

EVIDENCE FOR MULTIPLE HYDROGEN-ION DONOR SYSTEMS IN RAIN¹

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ABSTRACT

An integrated analytical system consisting of combined scanning electron microscopy and x-ray analysis, atomic absorption, colorimetry and coulometry was used to study rain water chemistry. The coulometry facilitated the determination in molarities of strong and non-volatile and volatile weak acids. The pH of individual rains in St. Paul - Minneapolis, Minnesota ranged from 4.0 to 5.65 during the summer of 1974. Samples of a given rain from different sites had different qualitative and quantitative bases for the measured pH. Increase in strong acid concentrations with a decrease in pH was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased with an increase in the acidity. Studies conducted on Twin Cities rain samples indicated that the total salt content expressed from the electrical conductivity could not be accounted for by the total concentrations of individual metals quantified (Fe, Pb, Zn, Mn, Cu, Cr, Cd, Ca, Mg, Na, and K). In addition, no correlation could be shown between the contents of SO_4^- , NO_3^- , Cl_2^- & PO_4^- and the observed changes in pH.

INTRODUCTION

Fall out of acidic rain may be a threat to the regional environment. Rainfall with a pH as low as 2.8 and 2.1 has been reported from Sweden (Odén, 1968) and the United States (Likens and Bormann, 1974) respectively.

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Barrett and Brodin (1955) stated that since SO_2 is a major constituent of atmospheric pollution, H_2SO_4 is the most likely cause for the acidity of rain water. Since then, almost all of the published reports are based on correlations between total sulfate and pH (Pearson and Fisher, 1971). Measurements of total sulfates do not differentiate the levels and extent to which sulfate is present in the particulate fraction, soluble fraction, as salts and as acid *per se*. Similar considerations are also important in the case of nitrate (Pearson and Fisher, 1971) and chloride (ref. Junge, 1963) and their status as HNO_3 and HCl respectively. Furthermore, pH measurements do not indicate the parent species for the hydrogen ions. In general, our current knowledge of the chemistry of rain water is inadequate.

In this paper we report the results of some of our efforts to understand the chemistry of rain water in the St. Paul - Minneapolis, Minnesota area and the origin of its acidity, as a prelude to the study and interpretation of acidic rain effects on Minnesota vegetation.

MATERIALS AND METHODS

Approximately 250 ml of rain water were sampled from individual rainfalls at several locations in the St. Paul-Minneapolis area in the U.S.A. Sampling was performed manually at approximately 5-6 ft. from the ground, away from trees, buildings, etc. Sampling was started from the time the first rain droplets fell on the ground and was terminated after approximately 30 minutes. Samples were collected in FEP-TEP teflon (DuPont Co. U.S.A.) trays and were immediately transferred to screw cap bottles made of TEP teflon. Precaution was taken to prevent any dead space between the sample and the cap of the bottle. Samples were frozen as quickly as possible in a conventional freezer. At the time of analysis, samples were allowed to thaw and equilibrate to the room temperature (20 C) without opening the bottle.

The analytical techniques used, along with their application, are summarized in Table I. For determining the morphology and gross composition of the inorganic particulate matter in each sample, 10 ml of the rain water were filtered through 0.22 μ Millipore (Millipore Corp. U.S.A.) or Nuclepore (Sargent Welch & Co., U.S.A.) filter. After drying the filter in a vacuum, discs were punched at random, mounted on scanning electron microscope (SEM) stubs, carbon coated and viewed under a Cambridge SEM at different magnifications. Whenever the gross inorganic composition was to be determined, the particle was bombarded for approximately 2 min with an energy beam from the internal electron source and the qualitative, relative composition was identified by a precalibrated x-ray analyzer.

TABLE 1

Some Techniques and Their Application in
Rainwater Analysis

| Technique | Description of its use |
|--------------------------------------|---|
| Coulometry | Quantification in molarities (M) of: 1) non-volatile strong acid, 2) non-volatile weak acid, and 3) volatile weak acid. |
| Scanning E.M. + x-ray analysis | Morphology and gross qualitative inorganic composition of particulate matter. |
| Atomic Absorption | Quantification of metallic components Eg: Ca, Mg, Na, K, Fe, Zn, Cu, Mn, Pb, Cd etc. |
| Colorimetry + Specific ion electrode | Quantification of SO ₄ , Cl, NO ₃ , NO ₂ , NH ₄ , PO ₄ , F, etc. |

Concentrations in molarities of different acids in the rain samples were determined by coulometry. The coulometric unit consists of a constant current source, a measuring cell located on a magnetic stirrer and a potentiometer (modified pH meter) with a four digit visual read out. Based on the relationship between Ψ (a function of the electromotive force) and time in seconds (t) in two portions of the same rain sample, with and without volatiles, the molarities of non-volatile strong, and non-volatile and volatile weak acids were calculated (Krupa et al. 1974). When a sample was to be freed of volatiles, the solution was bubbled vigorously with N₂ for 30 minutes with simultaneous stirring and kept under a blanket of N₂ throughout the analysis.

