CHEMICAL STABILITY OF WET-DEPOSITION SAMPLES SUBSAMPLED DAILY FOR ONE WEEK

By Timothy C. Willoughby, LeRoy J. Schroder, and Randolph B. See

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MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Chief, Branch of Quality Assurance
U.S. Geological Survey
Box 25046, Mail Stop 401
Federal Center
Denver, CO 80225-0046

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CONVERSION FACTORS

Metric units (International System) used in this report may be converted to inch-pound units by using the following conversion factors:

Multiply metric unit	*By*	*To obtain inch-pound unit*
millimeter (mm)	0.0394	inch
gram (g)	0.0353	ounce
liter (L)	1.057	quart, liquid
micrometer (μm)	0.00039	inch
milligram (mg)	0.000035	ounce
milliliter (mL)	0.0338	ounce, fluid
microliter (μL)	0.0000338	ounce, fluid

Temperature can be converted from degree Celsius (°C) to degrees Fahrenheit (°F) by using the following equation:

$$°F=9/5(°C)+32$$

The following terms and abbreviations also are used in this report:

Megohm per centimeter (MΩ/cm) is equal to 1 × 10^6 ohms per centimeter.
microequivalents per bucket (μequiv./bucket)

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ABSTRACT

During 1988, the U.S. Geological Survey examined the chemical changes that occur in wet-deposition samples stored in a collector for one week. Samples from ten storms that resulted in 1.3 millimeters or more of precipitation were collected in a wet-only collector using 13-liter polyethylene buckets. About 25 milliliters of the sample was removed daily from the bucket and filtered for each subsampling. After the pH and specific conductance for each daily subsample was determined, the remainder of the sample was preserved for ion chromatography and flame atomic absorption spectrometry or flame atomic emission spectrometry. Chloride, nitrate, and sulfate concentrations were determined by ion chromatography. Calcium concentrations were determined by flame atomic emission spectrometry, and magnesium, sodium, and potassium concentrations were determined by flame atomic absorption spectrometry. The subsamples were chilled at 4 degrees Celsius until all the subsamples for an individual storm were removed. All subsamples from an individual storm were then analyzed.

A Kendall's estimator was used to estimate the change in concentration versus the time the sample remained in the collection buckets for each analyte and a non-parametric regression equation was determined. A Kendall's tau measure of rank correlation was then used to determine if any statistically significant correlations existed between the analyte concentrations and the length of time the sample remained in the collection bucket. All of the analytes had positive slopes except hydrogen ion and specific conductance indicating increases in concentration. Only calcium and hydrogen ion had statistically significant correlations at a significance level of 0.05.

INTRODUCTION

Background

For the past decade, the acidity of wet deposition and the long-term effects it has on the environment has been of interest to scientific, environmental, and government organizations. Several programs established in the United States routinely collect, analyze, and monitor wet deposition. There are difficulties related to the collection of wet deposition; some of these are: (1) Measuring the effect of environmental conditions on sample chemistry, (2) choosing the most suitable methods to collect samples, (3) choosing suitable material for the construction of the sample collection vessels, and (4) defining the appropriate length of time between sample collections. Galloway and Likens (1976) concluded that polyethylene vessels were the best type for the collection of inorganic constituents and recommended using wet-only collectors. Peden and Skowron, 1978, examined the stability of major inorganic constituents in precipitation samples collected using various types of collection vessels and varying the time the sample remained in the collection vessel for as long as 6 weeks. Peden and Skowron determined that wet-only collectors were preferable for the collection of wet deposition over bulk collectors. Filtering the samples as soon as possible after sample collection resulted in the greatest assurance of retaining the ionic integrity of the collected samples.

The acid rain quality-assurance project of the U.S. Geological Survey is responsible for external quality assurance for the National Atmospheric Deposition Program (NADP) established in 1977 and the National Trends Network (NTN) established in 1983 (Schroder and Malo, 1984). The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) collects samples at more than 200 sites on a weekly basis, using 13-L polyethylene collection buckets and wet-only Aerochem Metrics[1] collectors (National Atmospheric Deposition Program, 1984).

Purpose and Scope

The U.S. Geological Survey studied the effects of environmental conditions on the sample chemistry for the time that the samples remained in the polyethylene buckets. To evaluate these effects, subsamples were removed each day for as long as 7 days following a sample collection to observe any changes in hydrogen ion, calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate concentrations and specific conductance.

Description of Site

The sampling site is in an urban environment in a northwest suburb of the Denver metropolitan area. The site, about 75 meters south of a major street, is between a residential area and a commercial area. A public garden is about 10 meters east and 3 to 4 meters lower than the location of the collectors. Mean wind direction for the site was determined for 1985. The prevailing wind is from the west; however, the wind direction during storms is from the west about 31 percent of the time, from the north 21 percent of the time, from the east 18 percent of the time, and from the south 30 percent of the time (Schroder and others, 1987).

Method of Sample Collection

Beginning in mid-April and continuing through October 1988, samples from single storms were collected in a clean 13-L polyethylene sample-collection bucket. The sample-collection buckets were cleaned by rinsing three times with ultrapure deionized water (greater than 16.7 MΩ/cm). Any remaining

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[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

debris in the bucket was then removed with a natural sponge. The buckets were rinsed three more times with ultrapure deionized water, filled with ultrapure deionized water and allowed to stand for at least 24 hours. The sample-collection buckets then were emptied, rinsed three more times with ultrapure deionized water, inverted, and allowed to dry. The clean sample-collection buckets then were covered with a clean polyethylene bag until they were transferred to the sampling site.

To allow more than one storm to be subsampled in a 7-day period, two wet-deposition collectors of the type described by Volchock and Graveson (1976) were used in this study. The first (north) collector was an Aerochem Metrics automatic wet-deposition collector that was used to collect the samples for the individual storms. The second (south) collector was located about 5 meters south of the north collector, and was manually operated; the sensor and motor box were disabled to prevent the collector from opening during storms. To simulate the conditions of the north collector when the collector was closed, the south collector was modified. The pressure applied to the top of the sampling bucket was measured for the north collector. An elastic cord was attached to the lid of the south collector and adjusted to apply the same amount of pressure to the lid on the south collector as was applied by the lid on the north collector.

Natural Wet-Deposition Samples

When a storm occurred, a sample was collected in the north collector. If there was no sample in the south collector, the bucket containing the sample from the north collector was transferred to the south collector and a clean bucket was placed in the north collector. This permitted for more than one sample to be subsampled at a time. If there already was a sample in the south collector, the sensor was disabled on the north collector to prevent activation by another storm. When the subsampling of the sample in the south collector was complete, the sample in the north collector was transferred to the south collector. If no wet deposition occurred within 7 days, the bucket in the north collector was replaced with a clean bucket.

Small volume storms (wet deposition less than 1.3 mm) allowed fewer than five subsamples and were not used for this study. Daily subsamples were taken from the bucket for storms that produced 1.3 mm or more precipitation. Twenty-five mL aliquots were removed daily from the bucket for up to 7 days. The aliquots were removed using a 60-mL polyethylene syringe that had been rinsed three times with ultrapure deionized water. Extreme care was taken to minimize contamination during removal of the aliquots. The aliquots were immediately filtered, with a 0.45 μm filter (that had been rinsed with at least 20 mL of the ultrapure deionized water and at least 2 mL of the sample), and placed into two precleaned polystyrene test tubes.

The pH and specific conductance were immediately measured and the remaining subsample was preserved for analysis. Analysis was by ion chromatography (IC) and flame atomic absorption spectrometry (FAAS) or flame atomic emission spectrometry (FAES). A 5-mL aliquot for ion chromatography was preserved with 10 μL of chloroform. A 10-mL aliquot for FAAS or FAES was preserved with 10 μL of ultrapure nitric acid. Both aliquots were chilled at 4 °C until all subsamples from each storm were removed. Experimental errors were minimized by analyzing the aliquots from each storm as a group using the same calibration curves. The instrumental accuracy was checked by periodically analyzing the Standard Reference Water Sample P-12 (Janzer, 1988, written communication). Chloride, nitrate, and sulfate were analyzed by ion chromatography. Magnesium, sodium, and potassium were analyzed by FAAS, and calcium was analyzed by FAES.

Blank Samples

Two types of blanks were analyzed: (1) Laboratory blanks and (2) onsite blanks. Three blanks of ultrapure deionized water were prepared to determine if contamination was present in the buckets. These ultrapure deionized water blanks had volumes of 100 mL, 200 mL, and 500 mL, and were placed in clean 13-L polyethylene buckets and stored in the laboratory. The buckets were covered with the same type of polyethylene-covered foam-pad bucket cover present on the wet-only collectors at the sampling site. The foam pads were weighted with about 1,000 grams to simulate the pressure applied to the lids of the onsite collectors. The three laboratory blank samples were subsampled daily using the same procedures used for the natural samples.

