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HOURLY VARIABILITY OF SAMPLE CHEMISTRY DURING PRECIPITATION EVENTS AND ITS RELATIONSHIP TO METEOROLOGICAL PARAMETERS

GILBERT S. RAYNOR AND JANET V. HAYES

August 1979

ATMOSPHERIC SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

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Printed in the United States of America
Available from

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy ~~\$4.00~~; Microfiche ~~\$3.00~~

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ABSTRACT

Data from hourly precipitation samples taken at Brookhaven National Laboratory from June 1976 to May 1979 were analyzed to determine the hourly variability within precipitation events with respect to the event means for each of the chemical measurements. These included conductivity and concentrations of hydrogen, nitrogen, sulfate, ammonium, chloride, and sodium ions. The coefficient of variation ($S.D./\bar{x}$) was found for each variable in each event of three hours or more. Events were then classified by length, season, precipitation rate, and by meteorological parameters and the variability of the coefficient of variation computed for each class. Results are presented in a series of tables.

INTRODUCTION

Hourly precipitation samples have been taken at Brookhaven National Laboratory (BNL) since June 1976, using an automatic sequential precipitation collector designed and built at the Laboratory.^{1,2} These samples are analyzed for pH, conductivity, and concentrations of nitrogen, sulfate, ammonium, chloride, and sodium ions.

A primary purpose of the sampling program is to document changes in precipitation chemistry within precipitation events and to relate these changes to causative or associated meteorological factors. Longer range objectives are to determine the mechanism by which pollutants are incorporated into precipitation and to determine the source regions of the pollutants.

Statistical analyses of first-year data and of data from the first two years have been reported.^{3,4} A brief description of the program with several case studies of changes within events was given by Raynor.⁵ The purpose of this report is to document the variability of hourly measurements of chemical constituents within precipitation events as a function of meteorological parameters without regard to the temporal sequence of changes. A later study will examine temporal changes in relation to changing meteorological conditions.

METHODS

Methods used for sampling and for chemical analyses were described previously, as was the information recorded with each sample.^{3,4} Methods used for statistical analyses of data were also explained in the same reports.

For this study, the hourly chemical measurements within each event of three hours or more were analyzed to find the arithmetic mean, standard deviation, minimum, maximum, and number of samples. The coefficient of variability ($S.D./\bar{x}$), where $\bar{x}$ is the arithmetic mean and S.D. is the arithmetic standard deviation, was selected as a measure of variability within the event, computed for each chemical measurement, and treated as a new variable.

The events were then classified by season, by meteorological parameters, by duration of the precipitation event, and by average precipitation rate. The class assigned for each event was that which occurred most frequently during the event. The mean and other statistics of the coefficients of variability were then computed for each class. As in previous reports,^{3,4} a few cases for which chemical measurements were doubtful and all measurements near the limit of detectability of the analytical instruments were excluded from the analyses.

RESULTS

Results are presented in tabular form. Table 1 shows the variability of hourly chemical measurements within precipitation events for all cases for the seven chemical measurements. Table 2 shows the same information

classified by length of event. The data are classified by season in Table 3 and by synoptic type in Table 4. In Table 5, the data are subdivided by precipitation type, and in Table 6 by precipitation rate. They are classified by wind direction in Table 7, by wind speed in Table 8, and by temperature in Table 9. These data are presented for the use of other investigators and as a base for future analytical studies which will be presented elsewhere.

ACKNOWLEDGMENTS

Numerous individuals made this study possible. John McNeil assisted in design and construction of the sampler. He and Rickey Petty were responsible for its operation and for collection of the samples. Chemical analyses were performed by Mary Kinsley, Cleveland Dodge, Tom McGee, Dan Spandau, and Robert Wilson. Continued support for this project was provided by Paul Michael, Leonard Newman, and George Hendrey.

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TABLE 1 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events for All Cases

Measurement	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)	0.53	0.27	0.02	1.67	149
H^+ ($\mu\text{eq/l}$)	0.63	0.31	0.08	1.46	170
N ($\mu\text{eq/l}$)	0.62	0.32	0.04	1.81	172
SO_4^{2-} ($\mu\text{eq/l}$)	0.47	0.22	0.02	1.37	155
NH_4^+ ($\mu\text{eq/l}$)	0.67	0.30	0.14	1.75	169
Cl^- ($\mu\text{eq/l}$)	0.61	0.31	0.07	1.74	125
Na^+ ($\mu\text{eq/l}$)	0.79	0.40	0.10	2.44	144

