gulf of Mexico by Brezonik (1968) indicated pH values ranging from 5.3 to 6.8 in 1967 and 1968. Previous studies by the Texas Air Control Board of rainfall acidity showed pH values of 6.0 in downtown Houston and 6.5 in Austin. Recent studies by the Clear Creek School District located between industrial areas along the Houston Ship Channel and in Texas City showed average rainfall pH values of 4.0 to 4.5. Extreme values as low as 3.5 were measured on two occasions, where it was desired to determine potential impacts on drinking water quality.

CHEMISTRY

The relative acidity or alkalinity of rainfall is affected by the presence of both acid-producing and alkali-producing constituents in rainfall. These constitutents may be present in either the gaseous or particulate forms and may be derived from either natural or manmade sources. In the absence of major manmade pollutants, raindrops falling through the atmosphere will reach an equilibrium with carbon dioxide which dissolves in water to produce the slightly acidic carbonic acid with an equilibrium pH of approximately 5.7.

The major constituent from manmade sources tending to produce acid rainfall is sulfur oxides emitted from combustion of coal or oil, where the amount released is directly proportional to the sulfur content of the fuel. The sulfur present in coal or oil is converted to sulfur dioxide during combustion, which can then be oxidized to form sulfuric acid either in the gaseous or liquid phase, as shown in Figure 1. The sulfuric acid formed either by hydrolysis of sulfur trioxide or oxidation of sulfurous acid can then react with the alkaline ammonia gas or calcium carbonate particulate matter to form ammonium sulfate or calcium sulfate, respectively.

Nitrogen oxides constitute an additional major source of rainfall acidity from combustion processes. Nitric oxide is formed at elevated temperatures by reaction of nitrogen and oxygen to produce nitric oxide, which can then be oxidized to form nitrogen dioxide in either the combustion zone or the atmosphere. The nitrogen dioxide can be hydrolized in the presence of water to form both nitrous and nitric acids. These acids can then react with either ammonia gas or calcium carbonate to form the respective ammonium or calcium nitrite or nitrate salts, as shown in Figure 1.

Other constituents present in the fuels can also affect the acidity levels of rainfall once the materials are emitted to the atmosphere. Chlorine and fluorine present in trace quantities of some coals react during combustion to produce their respective hydrochloric and

SULFUR OXIDES

$$S + O_2 \longrightarrow SO_2$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + \tfrac{1}{2}O_2 \xrightarrow{\text{Catalyst}} H_2SO_4$$

$$2SO_2 + O_2 \xrightarrow{\text{Catalyst}} 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O + CO_2$$

NITROGEN OXIDES

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$HNO_2 + NH_3 \longrightarrow NH_4NO_2$$

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

$$2HNO_2 + CaCO_3 \longrightarrow Ca(NO_2)_2 + H_2O + CO_2$$

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

Figure 1. Chemical Mechanisms of Acid Rainfall Formation in the Atmosphere

hydrofluoric acids. Trace metals present in coals such as iron, copper, manganese, vanadium and others can act as catalysts to promote the oxidation of sulfite to sulfate ion in solution, or of nitrite to nitrate ion. Other constituents present particularly in the fly ash released from combustion contain calcium, aluminium or silicon or other ions which are associated with the carbonate, silicate or oxide forms which can contribute to the alkalinity of rainfall. The ammonia present in the atmosphere from natural sources or from oil combustion can also act as a weak alkaline constituent.

METHODOLOGY

The purpose of the study was to determine background levels of rainfall acidity and factors affecting rainfall acidity in Austin, Texas in a city of about 300,000 population to provide a baseline for observing future changes. Existing rainfall chemical properties were measured in an area with little existing heavy industry, negligible sulfur oxides emission sources, and high natural background limestone (calcium carbonate) dust levels from adjacent deposits. The study was performed to obtain background information regarding rainfall composition affecting acidity prior to construction of a large coal-fired

power plant 35 miles southeast and upwind in the prevailing directions, and also prior to implementation of catalytic converter exhaust controls on new motor vehicles.