The two onsite blanks were 200 mL of ultrapure deionized water in 13-L polyethylene buckets. One ultrapure deionized water blank was placed on each of the collectors, and the north collector was disabled from opening if a storm occurred. These ultrapure deionized water blanks were used to determine if there was a measurable difference between the two sample collectors used for this experiment. The onsite blanks were subsampled using the same procedures used for the natural samples.

CHEMICAL STABILITY

Stability of Wet-Deposition Samples

Ten storms were subsampled from mid-April through October 1988 (table 1). The volume collected for each storm was determined by measuring the sample volume remaining in the bucket after all subsamples were removed and adding the volume that was removed for each subsampling.

The detection limit for each analyte was determined for the analytical methods used in this experiment for the duration of the experiment using the techniques described in National Atmospheric Deposition Program, 1988. Analyte concentrations less than the method detection limit were set equal to the detection limit. Table 2 lists the analytical method used and the detection limit for each analyte.

Samples from eight storms were subsampled for 7 days; however, only six subsamples were removed for the storms on April 20 and July 19, either because the sample was frozen or because it rained continuously on a day a sample was to be removed. The volume collected during the storms on June 13 and July 4

Table 1.--*Dates, volumes, days subsampled, and number of subsamples removed for the 10 storms*

Date of storm	Volume (milliliters)	Days subsampled	Number of subsamples removed
4/20/1988	396	7	6
5/5/1988	310	7	7
5/20/1988	5,007	7	7
6/9/1988	650	7	7
6/13/1988	105	5	5
7/4/1988	165	6	6
7/19/1988	155	7	6
8/16/1988	521	7	7
9/12/1988	1,249	7	7
9/14/1988	289	7	7

Table 2.--*Analytical method and detection limit for each analyte*

[Detection limit is in microequivalents per liter, analytical methods are flame atomic emission spectrometry (FAES), flame atomic absorption spectrometry (FAAS) and ion chromatography (IC)]

Analyte	Analytical method	Detection limit
Calcium	FAES	0.426
Magnesium	FAAS	.716
Sodium	FAAS	.470
Potassium	FAAS	.230
Chloride	IC	1.80
Nitrate	IC	.407
Sulfate	IC	.356

was insufficient for 7 days of subsamples. The sample from the June 13 storm was subsampled for 5 days, and the sample from July 4 was subsampled for 6 days. The mean, standard deviation, maximum, and minimum measured concentrations for the first day subsampled for the 10 storms are listed in table 3.

Measured analyte concentrations were converted to mass per bucket by multiplying the ion concentration by the volume of the sample in the bucket before each subsample was removed. Specific conductance determinations were not adjusted. The mass per bucket concentrations were then adjusted by adding the mass removed from the previous days subsamplings to the measured

Table 3.--*Mean, standard deviation, maximum, and minimum determinations for the first day subsampled for ten storms*

[All concentrations are in microequivalents per liter except specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Mean	Standard deviation	Maximum	Minimum
Calcium	39.3	62.0	233	1.75
Magnesium	4.69	4.89	20.3	.74
Sodium	6.18	6.51	24.8	.96
Potassium	3.13	2.16	8.95	.46
Chloride	32.3	30.3	86.5	4.34
Nitrate	27.5	16.4	77.9	7.10
Sulfate	42.7	36.7	133	7.60
Hydrogen ion	13.1	16.3	61.7	.06
Specific conductance	17.8	11.2	50.0	3.60

mass per bucket for each day subsampled. Equations summarizing the conversions are:

$$M_i = C_i \times V_i \qquad (1)$$

$$M_r = \Sigma C_{i-1} \times (V_i - V_{i-1}) \qquad (2)$$

$$M_a = M_i + M_r \qquad (3)$$

where M_i = calculated mass per bucket for each subsample, i,

C_i = measured concentration for each subsample, i,

V_i = volume remaining in the bucket prior to the removal of each subsample, i,

M_r = mass removed for a subsample, and

M_a = adjusted mass.

Linear regression analyses were done on the analyte concentrations for each day subsampled versus the time that the sample remained in the collection bucket. The residuals were then plotted to test for normality. It was determined that the analyte concentrations for each day subsampled were not normally distributed. A Kendall's estimator was then used to estimate the slopes and a non-parametric regression equation was determined for each analyte. Figures 1-9 are plots of the adjusted concentrations (equations 1-3) versus the time the sample remained in the collection bucket for each analyte. A Kendall's tau estimator of rank correlation was done on each analyte to determine if any statistically significant correlations existed (Lehmann and D'abrera, 1975). Calcium and hydrogen ion were determined to have statistically significant correlations at a significance level of 0.05 (table 4). Statistically significant correlations indicate that the sample chemistry is changing with respect to the length of time that the sample remained in the collection bucket.

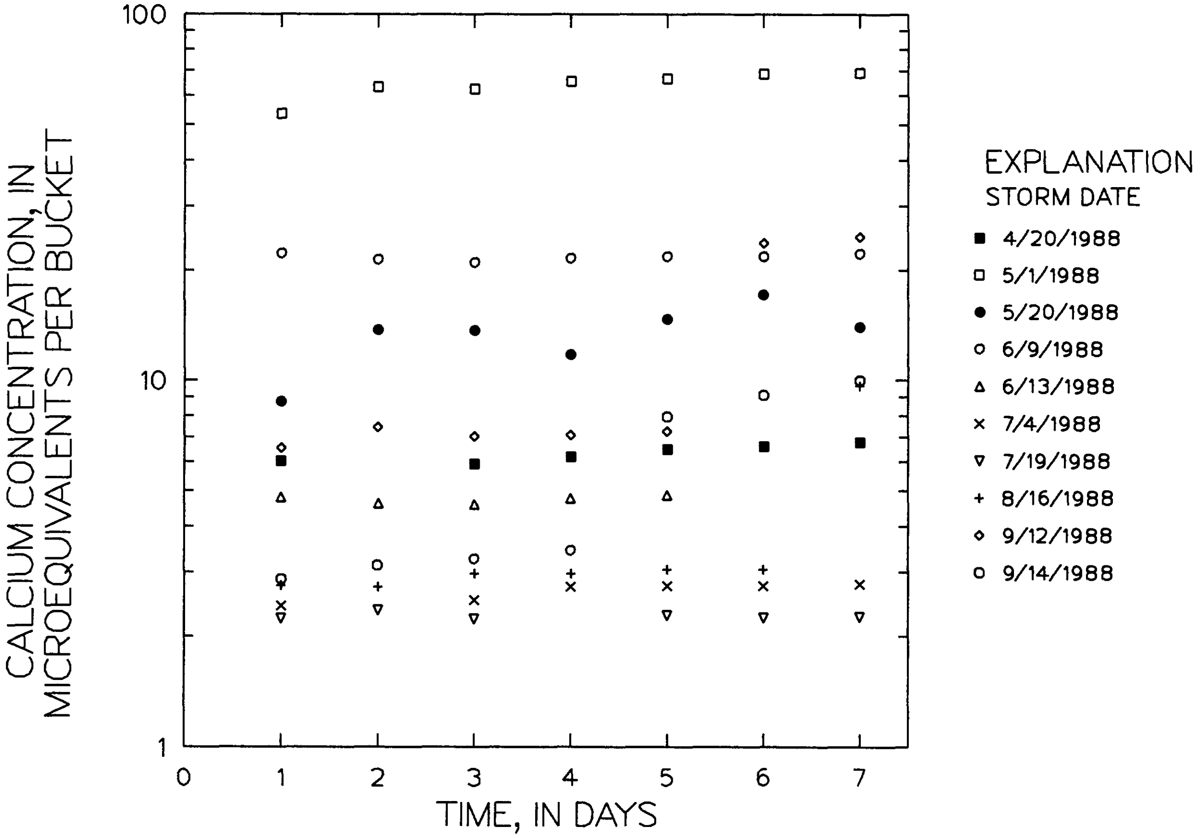

Figure 1.--Adjusted concentration versus time for the 10 storms, for calcium.

