



Project Summary

Analysis of Acid Precipitation Samples Collected by State Agencies

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This report presents the analytical data from the 31 acid precipitation collection sites in the State-Operated Network. Samples are collected weekly in plastic bag bucket liners and shipped in 500 mL polyethylene bottles to Global Geochemistry Corporation (the central laboratory for the network). The report contains maps showing the location of each site, plots of analytical data, tables of all field and analytical data, plots comparing field and laboratory pH and conductivity, and information on data quality.

Samples are analyzed for pH, strong acid, conductivity, fluoride, chloride, nitrite, phosphate, bromide, nitrate, sulfate, ammonium, sodium, potassium, calcium, and magnesium.

The central laboratory renders technical assistance to the collection sites on problems concerning pH and conductivity. Each of the 11 participating state agencies receive analytical reports for the samples analyzed the previous month. Analyte concentration data are sent to the Acid Deposition System (ADS) for inclusion in the National Acid Precipitation Data Base.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

As the central laboratory for the State-Operated Network, Global Geochemistry Corporation (GGC) analyzes acid precipitation samples for pH, strong acid, conductivity, fluoride, chloride, nitrite, phosphate, bromide, nitrate, sulfate, ammonium, sodium, potassium, calcium, and magnesium.

The central laboratory provides the collection sites with plastic bucket liners, 500 mL sample bottles, field data sheets, pH and conductivity solutions, and other supplies incidental to collecting and shipping a collected rain sample. The central laboratory also provides technical assistance whenever it is requested by the field sites. This assistance has consisted mostly of advice on field pH and conductivity measurement procedures and equipment.

The final report contains maps showing the location of each site, plots of analytical data during the time period, tables of all field and analytical data, a comparison of analyte concentration at deficient sites, precipitation weighted data for each site, plots comparing field and laboratory pH and conductivity, and quality control tables and plots.

Each participating state agency and sponsoring EPA Region receives an analytical report for the previous month's analyses.

Data is summarized on magnetic tape for inclusion in the yearly report of the national acid rain data base, the Acid Deposition System (ADS), funded by EPA.

Balance Accuracy

In the April 1987 survey of balance accuracy, the respondents reported differences from the expected value ranging from -8.8 g to 1.4 g for the large weight. Results from one site were excluded from average performance shown in Table 1 to avoid biasing the average. The average difference from the expected value was +0.01 grams. Using the small weight, the reported difference ranged from -0.39 g to +0.75 g. The average difference was +0.04 grams.

A second balance accuracy survey was conducted in March 1988. For 24 reporting sites, the differences from the expected value ranged from -16.3 g to 1.9 g for the large weight. The average difference from the expected value was -0.9 g, however, one site was excluded from the summary of average performance to avoid biasing the average.

The small weights were approximately 26 grams; the large weights 200 grams. In most instances, an individual set of 2 weights was sent to each site with no other field laboratory receiving the same set. The central laboratory determined the true mass of each weight.

pH and Conductivity

Semi-annual surveys of pH and conductivity were performed. The results of 3 survey periods are summarized in Table 2. The results showed that incorrect pH measurements (errors greater than 0.10 pH unit) may be occurring at least 10 percent of the time.

For conductivity measurements, errors in the range of 10 percent were evident at 20-25 percent of the sites in the April 1987 and March 1988 surveys.

The central laboratory assigned the true values for pH and conductivity in the surveys.

Discussion

There were 31 acid rain collection sites in operation during most of 1987. The State-Operated Network collects weekly samples using a wet/dry bucket collector. Samples are collected in a plastic bag bucket liner, and an aliquot is sent to the central laboratory unrefrigerated in a 500 mL polyethylene bottle.

The following analytes are measured: pH, conductivity, strong acidity, chloride, sulfate, phosphate, nitrate, ammonium, sodium, potassium, calcium, and magnesium. Plots are presented in the main report showing the weekly concentration of each analyte throughout the year. The amount of precipitation is given for each

weekly collection period. Each site conducts field measurements for pH and conductivity. Representative plots are presented in Table 3.

Once every two months the central laboratory sends each collection site replacement supplies, including 500 mL of pH reference solution and 500 mL of conductivity reference solution. Sites are instructed to measure the reference materials in the same way as a sample. This procedure provides the sites with on-going quality assurance self-checks of the accuracy of their measurements.

The analytical methods used by the central laboratory are shown in Table 4.

The occurrence of different concentration levels at each site are given in the main report. The concentration at which

100%, 75%, 50%, 25%, and 0% of samples have concentrations greater than the given values are listed for each site and for each analyte. This is illustrated in Table 5 for pH.

Quality Control

To validate the accuracy of routine analytical procedures, the central laboratory included duplicate and spike samples with all analyses. The duplicate samples were randomly chosen acid rain samples. Spike samples were prepared from stock solutions and were unknown to the analyst. Quality control plots for all analytes are presented in Appendix A of the main report.