Quantification of the cations and NH₄⁺ & anions were performed according to the conventional procedures using a Perkin-Elmer (U.S.A.) Model 330 atomic absorption unit and Technicon (U.S.A.) model II Auto-analyzer respectively.

RESULTS AND DISCUSSION

The pH of individual rains varied from 4.00 to 5.65 during the summer of 1974. Inorganic and organic particulate matter ranged in the samples at approximate ratios of 8 : 2 to 5 : 5. In the analysis of

Si > Al > Fe > K > S,Ca > Ti > P > Cl,F

Coulometric data on samples collected at five different sites during a representative rain event are shown in Figure 2. Strong acid(s)

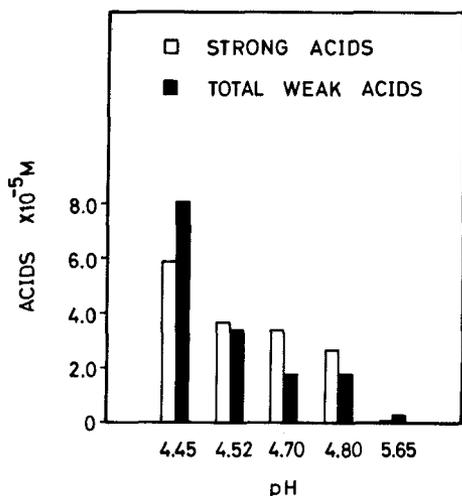


Figure 2. Relationships between pH and strong and weak acids in rain. Acid concentrations expressed as molarities.

concentration in the rain samples ranged from 0.0 to 5.89×10^{-5} M. There was an increase in the concentration of the strong acid component with a decrease in pH. However, this was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased (0.22 to 8.01×10^{-5} M) with an increase in the acidity.

The strong acid component may consist of different combinations of H_2SO_4 , HNO_3 , HCl and possibly dithionite. Figures 3, 4, and 5 illustrate the relationships between pH and SO_4^{2-} , NO_3^- and Cl^- when they exist as their corresponding acids and when each acts as the sole hydrogen ion donor. These values are based on known dissociation rates in aqueous systems. Barium chloride precipitable sulfur content (expressed as sulfate units) ranged in the rain samples from 1.2 mg/l to 2.4 mg/l. There was no correlation between the changes in the strong acid concentration and SO_4^{2-} levels (Figure 6). Patterns of change in NO_3^- concentration paralleled the SO_4^{2-} change in relation to pH. One of the most effective methods of SO_2 oxidation and neutralization is considered to be the " SO_2 - NH_3 - H_2O " system (Scott and Hobbs, 1967; ref. Krupa and Wood, 1974). NH_4 -N content in our samples ranged from 0.7 mg/l to 0.82 mg/l. No definite correlations could be found when ratios between $(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-)$ and NH_4^+ or ratios between SO_4^{2-} and NH_4^+ were plotted against pH (Figure 7). pH of rain samples varied irrespective of the calculated levels of NH_3 neutralization. Inorganic acid forming groups other than SO_4^{2-} varied in their concentration as

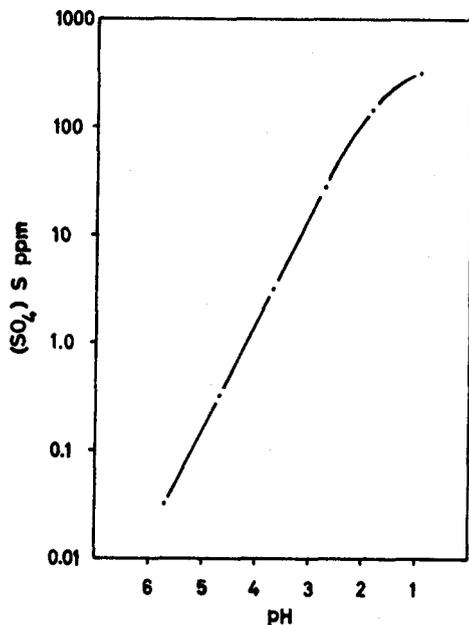


Figure 3. Relationship between pH and $\text{SO}_4\text{-S}$ based on the values for the two step dissociation of H_2SO_4 . $\text{SO}_4\text{-S}$ should be multiplied by 3 to obtain SO_4 values.