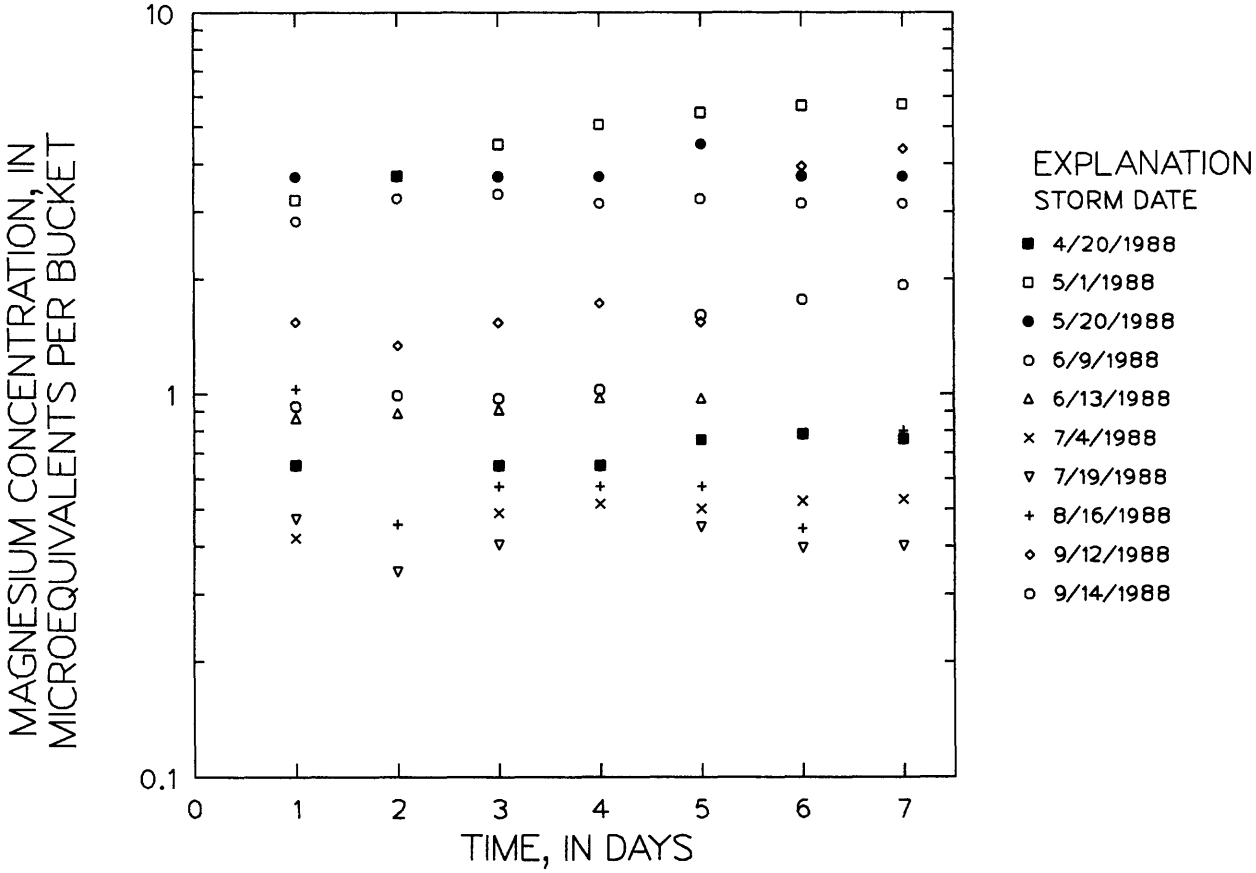

Figure 2.--Adjusted concentration versus time for the 10 storms, for magnesium.

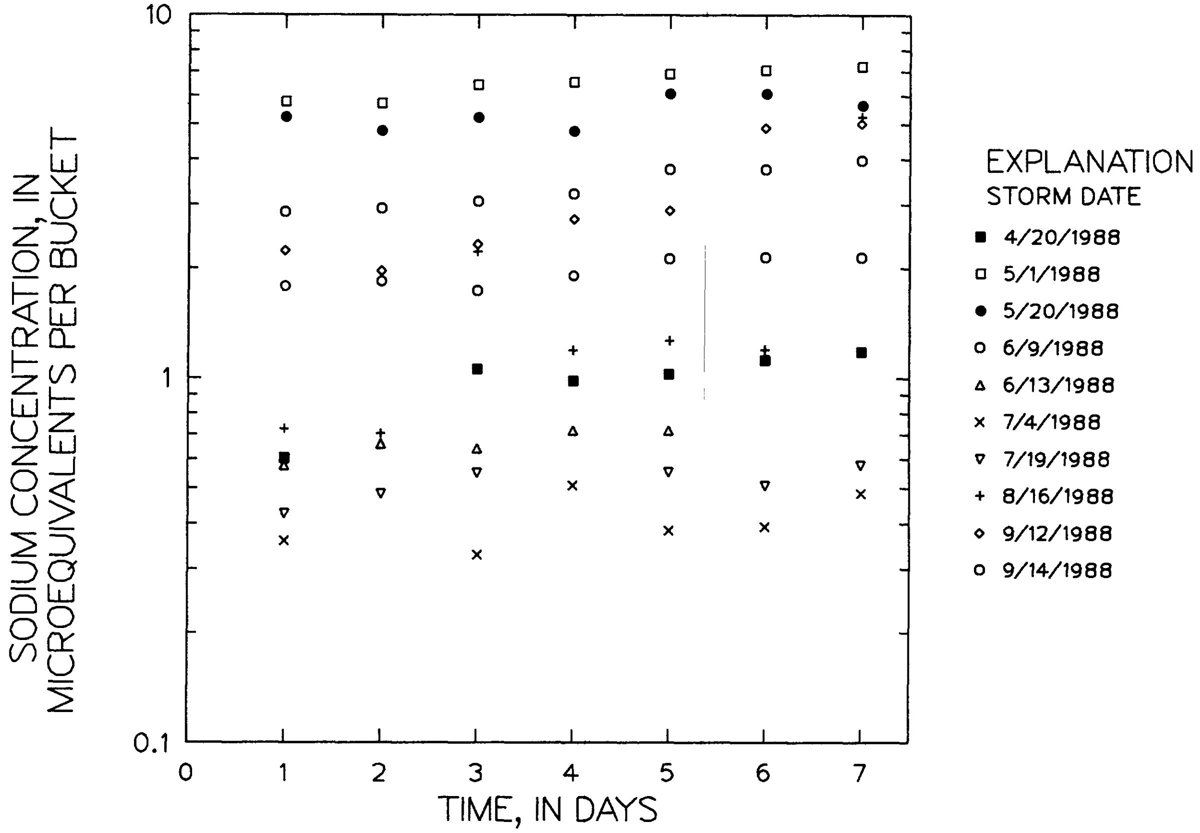

Figure 3.--Adjusted concentration versus day for the 10 storms, for sodium.

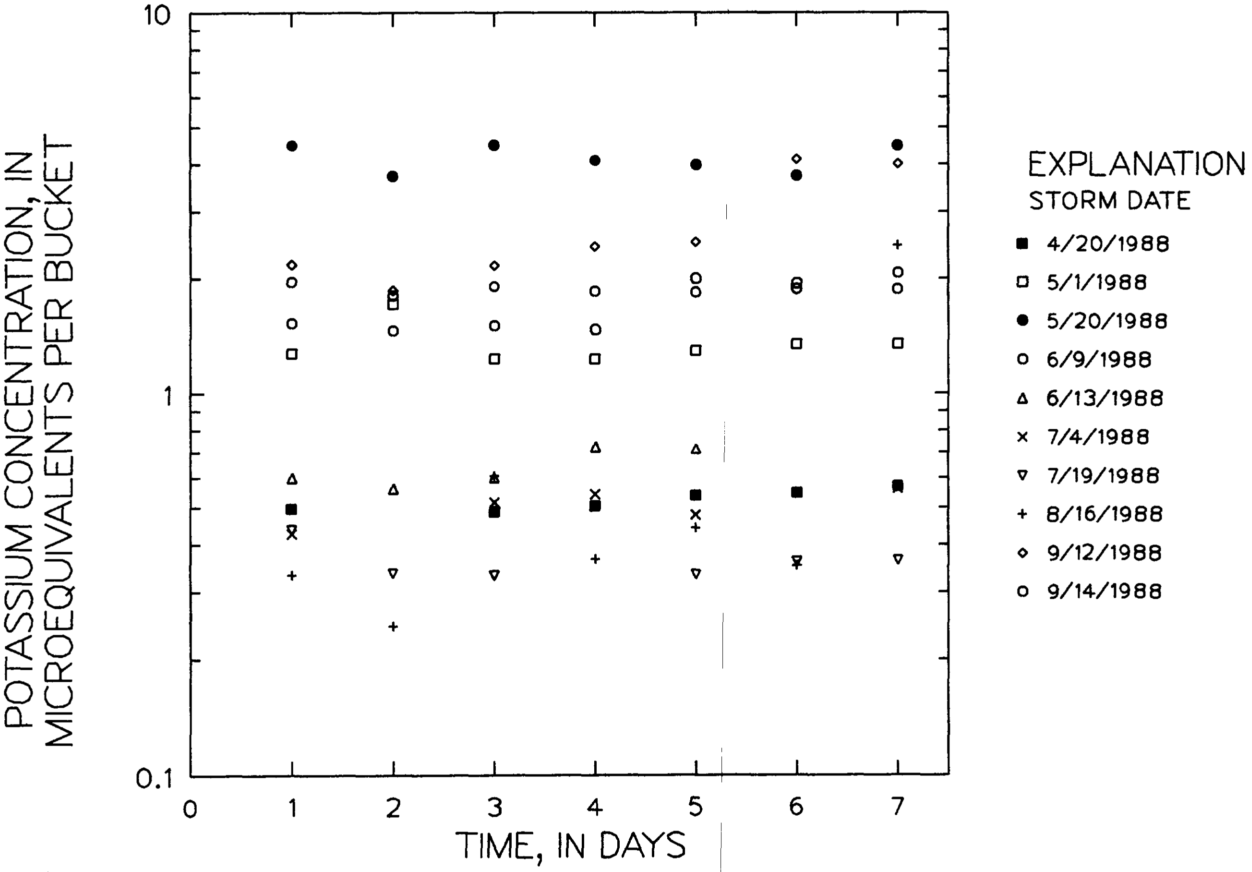

Figure 4.--Adjusted concentration versus time for the 10 storms, for potassium.

