CHEMICAL COMPOSITION OF ACID PRECIPITATION IN CENTRAL TEXAS

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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 Ca levels of 1 to 4 mg l\(^{-1}\) 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.

1. Introduction

The increasingly serious problems of availability of domestic petroleum energy resources are 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 MW in 1973 to over 400,000 MW by 1990. Coal-fired generating capacity in the State of Texas is expected to increase from 1100 MW to almost 17,000 MW by the year 1990. Major increases in oil-fired electric generating capacities in Texas are expected to occur from 900 MW in 1973 to above 4,000 MW 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 × 10\(^6\) t n 1968 to 94 × 10\(^6\) t by 1980. Sulfur oxides emissions in the United States are projected to increase from 33 × 10\(^6\) t in 1968 to 50 × 10\(^6\) t by 1980, and nitrogen oxides emissions are projected to increase from the present 20 × 10\(^6\) t to 30 × 10\(^6\) t yr\(^{-1}\). The burning of coal and oil for electric power generation in Texas is expected to increase sulfur oxides emissions by more than 3 × 10\(^6\) t yr\(^{-1}\) 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 SO\(_2\) in ambient air without attempting to reduce the quantities emitted to the atmosphere. The result has been to minimize the ambient SO\(_2\) 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.

2. 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 (1974) and Likens et al. (1972) indicate increasing rainfall acidity values in the northeastern United States over the past 20 yr 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 et al. (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.

3. Chemistry

The relative acidity or alkalinity of rainfall is affected by the presence of both acid-producing and alkali-producing constituents in rainfall. These constituents 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 CO₂ 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 S content of the fuel. The S present in coal or oil is