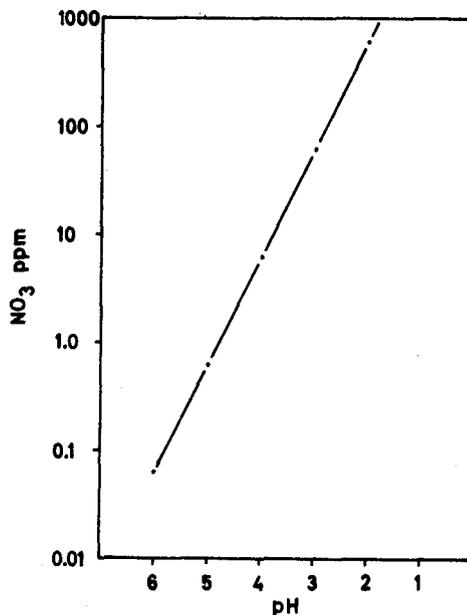


Figure 4. Relationship between pH and NO_3 based on the single step dissociation of HNO_3 .

follows: $\text{NO}_3\text{-N}$ - 0.063 mg/l to 0.450 mg/l; Cl - 0.10 mg/l to 0.60 mg/l; and $\text{PO}_4\text{-P}$ - 0.002 mg/l to 0.009 mg/l.

Approximate total salt concentration expressed from electrical conductivity measurements (3.47 mg/l to 11.10 mg/l) could not be accounted by the total concentration of the individual cations quantified by atomic absorption (Table 2).

As mentioned previously the weak acid component also increased with a decrease in pH. Figure 8 illustrates the relationship between non-volatile and volatile weak acids and pH of our rain samples. It is not clear at this time as to what extent the volatile acid component is constituted by $\text{CO}_2\text{-H}_2\text{O-H}_2\text{CO}_3\text{-HCO}_3$ system. The $\text{CO}_2\text{-H}_2\text{O}$ system can be influenced by the SO_2 dissolved species, HSO_3^- .

The aforementioned results demonstrate a multiple hydrogen-ion donor system in rain. These includes: 1) a strong acid component (H_2SO_4 , HNO_3 , HCl , and possibly dithionate); 2, a non-volatile weak acid component (HF , organic acids, hydrolysable salts etc.); and 3) a

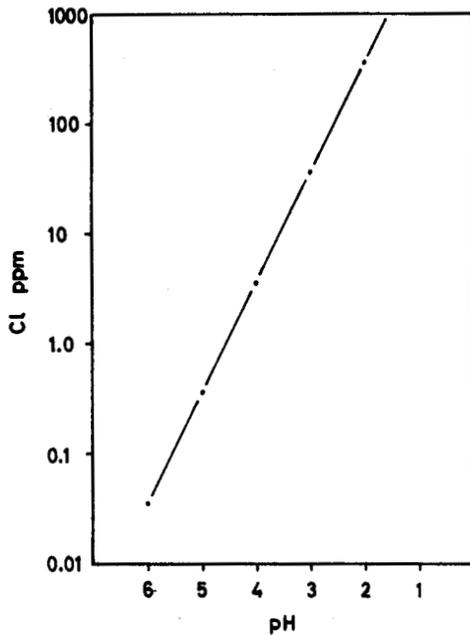


Figure 5. Relationship between pH and Cl based on the single step dissociation of HCl.

volatile weak acid component ($\text{CO}_2\text{-H}_2\text{O}$ system and unknowns). Sulfur in the atmosphere may exist in several different forms: SO_2 , SO_3 , SO_4 ,

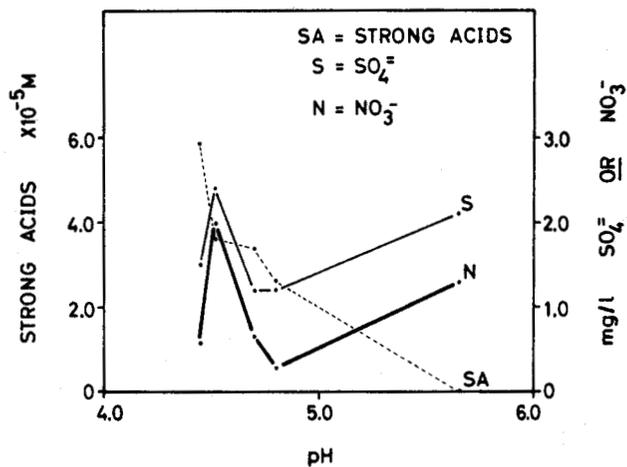


Figure 6. Relationship between pH and 1) molarities of strong acids, 2) SO_4^{2-} concentrations, and 3) NO_3^- concentrations in rain samples.