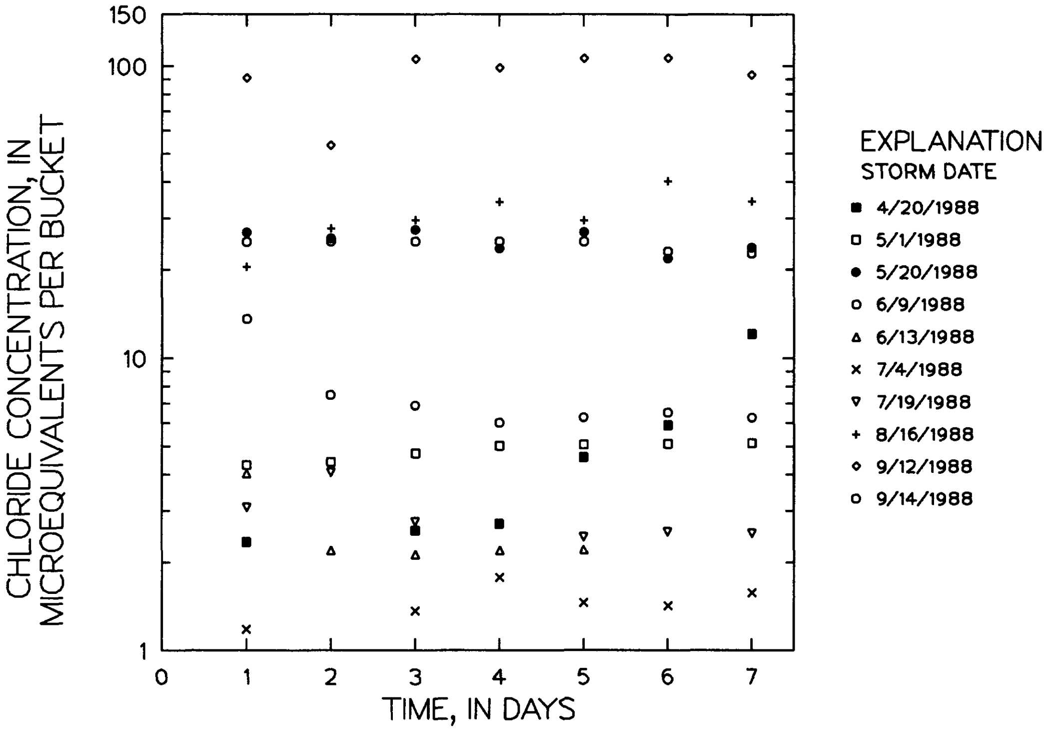

Figure 5.--Adjusted concentration versus time for the 10 storms, for chloride.

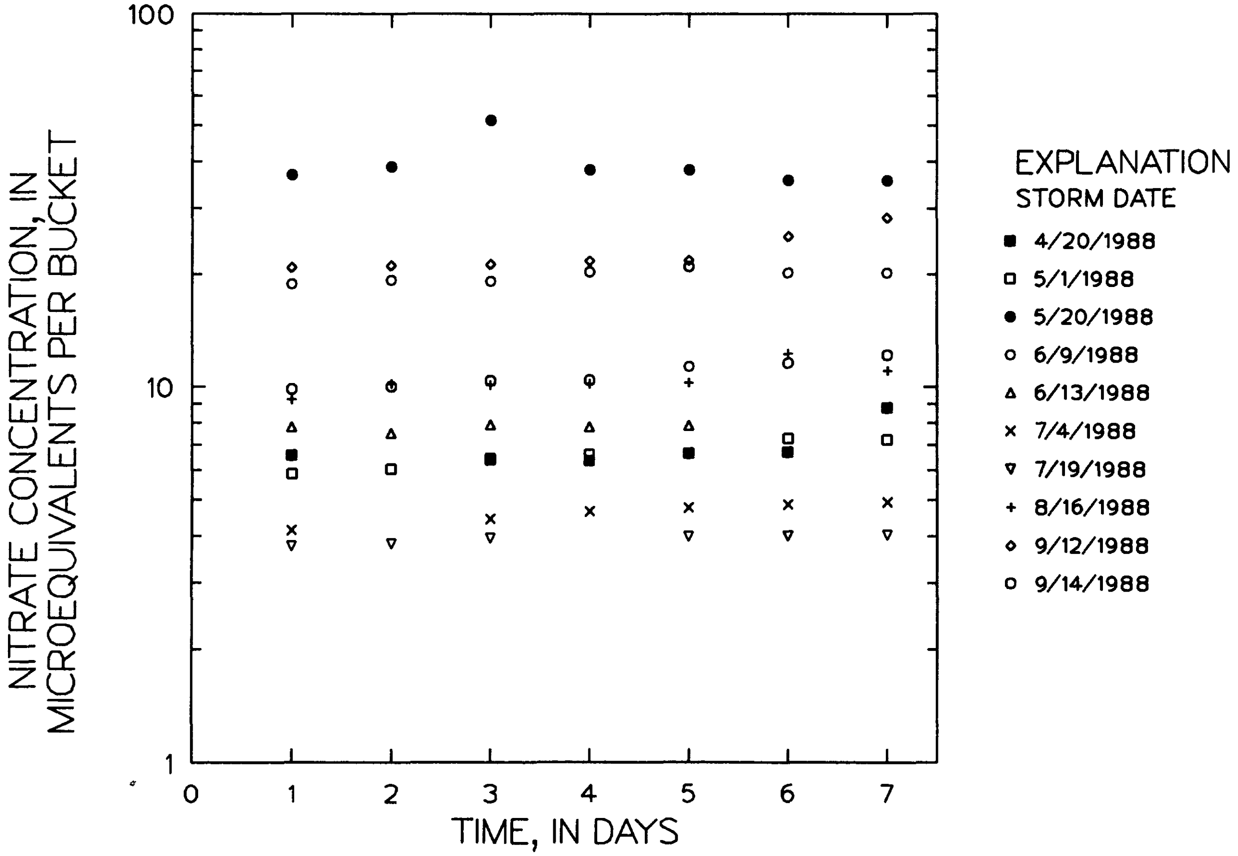

Figure 6.--Adjusted concentration versus time for the 10 storms, for nitrate.