Rainfall collection stations were located at three points in Austin in a generally south-north line at a residence along Town Lake, atop the Civil Engineering Building at the University of Texas, and at the Texas Air Control Board. Sequential static units were used for collection of rainfall samples through funnels consecutively into 300 milliliter plastic collection bottles, as shown in Figure 2. Following

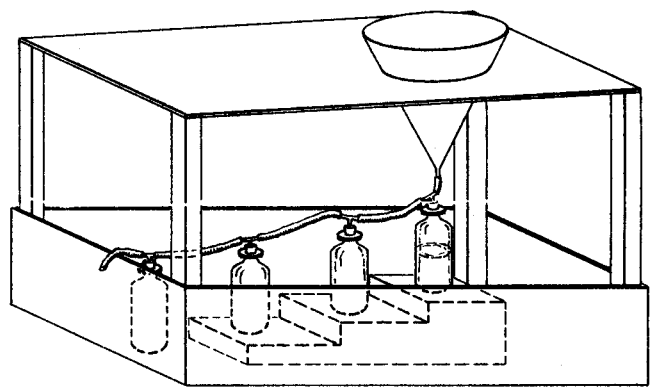

Figure 2. Sequential Rainfall Sample Collection Unit

collection, the rainfall samples were taken to the laboratory for subsequent chemical analyses. Collection bottles could also be removed for intermittent analysis of liquid pH.

Chemical measurements during the studies were made for liquid pH, total solids, total dissolved solids, sulfate ion, nitrate ion, nitrite ion, calcium ion and trace metals using established analytical techniques. The barium chloride turbidometric method was used for sulfate ion determination. While the reduction-diazotization method was used for nitrate and nitrite ion measurements. Calcium ion measurements were made by means of atomic absorption spectrophotometry while trace metal measurements were made using X-ray fluorescence.

RESULTS

Rainfall samples were collected during rainstorms in Austin, Texas on February 1-4, March 1-3 and April 28-29, 1975. An additional rain

sample was taken in Laredo, Texas on March 11-12, 1975 and a snow sample was collected in Austin, Texas on January 8, 1975.

Rainfall pH measurements were made periodically at the Town Lake sampling station during a prolonged four day rainstorm which began on January 31st and ended on February 4th of 1975. Initial rainfall pH values were about 6.6 at the start of the rain which gradually increased to 7.4 and then dropped dramatically to almost 5.7 during a heavy rain with a strong north wind. The rain pH then gradually increased to 6.6 over the next two days with a reduced rainfall intensity and a return to southerly winds, as shown in Figure 3. Soils to the

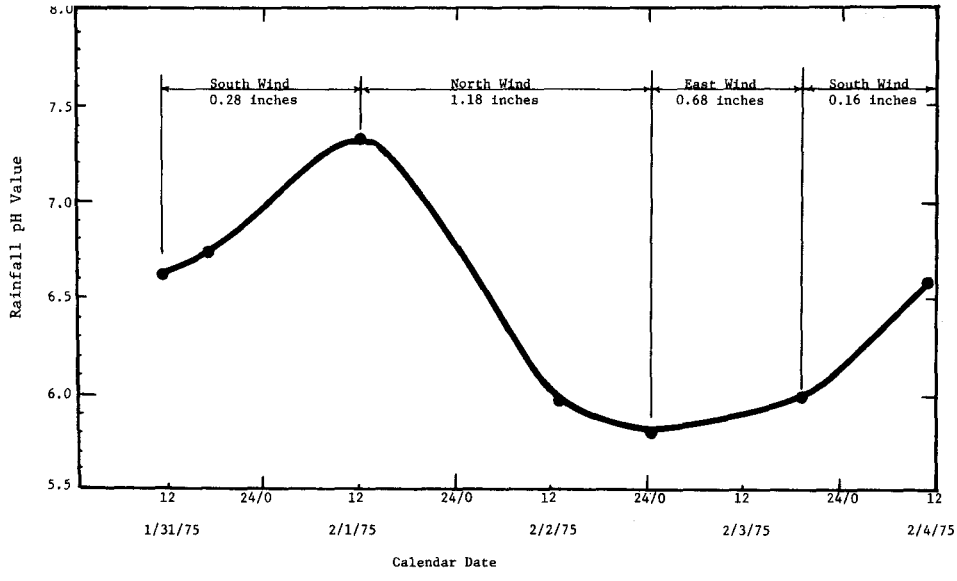

Figure 3. Variation of Rainfall pH during a Storm in Austin, Texas January 31 - February 4, 1975

South and West of the sampling location generally contained high calcium carbonate contents which probably increased the entrained limestone dust and resultant rainfall pH values.

The pH of the rainfall during a second storm on March 1-4, 1975 varied between 6.6 and 7.7. Samples taken at the University sampling station showed a decrease in pH from 6.6 to 5.9 during the course of a recent rainstorm on April 28-29, 1975 characterized by thunderstorms and medium rainfall intensity. An additional rainfall sample taken during a thunderstorm in Laredo, Texas indicated a pH value 6.66 while a snowfall sample taken in Austin showed a pH of 7.65.