TABLE 2 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Length of Event

Length (hr)	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
3-5	0.30	0.16	0.02	0.65	22
6-10	0.42	0.20	0.14	0.94	39
>10	0.63	0.27	0.08	1.67	88
H^+ ($\mu\text{eq/l}$)					
3-5	0.46	0.23	0.14	1.03	35
6-10	0.49	0.28	0.08	1.12	46
>10	0.77	0.30	0.17	1.46	89
N ($\mu\text{eq/l}$)					
3-5	0.38	0.24	0.04	0.93	35
6-10	0.55	0.28	0.08	1.09	46
>10	0.76	0.31	0.17	1.81	91
SO_4^{2-} ($\mu\text{eq/l}$)					
3-5	0.40	0.25	0.02	0.99	27
6-10	0.40	0.18	0.13	1.08	44
>10	0.52	0.21	0.13	1.37	84
NH_4^+ ($\mu\text{eq/l}$)					
3-5	0.50	0.26	0.14	1.15	33
6-10	0.62	0.26	0.16	1.07	45
>10	0.76	0.29	0.23	1.75	91
Cl^- ($\mu\text{eq/l}$)					
3-5	0.44	0.25	0.08	0.93	19
6-10	0.52	0.26	0.07	1.03	30
>10	0.69	0.31	0.11	1.74	76
Na^+ ($\mu\text{eq/l}$)					
3-5	0.45	0.22	0.10	0.88	20
6-10	0.63	0.32	0.17	1.37	37
>10	0.94	0.40	0.15	2.44	87

TABLE 3 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Season

Season	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
Winter	0.55	0.33	0.08	1.67	46
Spring	0.50	0.25	0.02	0.94	38
Summer	0.52	0.29	0.17	1.48	25
Fall	0.52	0.20	0.23	1.04	40
H^+ ($\mu\text{eq/l}$)					
Winter	0.58	0.32	0.08	1.43	47
Spring	0.55	0.26	0.14	1.34	44
Summer	0.66	0.28	0.20	1.40	30
Fall	0.73	0.34	0.19	1.46	49
N ($\mu\text{eq/l}$)					
Winter	0.67	0.31	0.07	1.29	52
Spring	0.61	0.30	0.11	1.52	47
Summer	0.56	0.29	0.07	1.09	28
Fall	0.63	0.38	0.04	1.81	45
SO_4^{2-} ($\mu\text{eq/l}$)					
Winter	0.50	0.25	0.15	1.37	41
Spring	0.45	0.22	0.02	1.08	46
Summer	0.46	0.16	0.21	0.74	26
Fall	0.46	0.22	0.13	1.00	42
NH_4^+ ($\mu\text{eq/l}$)					
Winter	0.71	0.30	0.22	1.75	50
Spring	0.63	0.29	0.16	1.55	47
Summer	0.65	0.31	0.18	1.22	27
Fall	0.70	0.30	0.14	1.59	45
Cl^- ($\mu\text{eq/l}$)					
Winter	0.64	0.32	0.07	1.53	41
Spring	0.59	0.31	0.08	1.49	35
Summer	0.65	0.41	0.22	1.74	13
Fall	0.59	0.25	0.11	1.03	36
Na^+ ($\mu\text{eq/l}$)					
Winter	0.94	0.42	0.27	1.89	45
Spring	0.73	0.35	0.10	1.43	41
Summer	0.70	0.53	0.17	2.44	19
Fall	0.73	0.34	0.15	1.75	39