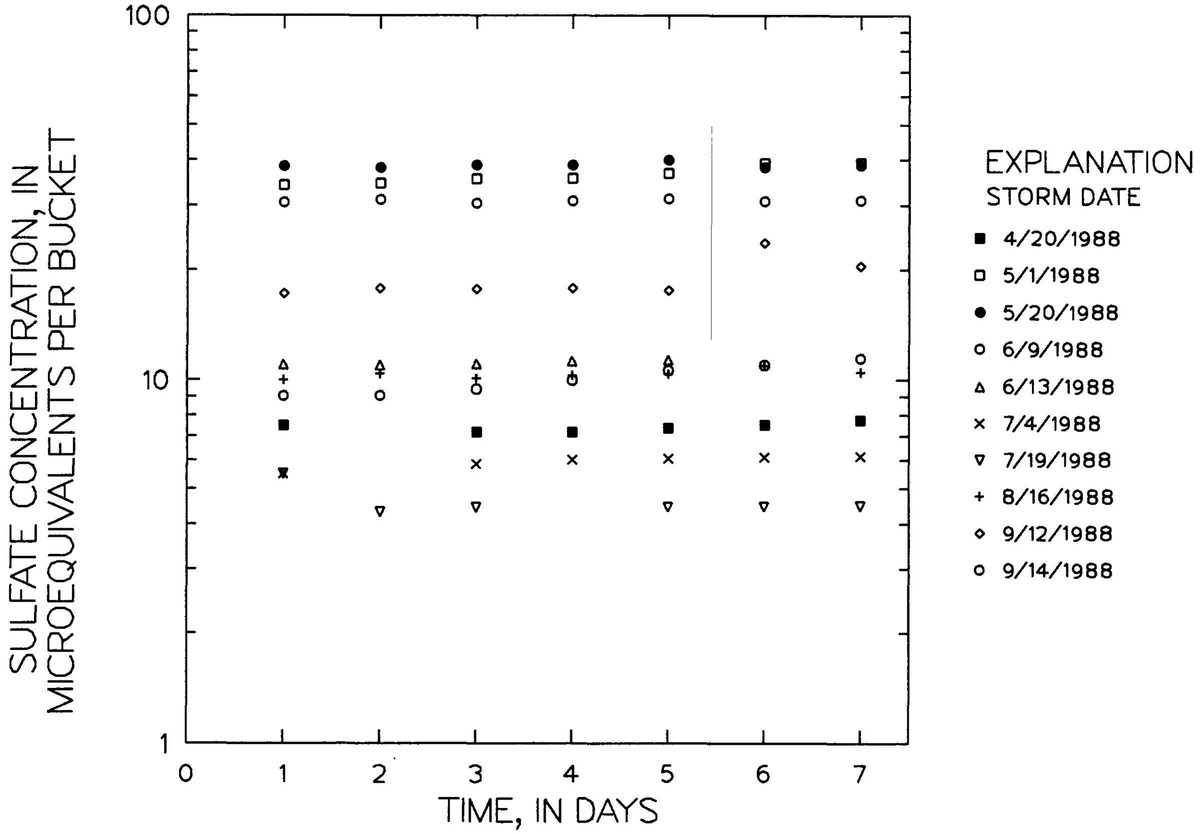

Figure 7.--Adjusted concentration versus time for the 10 storms, for sulfate.

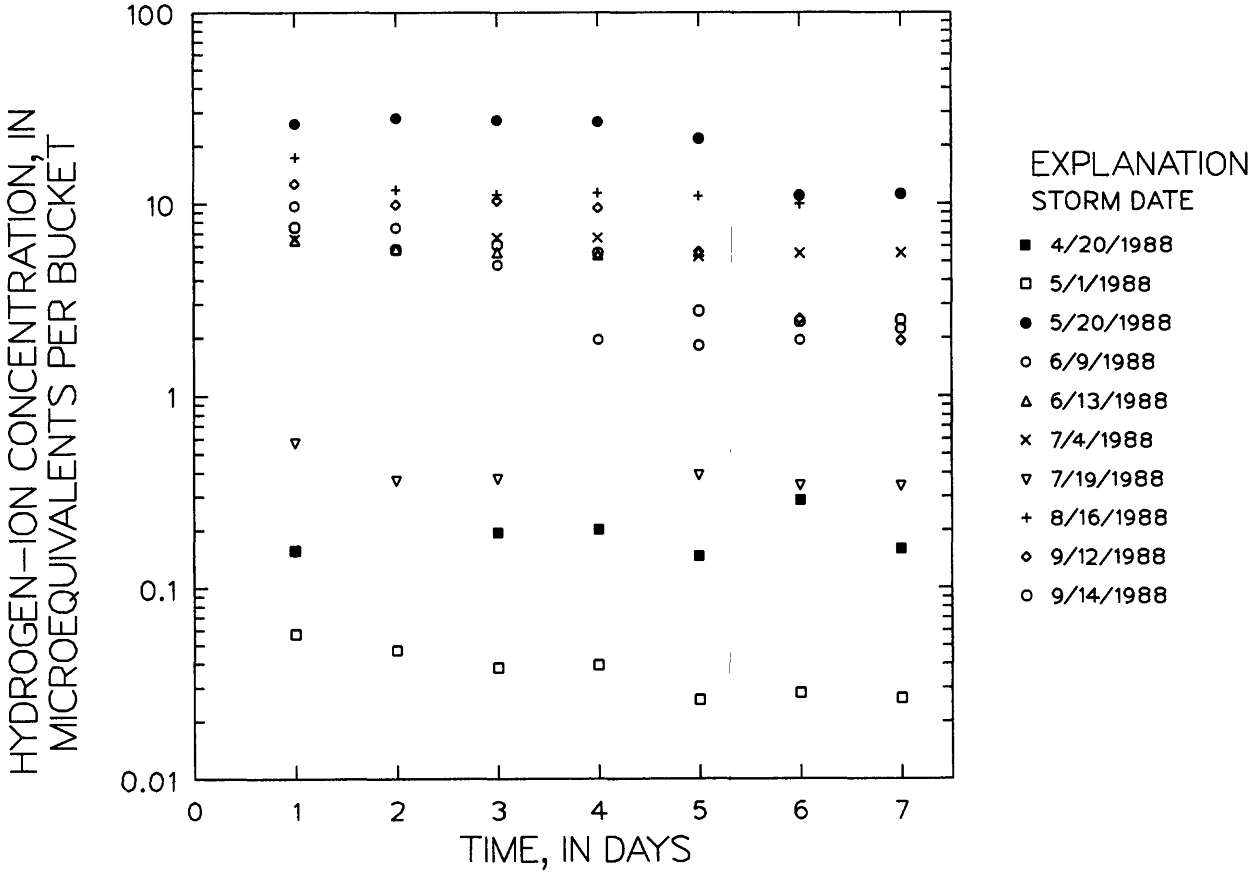

Figure 8.--Adjusted concentration versus time for the 10 storms, for hydrogen ion.

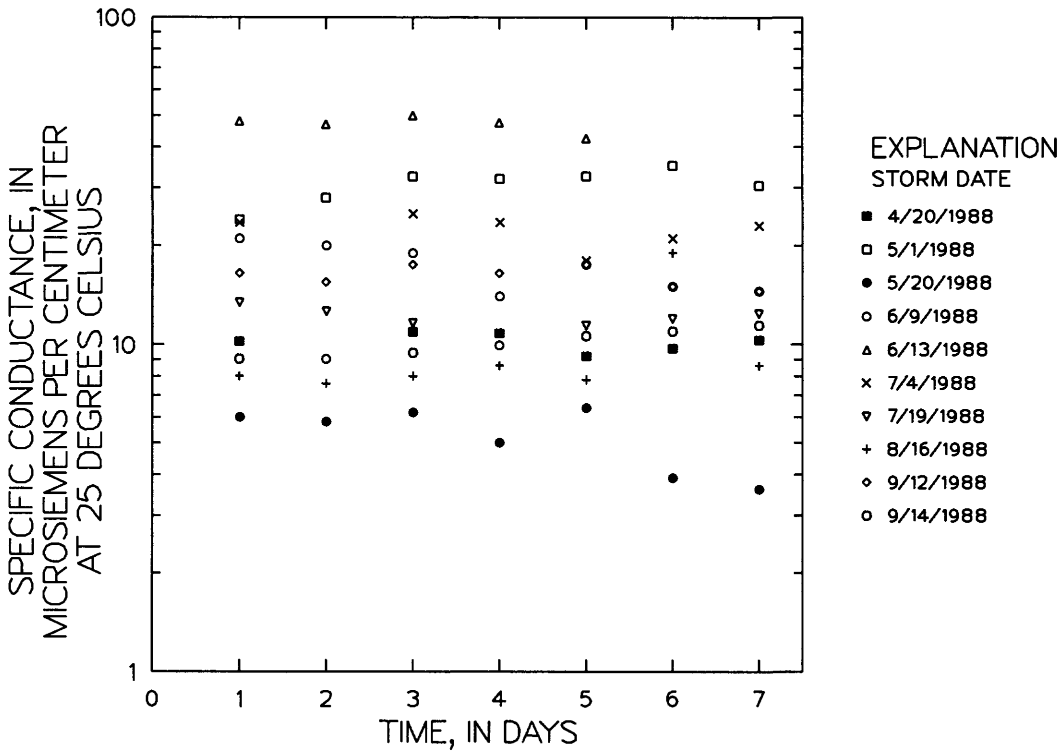

Figure 9.--Specific conductance versus time for the 10 storms.