Table 1. Summary of Survey of Balance Accuracy

Date	Large weight (grams)		Small weight (grams)	
	Average difference*	Range of difference	Average difference	Range of difference
April 1987	0.01	-8.8 to 1.4	0.04	-0.39 to 0.75
March 1988	-0.9	-16.3 to 1.9	0.00	-1.63 to 2.61

*Excluded ALMOB

Table 2. Summary of Survey of pH and Conductivity Accuracy

Date	Survey averages				Expected values	
	pH	Std. dev.	Conductivity (μS/cm)	Std. dev.	pH	Conductivity
April 1987	4.22	0.14	39.0	2.2	4.26	37.8
Sept. 1987	4.24	0.04	39.7	1.3	4.26	37.8
March 1988	4.24	0.06	37.6	2.2	4.28	37.4

Table 3. pH and Conductivity — Field vs. Laboratory

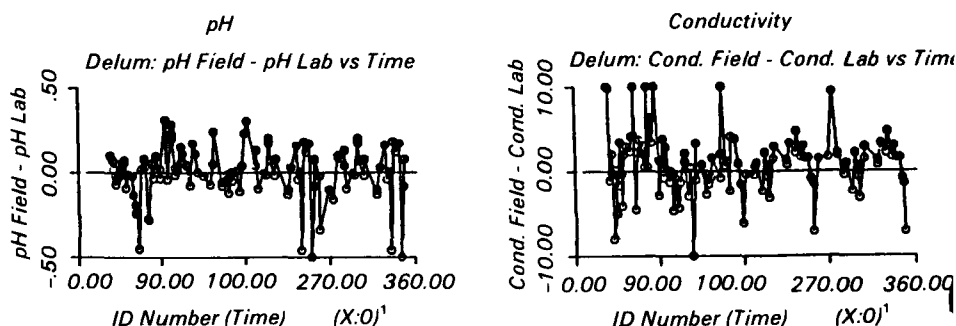


Table 4. Analytical Methods

Analyte	Analytical Method
ph	EPA Method 150.1
Conductivity	EPA Method 120.1
Acidity	Gran Titration
Cl ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , NO ₃ ⁻	Ion Chromatography
NH ₄ ⁺	EPA Method 350.1
Na ⁺ , K ⁺ , Ca ⁺² , Mg ⁺²	EPA Methods 273.1, 258.1, 215.1, 242.1

Table 5. Cumulative Frequency of Occurrence: pH

Site	#Pts	% of Samples Greater Than Given Value				
		100%	75%	50%	25%	0%
ALTAL	19	4.11	4.30	4.54	4.60	4.90
ALMOB	28	3.70	4.20	4.38	4.62	5.67
DEGEO	45	3.21	4.11	4.38	4.75	5.96
DELUM	43	3.48	3.97	4.18	4.43	4.91
GADAW	31	4.00	4.25	4.38	4.55	5.20
GADUP	22	3.91	4.21	4.50	4.73	5.07
GAHIW	23	3.99	4.20	4.38	4.70	5.02
GASUM	37	3.74	4.18	4.34	4.50	4.89
GAWAY	24	4.03	4.44	4.67	4.78	5.24
GABFG	23	3.74	4.22	4.41	4.63	5.00
KYGRA	43	3.71	3.94	4.17	4.36	5.51
KYMAM	37	3.84	4.21	4.32	4.48	6.37
LACAR	19	4.15	4.64	5.05	5.45	6.07
LACHS	29	4.22	4.51	4.69	4.85	5.27
LAROS	34	3.97	4.49	4.74	4.98	5.51
MDRGP	39	3.55	3.94	4.03	4.31	4.72
MDBBC	32	3.51	4.02	4.34	4.52	5.45
MSUNI	34	4.00	4.39	4.55	4.72	6.50
SCCAP	36	4.02	4.30	4.53	4.81	5.16
SCCON	35	3.64	4.29	4.45	4.70	4.97
SCDEL	30	3.87	4.21	4.41	4.70	6.85
SCLON	34	3.81	4.16	4.32	4.56	5.00
TNCEN	26	3.84	4.22	4.34	4.67	4.79
WVAPC	0	0.00	0.00	0.00	0.00	0.00
WVGRN	1	4.69	1.17	2.35	3.52	4.69
WVNEW	4	4.02	4.02	4.03	4.22	4.43
WVWAR	5	3.93	3.94	4.01	4.18	4.44
SDAPR	32	4.47	5.03	5.49	5.65	6.44
SDBGP	1	5.83	1.46	2.92	4.37	5.83
SDBPR	33	4.46	5.09	5.46	5.72	6.50
SDCUS	8	4.98	5.14	5.40	5.69	6.33

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Berne I. Bennett is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Acid Precipitation Samples Collected by State Agencies," (Order No. PB 89-155 279/AS; Cost: \$42.95, subject to change) will be available only from:

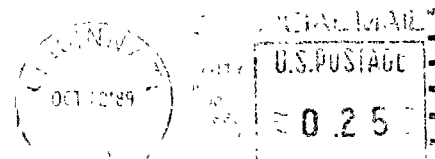
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