TABLE 4 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Synoptic Type

Type	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
Low	0.41	0.13	0.11	0.59	12
Warm Front	0.60	0.27	0.14	1.48	67
Cold Front	0.45	0.30	0.02	1.67	35
Occluded Front	0.49	0.33	0.08	1.03	11
Stationary Front	0.53	0.20	0.14	0.79	17
Squall Line	0.48	0.26	0.20	0.81	5
H^+ ($\mu\text{eq/l}$)					
Low	0.57	0.30	0.14	1.46	18
Warm Front	0.65	0.32	0.09	1.43	73
Cold Front	0.60	0.30	0.08	1.35	41
Occluded Front	0.51	0.25	0.17	0.91	11
Stationary Front	0.69	0.30	0.27	1.30	19
Squall Line	0.63	0.42	0.19	1.34	6
N ($\mu\text{eq/l}$)					
Low	0.48	0.31	0.08	1.03	19
Warm Front	0.69	0.34	0.07	1.81	74
Cold Front	0.55	0.26	0.04	1.04	40
Occluded Front	0.60	0.29	0.29	1.20	13
Stationary Front	0.69	0.36	0.16	1.51	18
Squall Line	0.60	0.37	0.07	1.05	6
SO_4^{2-} ($\mu\text{eq/l}$)					
Low	0.37	0.17	0.13	0.69	15
Warm Front	0.49	0.20	0.18	1.01	69
Cold Front	0.46	0.25	0.02	1.08	37
Occluded Front	0.52	0.32	0.20	1.37	12
Stationary Front	0.44	0.17	0.13	0.74	14
Squall Line	0.51	0.23	0.23	0.74	5
NH_4^+ ($\mu\text{eq/l}$)					
Low	0.58	0.25	0.19	0.93	18
Warm Front	0.72	0.31	0.22	1.59	74
Cold Front	0.63	0.27	0.14	1.15	40
Occluded Front	0.70	0.41	0.16	1.75	12
Stationary Front	0.66	0.25	0.25	1.09	17
Squall Line	0.62	0.32	0.37	1.16	5
Cl^- ($\mu\text{eq/l}$)					
Low	0.55	0.24	0.11	0.99	14
Warm Front	0.69	0.31	0.22	1.74	58
Cold Front	0.51	0.27	0.08	1.15	29
Occluded Front	0.60	0.41	0.20	1.53	11
Stationary Front	0.52	0.37	0.07	1.11	8
Squall Line	0.53	0.14	0.40	0.67	3

TABLE 4 - Synoptic Type (continued)

Type	Mean	S.D.	Min	Max	No.
	Na ⁺ (μeq/l)				
Low	0.68	0.30	0.13	1.30	15
Warm Front	0.89	0.43	0.17	2.44	67
Cold Front	0.66	0.33	0.10	1.38	34
Occluded Front	0.69	0.44	0.26	1.77	12
Stationary Front	0.81	0.55	0.15	1.75	10
Squall Line	0.81	0.22	0.51	0.97	4

TABLE 5 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Precipitation Type

Type	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
Rain	0.58	0.28	0.11	1.67	106
Rainshower	0.36	0.17	0.02	0.67	22
Thundershower	0.67	0.11	0.55	0.76	4
Mixed	0.27	0.12	0.14	0.38	3
Sleet	0.38	-	-	-	1
Snow	0.36	0.22	0.08	0.77	13
H^+ ($\mu\text{eq/l}$)					
Rain	0.69	0.32	0.08	1.46	117
Rainshower	0.50	0.27	0.14	1.10	29
Thundershower	0.61	0.09	0.54	0.75	4
Mixed	0.46	0.09	0.38	0.56	3
Sleet	0.35	-	-	-	1
Snow	0.42	0.26	0.09	0.86	15
N ($\mu\text{eq/l}$)					
Rain	0.67	0.32	0.15	1.81	115
Rainshower	0.48	0.30	0.04	1.05	29
Thundershower	0.79	0.28	0.35	1.09	5
Mixed	0.73	0.41	0.39	1.27	4
Sleet	0.96	-	-	-	1
Snow	0.44	0.27	0.07	0.96	18
SO_4^{2-} ($\mu\text{eq/l}$)					
Rain	0.49	0.22	0.02	1.37	108
Rainshower	0.42	0.26	0.02	1.08	26
Thundershower	0.56	0.22	0.27	0.74	4
Mixed	0.44	0.31	0.23	0.79	3
Sleet	0.48	-	-	-	1
Snow	0.38	0.11	0.19	0.56	13
NH_4^+ ($\mu\text{eq/l}$)					
Rain	0.71	0.30	0.16	1.75	113
Rainshower	0.59	0.30	0.14	1.16	30
Thundershower	0.79	0.32	0.32	1.01	4
Mixed	0.74	0.17	0.61	0.98	4
Sleet	0.42	-	-	-	1
Snow	0.59	0.25	0.22	1.05	17
Cl^- ($\mu\text{eq/l}$)					
Rain	0.65	0.31	0.11	1.74	93
Rainshower	0.46	0.24	0.08	0.86	16
Thundershower	1.03	-	-	-	1
Mixed	0.62	0.54	0.07	1.15	3
Sleet	0.53	-	-	-	1
Snow	0.48	0.24	0.20	0.94	11

TABLE 5 - Precipitation Type (continued)

Type	Mean	S.D.	Min	Max	No.
	Na ⁺ (μeq/l)				
Rain	0.85	0.41	0.15	2.44	106
Rainshower	0.57	0.27	0.10	0.97	19
Thundershower	0.61	0.66	0.23	1.37	3
Mixed	0.97	0.13	0.88	1.06	2
Sleet	0.76	-	-	-	1
Snow	0.68	0.38	0.27	1.68	13