Table 4.--*Results of Kendall's estimator for slope, the calculated intercept, and the Kendall's tau estimator of rank correlation for adjusted concentration versus day subsampled for each analyte*

[All data were included from the 10 storms. Slope is in microequivalents per bucket-day except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius; intercept is in microequivalents per bucket except specific conductance, in microsiemens per centimeter at 25 degrees Celsius; Kendall's tau (Υ) and significance level are in units]

Analyte	Intercept	Slope	Kendall's Υ	Significance level
Calcium	5.16	0.357	0.149	0.040
Magnesium	1.03	.027	.079	.176
Sodium	1.54	.106	.135	.057
Potassium	1.20	.021	.098	.124
Chloride	6.26	.066	.039	.324
Nitrate	9.36	.167	.084	.163
Sulfate	10.8	.109	.058	.248
Hydrogen ion	7.50	-.496	-.197	.010
Specific conductance	14.5	-.450	-.103	.109

Stability of Blank Samples

Ultrapure deionized water blanks of 100, 200, and 500 mL, were placed in clean buckets and stored in the laboratory to determine if there was any contamination related to volume introduced into the sample by the polyethylene buckets. The 200 and 500 mL blanks were subsampled for 7 days. The 100 mL sample had insufficient volume to subsample for 7 days, and was therefore subsampled for 5 days. The subsamples were removed, filtered, preserved, and analyzed after all of the subsamples were removed, using the same techniques as was used for the natural samples. Table 5 lists the median determinations for the three ultrapure deionized water blanks which were stored in the laboratory.

Table 5.--*Median determinations for the 100-, 200-, and 500-mL blanks stored in the laboratory*

[All concentrations are in microequivalents per liter except specific conductance, which is in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Median concentration by volume 100-mL blank	200-mL blank	500-mL blank
Calcium	0.52	1.12	0.62
Magnesium	.74	.74	.74
Sodium	.74	2.20	1.54
Potassium	.23	.23	.23
Chloride	5.11	4.82	4.51
Nitrate	1.50	1.03	.83
Sulfate	.64	.57	.64
Hydrogen ion	1.73	1.19	1.47
Specific conductance	2.08	1.98	1.88

The median measured determination for chloride, nitrate, and specific conductance decreased as volume increased for each of the three laboratory blanks. However, the changes observed for chloride, nitrate, and specific conductance determinations were considerably smaller than the changes observed in the natural samples. None of the other constituents had a consistent concentration change as volume increased.

The measured concentrations from the three laboratory blanks then were converted to mass per bucket and adjusted to compensate for the mass that was being removed for each subsampling using the same techniques used for the natural samples (equations 1-3). Figures 10-12 are plots of the adjusted concentrations versus the time the samples remained in the collection buckets. A Kendall's estimator of slope was used to estimate the slope and the corresponding non-parametric regression equation was determined. A Kendall's tau

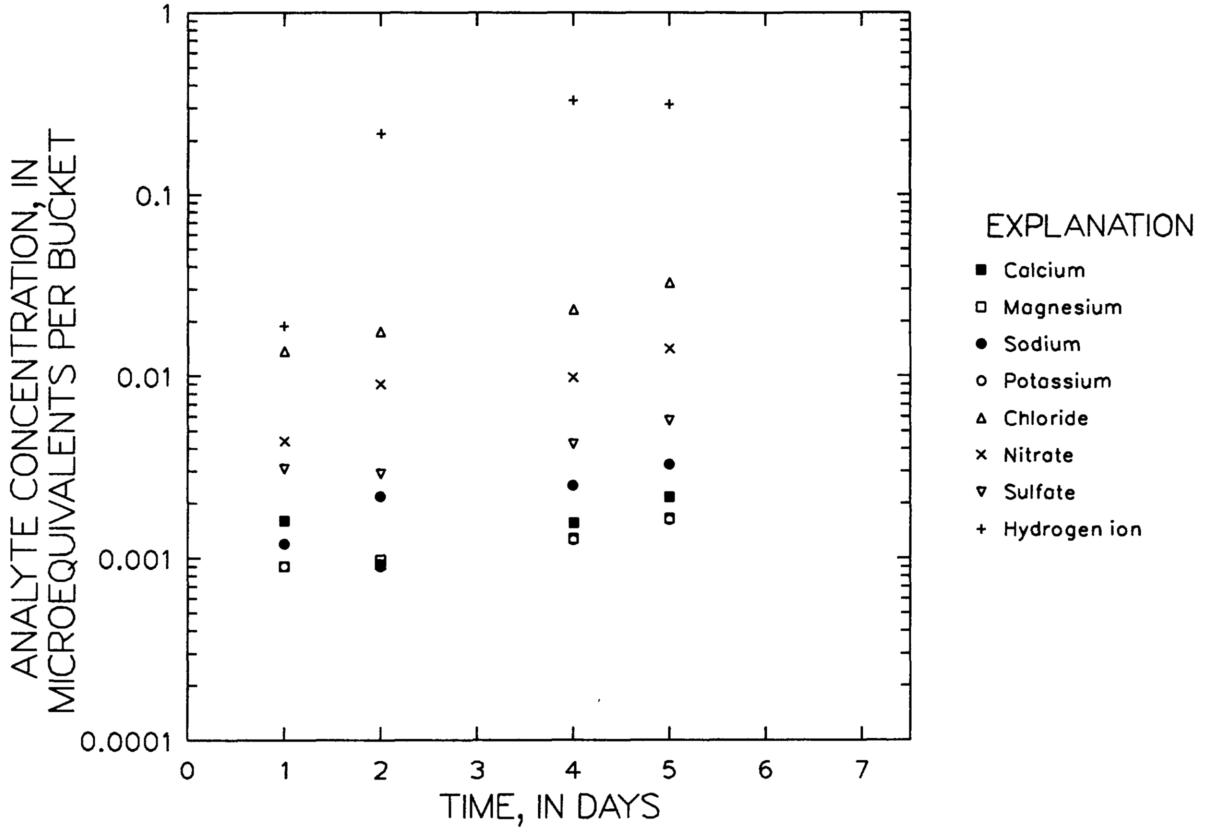

Figure 10.--Adjusted concentration of analytes versus time for the 100-milliliter blank stored in the laboratory.

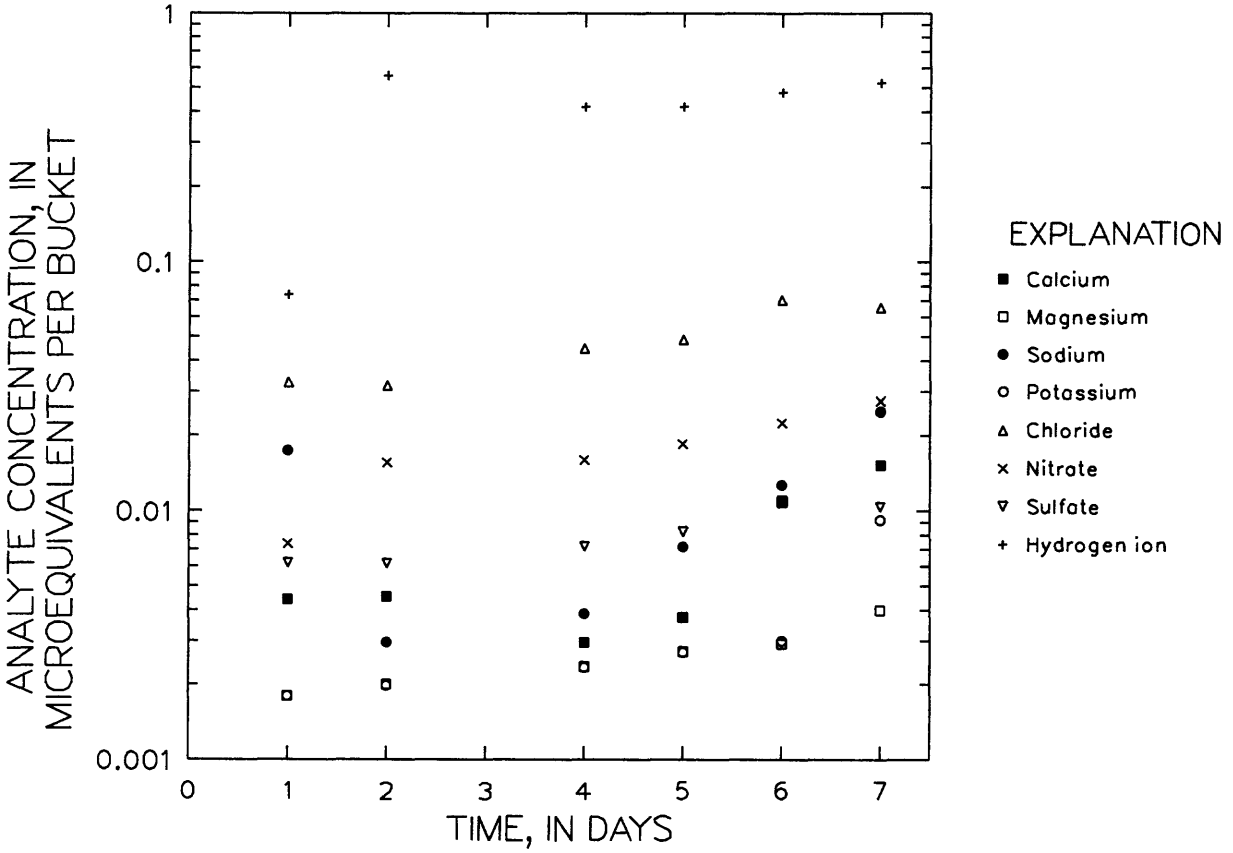

Figure 11.--Adjusted concentration of analytes versus time for the 200-milliliter blank stored in the laboratory.