A series of chemical analyses were made to characterize the chemical composition of rainfall samples taken during the February and March rainstorms. Sulfate ion levels observed during the February rainstorm generally decreased from 7.5 to 2.0 milligrams per liter during the storm as shown in Table I. Sulfate ion levels in the March rainstorm generally decreased from 12.5 to 3.0 milligrams per liter. The

TABLE 1

CHEMICAL COMPOSITION OF RAINFALL COLLECTED IN AUSTIN, TEXAS

January 31 - February 4, 1975

SAMPLE DATE	TIME INTERVAL	DISSOLVED SOLIDS mg/liter	TOTAL SOLIDS mg/liter	CALCIUM ION mg/liter	SULFATE ION mg/liter	NITRATE + NITRITE mg/liter
1/31/75	1030-1700	136.0	140.0	4.10	7.50	1.74
1/31/75	1700-2400	110.0	114.0	2.30	4.25	1.63
2/1/75	0000-0900	138.0	138.0	1.35	2.00	0.88
2/1/75	0900-2300	---	140.0	3.32	3.50	0.64
2/2/75	0100-1030	96.0	100.0	3.80	6.00	1.08
2/2/75	1100-2400	---	96.0	2.10	3.00	1.36
2/3/75	0030-1930	92.0	92.0	1.70	0.00	0.80
2/3/75	1930-0400 (2/3)	---	94.0	1.00	2.00	0.45
2/4/75	0400-1200	---	92.0	0.20	2.00	0.17
2/4/75	0400-1200	---	---	0.20	---	0.17

sulfate ion concentration in snow was 21.5 milligrams per liter as shown in Table II. This trend corresponded to the higher total solids level in snow of 210 milligrams per liter, which was significantly higher than the initial value of 140 milligrams per liter reported for the February rain.

The calcium ion concentrations in rain generally decreased from a maximum of 4.1 to a minimum of 0.2 milligrams per liter during the progress of the rainstorm on February 1-4, 1975. Significantly higher calcium levels were observed during the March rainstorm, which may have occurred because of the prolonged air stagnation period prior to the rain. A general decrease in pH of rainfall was observed during the progress of rains as the weight ratio of calcium-to-sulfate contents of rainfall decreased, as shown in Figure 4. These results showed that decreases in the amount of available calcium associated with the alkaline calcium carbonate in relation to the sulfate content of rainfall caused a decrease in the pH.

TABLE 2

CHEMICAL COMPOSITION OF RAIN COLLECTED IN AUSTIN, TEXAS

March 1-4, 1975

SAMPLE	LIQUID pH	TOTAL SOLIDS mg/liter	CALCIUM ION mg/liter	SULFATE ION mg/liter	NITRATE + NITRITE mg/liter
1A	7.72	206	15.0	12.5	1.28
2A	7.17	100	4.5	3.0	0.44
3A	—	96	3.4	—	—
1B	—	—	8.7	8.5	2.54
2B	7.52	138	10.5	3.5	1.12
3B	—	92	2.5	3.5	0.36
1C	6.69	—	—	4.0	0.84
1D	6.65	—	—	—	—
Laredo	6.66	—	—	5.0	0.00
Snow	7.65	210.0	11.0	21.5	2.52

Values for total nitrite plus nitrate content of rainfall decreased from 1.74 to 0.17 milligrams per liter during the February