TABLE 6 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Average Precipitation Rate

Rate (mm/hr)	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
0.0-1.0	0.51	0.26	0.02	1.48	115
1.1-2.5	0.53	0.23	0.24	0.98	17
2.6-6.0	0.82	0.25	0.55	1.03	3
6.1-12.0	0.38	-	-	-	1
H^+ ($\mu\text{eq/l}$)					
0.0-1.0	0.65	0.33	0.08	1.46	135
1.1-2.5	0.60	0.27	0.24	1.34	18
2.6-6.0	0.46	0.21	0.25	0.66	3
6.1-12.0	0.40	-	-	-	1
N ($\mu\text{eq/l}$)					
0.0-1.0	0.63	0.34	0.04	1.81	137
1.1-2.5	0.51	0.26	0.18	1.08	18
2.6-6.0	0.74	0.09	0.68	0.80	2
6.1-12.0	0.80	-	-	-	1
SO_4^{2-} ($\mu\text{eq/l}$)					
0.0-1.0	0.47	0.23	0.02	1.37	125
1.1-2.5	0.42	0.20	0.02	0.76	15
2.6-6.0	0.54	0.14	0.44	0.64	2
6.1-12.0	0.23	-	-	-	1
NH_4^+ ($\mu\text{eq/l}$)					
0.0-1.0	0.67	0.31	0.14	1.75	136
1.1-2.5	0.63	0.25	0.32	1.10	17
2.6-6.0	0.67	0.13	0.58	0.76	2
6.1-12.0	0.51	-	-	-	1
Cl^- ($\mu\text{eq/l}$)					
0.0-1.0	0.59	0.30	0.07	1.74	102
1.1-2.5	0.56	0.27	0.16	1.03	12
2.6-6.0	1.31	0.32	1.08	1.53	2
6.1-12.0	0.43	-	-	-	1
Na^+ ($\mu\text{eq/l}$)					
0.0-1.0	0.79	0.41	0.10	2.44	114
1.1-2.5	0.69	0.25	0.23	1.14	16
2.6-6.0	1.08	0.75	0.28	1.77	3
6.1-12.0	1.10	-	-	-	1

TABLE 7 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Wind Direction

Direction	Mean	S.D.	Min	Max	No.
Conductivity ($\mu\text{mhos/cm}$)					
N	0.43	0.18	0.20	0.74	11
NE	0.50	0.22	0.08	1.04	31
E	0.62	0.28	0.15	1.10	27
SE	0.52	0.30	0.11	1.16	13
S	0.61	0.38	0.02	1.67	20
SW	0.47	0.20	0.14	0.84	20
W	0.42	0.23	0.21	0.64	4
NW	0.36	0.18	0.11	0.65	7
H^+ ($\mu\text{eq/l}$)					
N	0.67	0.24	0.14	1.11	12
NE	0.68	0.33	0.17	1.30	35
E	0.67	0.33	0.09	1.46	30
SE	0.72	0.38	0.30	1.43	14
S	0.58	0.29	0.20	1.34	21
SW	0.62	0.32	0.14	1.35	25
W	0.57	0.32	0.08	0.90	6
NW	0.41	0.16	0.15	0.64	9
N ($\mu\text{eq/l}$)					
N	0.53	0.38	0.04	1.15	14
NE	0.65	0.34	0.07	1.51	37
E	0.73	0.31	0.25	1.52	31
SE	0.59	0.32	0.15	1.26	14
S	0.59	0.38	0.11	1.81	22
SW	0.60	0.25	0.07	1.05	22
W	0.66	0.28	0.25	1.01	7
NW	0.48	0.34	0.08	1.00	10
SO_4^{2-} ($\mu\text{eq/l}$)					
N	0.39	0.17	0.13	0.69	10
NE	0.43	0.17	0.13	0.76	29
E	0.53	0.25	0.23	1.37	30
SE	0.51	0.26	0.14	1.08	14
S	0.45	0.26	0.02	1.00	19
SW	0.49	0.21	0.23	1.01	23
W	0.41	0.20	0.26	0.74	6
NW	0.46	0.30	0.02	0.99	9
NH_4^+ ($\mu\text{eq/l}$)					
N	0.57	0.26	0.25	0.93	12
NE	0.66	0.29	0.14	1.26	35
E	0.83	0.36	0.22	1.75	30
SE	0.60	0.29	0.18	1.04	14
S	0.65	0.30	0.16	1.42	22
SW	0.66	0.23	0.35	1.16	24
W	0.60	0.25	0.27	0.86	6
NW	0.66	0.26	0.34	1.05	10