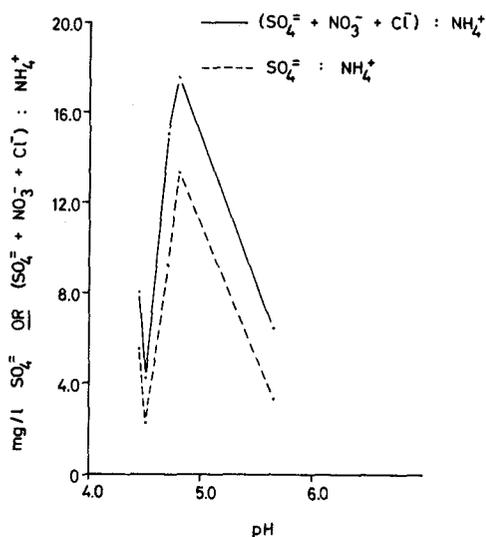


Figure 7. Relationship between pH and ratios of (SO₄²⁻ + NO₃⁻ + Cl⁻) and NH₄⁺ or ratios of SO₄²⁻ and NH₄⁺. Ratios calculated on the basis of mg/l of different components in rain.

TABLE 2

Metallic components in the same rain collected at
different locations in the Twin Cities area

Date of collection: June 6, 1974

| Sampling Location | Concentration in ppm | | | | | | | | | | |
|----------------------|----------------------|------|-------|-------|-------|-------|------|-------|-------|------|------|
| | Cu | Fe | MN | Zn | Cd | Cr | Pb | Mg | Ca | Na | K |
| Golden Valley | <0.01 | <0.1 | <0.01 | 0.02 | <0.02 | <0.02 | <0.2 | 0.016 | 0.055 | 0.03 | 0.03 |
| Mound | <0.01 | <0.1 | <0.01 | <0.02 | <0.02 | <0.02 | <0.2 | 0.053 | 0.529 | 0.04 | 0.11 |
| Delaware Ave. | <0.01 | <0.1 | <0.01 | 0.02 | <0.02 | <0.02 | <0.2 | 0.011 | 0.115 | 0.10 | 0.06 |
| N.E. University Ave. | <0.01 | <0.1 | <0.01 | <0.02 | <0.02 | <0.02 | <0.2 | 0.012 | 0.020 | 0.05 | 0.07 |
| Jonathan | <0.01 | <0.1 | <0.01 | <0.02 | <0.02 | <0.02 | <0.2 | 0.203 | 1.23 | 0.38 | 0.23 |

S₂O₅, S₂O₆, H₂S, dithionates, mercaptans, thionyls, (NH₄)₂SO₄, metallic salts, H₂SO₄ etc. Components such as organic acids form weak acids and may be part of the non-volatile weak acid component. Our results also show that samples of a given rain from different sites have different qualitative and quantitative bases for the measured pH. Semonin (1973) was unable to find correlations between point sources and pH of rain in the St. Louis, Missouri area and found that pH varied widely during the same rain at different sampling sites.

These considerations are important with reference to any direct vegetational effects. Shriner (1974) was able to demonstrate adverse effects on terrestrial vegetation by subjecting plants to pH 3.2 H₂SO₄ simulated to fall as rain. While acidity can have influence on plants through nutrient leaching etc., more recent evidence by Wood and

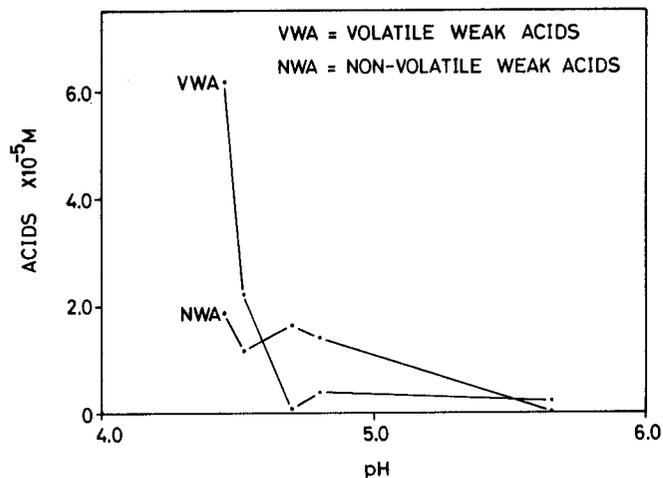


Figure 8. Relationship between pH and molarities of non-volatile and volatile weak acids in rain.

Pennypacker (1975) indicates that anions may play an important role in direct effects on foliage. The chemistry of rain in a given geographic region should be evaluated on per rain basis as a prelude to vegetational studies.

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