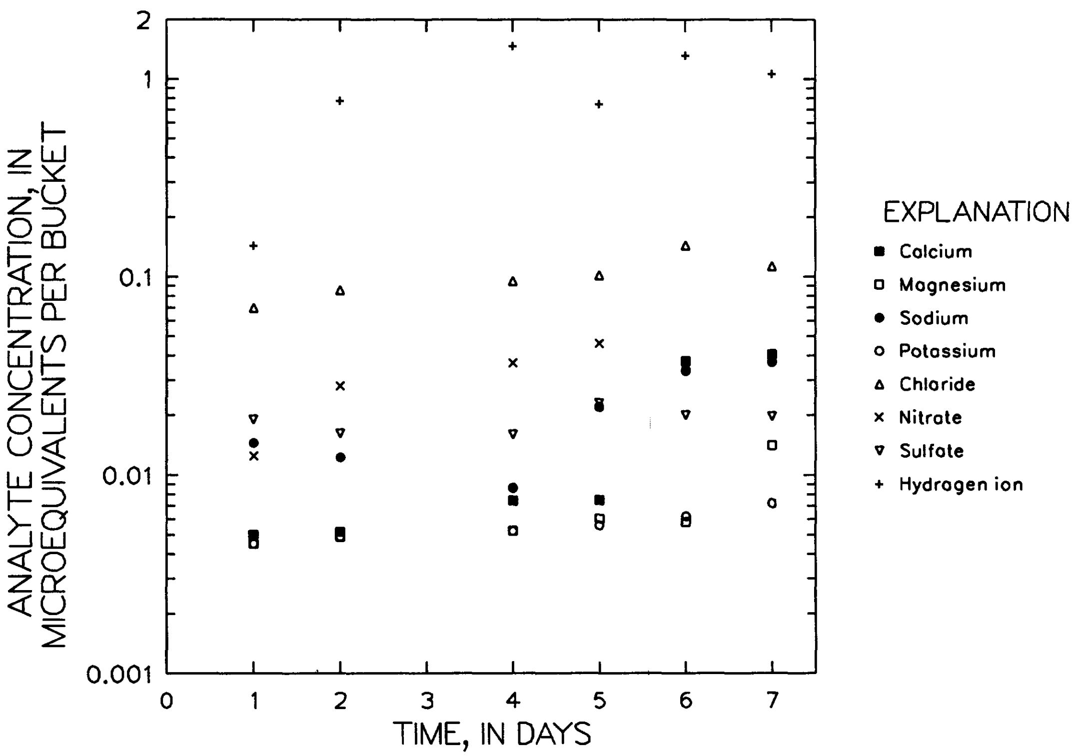

Figure 12.--Adjusted concentration of analytes versus time for the 500-milliliter blank stored in the laboratory.

estimator of rank correlation was done on each analyte to determine if there were any statistically significant correlations between the analyte concentrations and the length of time the sample remained in the collection bucket. Statistically significant correlations were determined for calcium, magnesium, sodium, potassium, chloride, nitrate, and hydrogen ion at a significance level of 0.05, indicating that the sample chemistry was changing with respect to the length of time that the sample remained in the collection bucket. However, the magnitude of the slopes for the laboratory blanks were smaller than the slopes determined for the natural wet-deposition samples (table 6).

Two 200-mL ultrapure deionized water blanks were placed simultaneously in clean buckets on the wet-only collectors to determine if there were any statistically significant differences between the two collectors. The blank samples were subsampled, filtered, preserved, and analyzed after all the subsamples were removed, using the same techniques as were used for the natural samples. Six subsamples were removed for the 7 days the samples remained on the collectors. No subsamples were removed on the sixth day because it rained.

The measured concentrations were then converted to mass per bucket using the same techniques used for the natural samples (equations 1-3). Figures 13 and 14 are plots of the adjusted concentrations versus the time the samples remained in the collection buckets. A Wilcoxon signed ranks test (Iman and Conover, 1983) was done on the adjusted concentrations and specific conductance determinations for both samplers to determine if there was a statistically significant difference between the two collectors. At a significance level of a=0.01 there were no statistically significant differences between the two collectors; however, the adjusted concentrations for all the

Table 6.--*Results of Kendall's estimator for slope, the calculated intercept, and the Kendall's tau estimator of rank correlation for adjusted concentration versus day subsampled for each analyte for the three blanks stored in the laboratory*

[Slope is in microequivalents per bucket-day except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius; intercept is in microequivalents per bucket except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius; Kendall's tau (τ) and significance level are in units]

Analyte	Intercept	Slope	Kendall's τ	Significance level
Calcium	-0.006	0.061	0.497	0.004
Magnesium	.140	.023	.443	.008
Sodium	.167	.074	.427	.011
Potassium	.033	.010	.543	.002
Chloride	.734	.220	.443	.008
Nitrate	.059	.055	.568	.001
Sulfate	.115	.020	.302	.052
Hydrogen ion	.134	.079	.479	.005
Specific conductance	1.8	.050	.371	.022

constituents--especially calcium, magnesium, nitrate, and the mean determination for specific conductance--were larger on the south collector than on the north collector (table 7). However, the changes which occurred in sample chemistry on the seventh day for the south sampler were considerably larger than the changes observed on the seventh day for the north sampler which influenced the adjusted concentrations for the south sampler. This may be due to differences in the lid pressure on the top of the bucket for each sampler. The changes in sample chemistry which were observed for days 1-5 were very similar for both samplers.

A Kendall's estimator was used to estimate the slope and a non-parametric regression equation was determined for each analyte. A Kendall's tau estimator of rank correlation was used to determine if there were any statistically significant correlations between the analyte concentration and the time that the sample remained in the collection bucket. Statistically significant correlations were determined for calcium, magnesium, potassium, chloride, nitrate, and sulfate, indicating that these analytes were changing with respect to the time that the sample remained in the collection bucket (table 8).

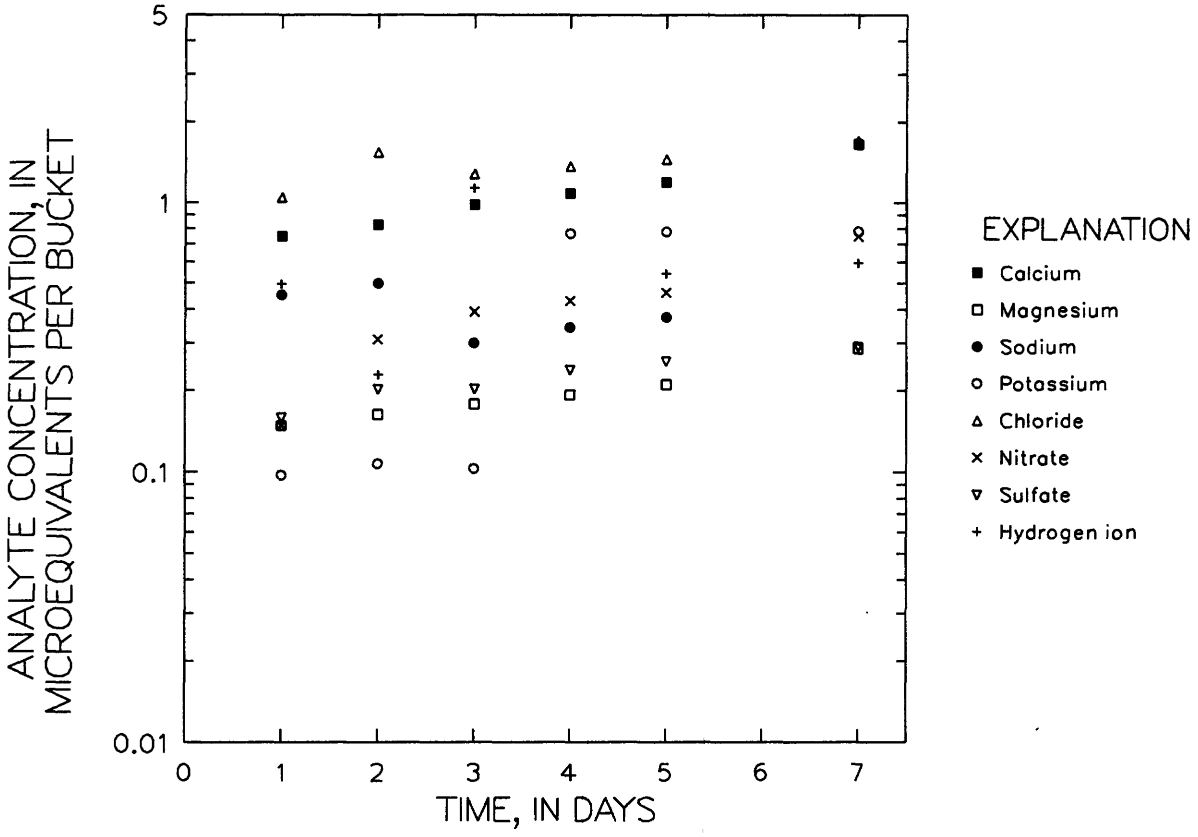

Figure 13.--Adjusted concentration of analytes versus time for the 200-milliliter blank stored in the north collector.