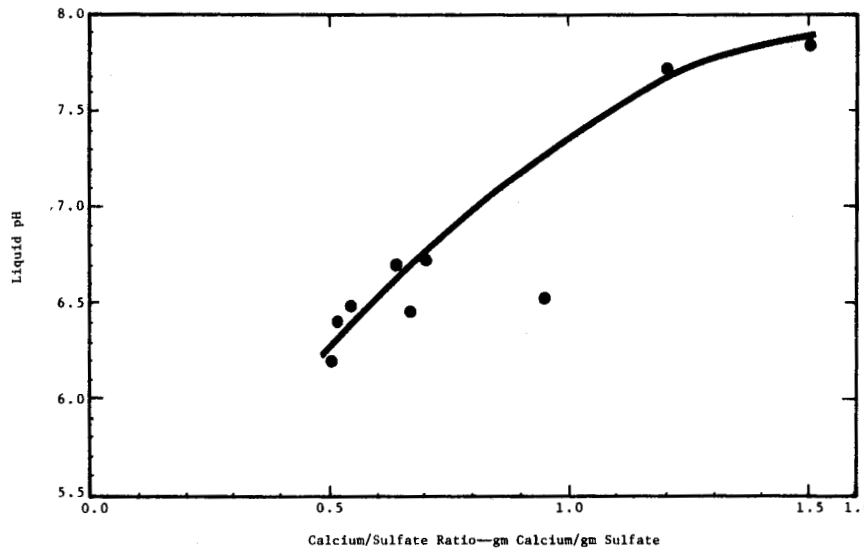

Figure 4. Effect of Calcium/Sulfate Concentration on Final Rainfall pH Value.

rainstorm as the nitrogen was gradually removed from the atmosphere, with a similar trend noted during the March rain. Further analyses showed that the major portion of the nitrogen was present in the nitrate ion form, with only a residual 0.1 milligrams per liter present in the nitrite ion form as shown in Table III. The nitrate ion is

TABLE 3

NITRITE AND NITRATE ION CONTENTS OF RAINFALL

IN AUSTIN, FEBRUARY 1-4, 1975

RAIN SAMPLE	Ionic Concentration—mg/liter		
	NO_2^-	NO_3^-	$NO_2^- + NO_3^-$
1A	0.10	1.80	1.90
4A	0.10	0.70	0.80
1B	0.10	1.10	1.20
4B	0.10	0.35	0.45
1C	0.10	0.00	0.10
2C	0.10	0.00	0.10

significant not only for acid rainfall formation, but also as a nutrient for algae and for soils, while the nitrite ion is significant in terms of potential oxygen demands in receiving waters.

A limited number of measurements have been made of the trace metal contents of rainfall samples using both atomic absorption spectrophotometry and X-ray fluorescence techniques. Analyses for calcium using cationic and anionic membrane ion exchange filters showed that materials tended to leach from the cationic filter and tended to be uncollected with the anionic filter. It was noted that small amounts of lead and bromine from automobile exhaust were detected, as well as trace quantities of vanadium, arsenic, copper, iron, potassium and zinc, as shown in Table IV. Additional work is necessary to evaluate the potential suitability of X-ray fluorescence for trace metal analyses in rainfall.

TABLE 4

COMPOSITION OF AUSTIN RAINFALL ON SAMPLE 1A

February 1-4, 1975

	METAL COMPOSITION mg/liter		
METAL	ATOMIC ABSORPTION	X-RAY CATIONIC	X-RAY ANIONIC
Calcium	2.72	2.850	0.042
Arsenic	——	——	0.004
Copper	——	——	0.002
Bromine	——	——	0.008
Iron	——	0.060	0.083
Lead	——	0.016	0.004
Potassium	——	0.230	0.054
Vanadium	——	——	0.002
Zinc	——	0.190	0.003

CONCLUSIONS

Existing rainfall acidity levels in Austin, Texas were determined through a series of measurements taken during the period January-April, 1975 to determine background levels in an area removed from major industrial activity. Results showed rainfall pH values to vary between 5.7 and 7.7 with average values of 6.6, where the pH tended to decrease during the progress of rainstorms as the alkaline calcium carbonate-bearing particulate materials were gradually removed. Sulfate ion levels in rain and snow ranged from 2.0 to 21.5 milligrams per liter while nitrate levels ranged from 0.2 to 2.5 milligrams per liter. Small quantities of lead and bromine from automobile exhausts, plus vanadium and other trace metals were also noted in the rain.

A possible solution to the problem of acid rainfall lies in the removal of sulfur dioxide from flue gas streams through regenerative emission control systems followed by conversion to liquid sulfur dioxide, sulfuric acid or elemental sulfur. The sulfur byproducts could then be transported from surplus generation points in the eastern United States by railroad to arid areas of the western United States. The sulfur byproducts could be added as sulfuric acid or sulfurous acid either through irrigation water or directly to these alkaline soils as neutralization agents to enhance agricultural productivity in these

areas. Recovery of the sulfur dioxide as elemental sulfur is indicated to minimize the amounts of material moved, and to enable the sulfur to be loaded into the same hopper cars used for the shipment of coal to be returned by unit trains to points adjacent to mining areas.

ACKNOWLEDGEMENT

The authors are indebted to the Bureau of Engineering Research at the University of Texas at Austin and the Texas Air Control Board for their support of the present research project.

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