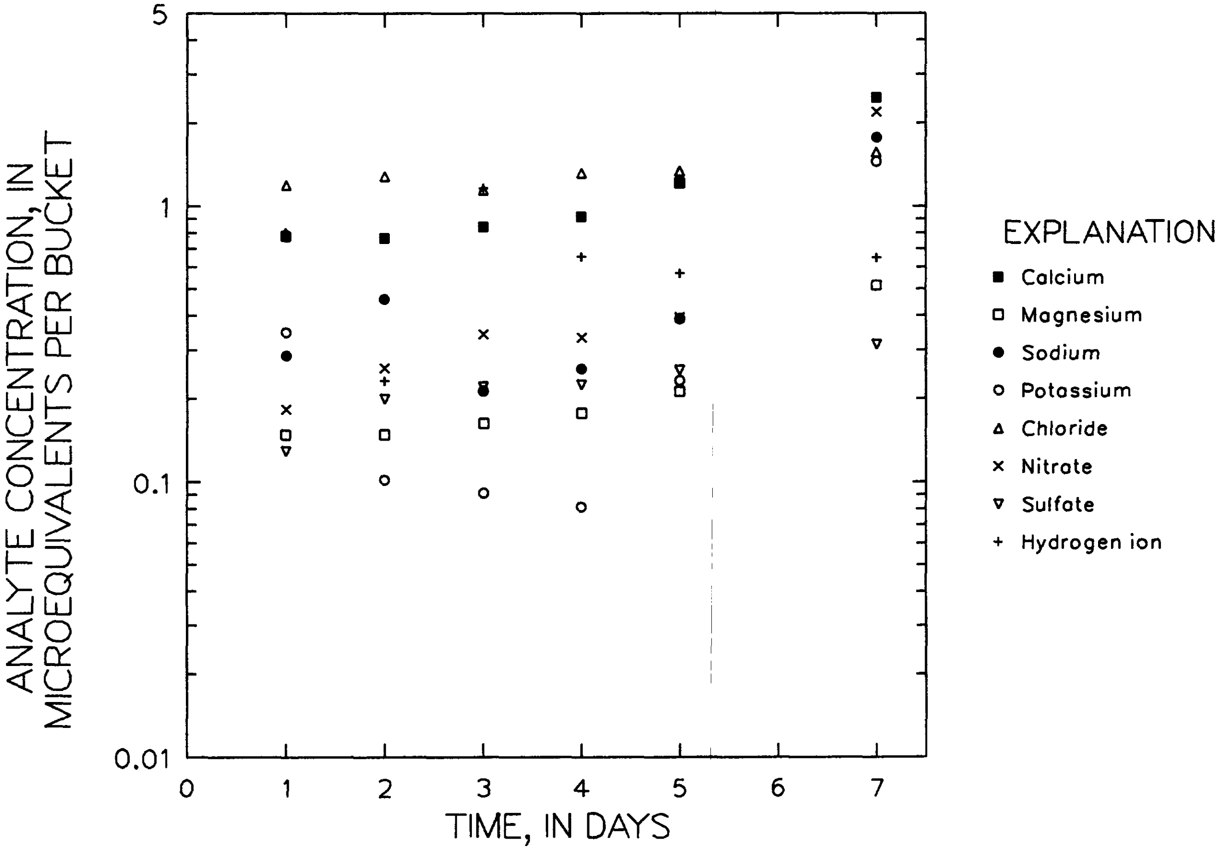

Figure 14.--Adjusted concentration of analytes versus day for the 200-milliliter blank stored in the south collector.

Table 7.--*Median determination for the two 200-milliliter field blanks*

[All concentrations are in microequivalents per liter except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius]

Analyte	North collector	South collector	Number of subsamples removed
Calcium	3.87	4.34	6
Magnesium	.74	.74	6
Sodium	1.50	1.72	6
Potassium	.59	1.62	6
Chloride	5.65	5.12	6
Nitrate	1.47	1.64	6
Sulfate	1.03	.91	6
pH	1.87	1.69	6
Specific conductance	7.08	2.25	6

Table 8.--*Results of Kendall's estimator for slope, the calculated intercept, and the Kendall's tau estimator of rank correlation for adjusted concentration versus day subsampled for each analyte for the two field blanks*

[Slope is in microequivalents per bucket-day except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius; intercept is in microequivalents per bucket except specific conductance which is in microsiemens per centimeter at 25 degrees Celsius; Kendall's tau (Υ) and significance level are in units]

Analyte	Intercept	Slope	Kendall's Υ	Significance level
Calcium	0.535	0.118	0.890	0.000
Magnesium	.122	.016	.926	.000
Sodium	.144	.024	.286	.098
Potassium	-.068	.068	.445	.022
Chloride	1.12	.061	.636	.002
Nitrate	.091	.079	.858	.000
Sulfate	.139	.024	.954	.000
Hydrogen ion	.571	.015	.032	.443
Specific conductance	-1.6	1.2	.144	.257

The two analytes with statistically significant correlations for the natural samples were calcium and hydrogen at a significance level of 0.05. The slope for calcium was over twice the magnitude as the calcium slope observed for the field blanks, which may be due to the larger hydrogen ion concentration observed for the first day subsampled for the natural samples. A decrease in the hydrogen ion concentration was observed for the natural samples while no statistically significant correlations for hydrogen ion were observed for the field blanks.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey conducted a study to examine the chemical changes that occur in wet-deposition samples subsampled daily for 7 days. Each sample was collected in a 13-L polyethylene collection bucket using a wet-only collector. Subsamples were removed, filtered, and preserved for analysis. Specific conductance and pH were measured immediately after each sample was removed from the collection bucket. Calcium was analyzed by flame atomic emission; magnesium, sodium, and potassium were analyzed by flame atomic absorption spectrometry; and chloride, nitrate, and sulfate were analyzed by ion chromatography after all of the subsamples for each storm were removed.

The measured concentrations were converted to mass per bucket and adjusted to account for the mass that was removed for each subsampling. A Kendall's estimator was used to estimate the slope and the non-parametric regression equation was determined. A Kendall's tau estimator of rank correlation was used to determine if there were any statistically significant correlations between analyte concentrations and the length of time that the sample remained at the collection site.

All of the regression equations for the natural samples had positive slopes except hydrogen ion and specific conductance; however, only hydrogen ion and calcium had a statistically significant correlation at a significance level of 0.05 when a Kendall's tau estimator of rank correlation was determined.

Laboratory ultrapure deionized water blanks that had volumes of 100, 200, and 500 mL were subsampled daily for up to 7 days to determine if there was any volume-related contamination resulting from the buckets. The mean measured concentration for nitrate decreased and the mean measured concentration for hydrogen ion increased as volume increased. None of the other constituents had a consistent change in concentration as volume increased. The measured concentrations were adjusted using the same techniques as those used for the natural samples.

A Kendall's tau estimator of rank correlation was used to determine if there were any statistically significant correlations between the analyte concentration and the time that the sample remained in the collection bucket. Statistically significant correlations were determined for calcium, sodium, potassium, chloride, nitrate, and hydrogen ion.

Two 200-mL ultrapure deionized water field blanks were used to determine if changes in sample chemistry occurred between collectors. The adjusted analyte concentrations for each of the collectors were compared using a paired Wilcoxon signed ranks test. At $\alpha=0.01$ there were no statistically significant differences between the two collectors for any of the analytes; however, the mean measured concentrations for the south collector were considerably larger than was determined for the north collector, which was probably due to the differences in the way the sampler lid covered the collection bucket.

Statistically significant decreases in hydrogen ion and increases in calcium can be observed in wet-deposition samples collected weekly using a polyethylene collection vessel and wet-only collector. Wet deposition monitoring projects like the National Atmospheric Deposition Program/National Trends Network might underestimate the hydrogen ion concentrations and overestimate calcium concentrations for samples that remain in a wet-only collector for as long as one week.

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