TABLE 7 - Wind Direction (continued)

Direction	Mean	S.D.	Min	Max	No.
Cl^- ($\mu\text{eq}/\ell$)					
N	0.46	0.26	0.22	0.82	6
NE	0.58	0.28	0.07	1.15	28
E	0.69	0.26	0.31	1.53	26
SE	0.63	0.32	0.11	1.13	11
S	0.64	0.34	0.08	1.15	19
SW	0.51	0.24	0.11	1.03	19
W	0.49	0.11	0.41	0.56	2
NW	0.51	0.32	0.16	0.81	4
Na^+ ($\mu\text{eq}/\ell$)					
N	0.73	0.44	0.15	1.44	8
NE	0.75	0.35	0.26	1.75	31
E	0.88	0.38	0.18	1.77	28
SE	0.69	0.39	0.13	1.30	13
S	0.84	0.45	0.10	1.50	21
SW	0.77	0.34	0.27	1.37	18
W	0.74	0.21	0.57	0.97	3
NW	0.61	0.37	0.27	1.33	7

TABLE 8 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Wind Speed

Speed (msec ⁻¹)	Mean	S.D.	Min	Max	No.
Conductivity (μmhos/cm)					
0-2	0.25	0.13	0.11	0.48	8
3-5	0.49	0.25	0.14	1.48	48
6-9	0.53	0.27	0.02	1.67	63
≥10	0.73	0.24	0.26	1.10	15
H ⁺ (μeq/l)					
0-2	0.43	0.22	0.09	0.76	10
3-5	0.65	0.34	0.20	1.46	61
6-9	0.60	0.28	0.08	1.25	68
≥10	0.77	0.30	0.34	1.34	16
N (μeq/l)					
0-2	0.36	0.14	0.11	0.63	12
3-5	0.59	0.30	0.16	1.51	56
6-9	0.64	0.29	0.04	1.29	73
≥10	0.72	0.40	0.08	1.52	16
SO ₄ ²⁻ (μeq/l)					
0-2	0.36	0.18	0.14	0.79	11
3-5	0.41	0.16	0.13	0.82	49
6-9	0.50	0.25	0.02	1.37	65
≥10	0.53	0.17	0.23	0.81	16
NH ₄ ⁺ (μeq/l)					
0-2	0.51	0.26	0.16	0.93	12
3-5	0.61	0.28	0.14	1.31	54
6-9	0.70	0.30	0.16	1.75	72
≥10	0.72	0.32	0.23	1.55	16
Cl ⁻ (μeq/l)					
0-2	0.31	0.23	0.07	0.65	6
3-5	0.56	0.30	0.11	1.74	36
6-9	0.62	0.31	0.08	1.53	57
≥10	0.71	0.25	0.31	1.03	15
Na ⁺ (μeq/l)					
0-2	0.48	0.27	0.13	0.88	8
3-5	0.72	0.43	0.15	2.44	43
6-9	0.81	0.38	0.10	1.77	63
≥20	0.91	0.41	0.34	1.89	16

TABLE 9 Variability of Coefficient of Variation of Hourly Chemical Measurements Within Precipitation Events by Air Temperature

Speed (msec ⁻¹)	Mean	S.D.	Min	Max	No.
Conductivity (μmhos/cm)					
<0.0	0.36	0.22	0.08	0.77	12
0.0-9.9	0.54	0.27	0.11	1.10	57
10.0-19.9	0.54	0.27	0.02	1.67	60
20.0-29.9	0.54	0.32	0.20	1.48	16
H ⁺ (μeq/l)					
<0.0	0.46	0.31	0.09	1.11	15
0.0-9.9	0.59	0.27	0.08	1.30	64
10.0-19.9	0.71	0.32	0.17	1.43	66
20.0-29.9	0.63	0.34	0.19	1.46	20
N (μeq/l)					
<0.0	0.47	0.32	0.07	1.27	19
0.0-9.9	0.69	0.32	0.04	1.52	64
10.0-19.9	0.62	0.28	0.11	1.26	64
20.0-29.9	0.57	0.40	0.07	1.81	20
SO ₄ ²⁻ (μeq/l)					
<0.0	0.41	0.16	0.19	0.79	13
0.0-9.9	0.46	0.24	0.02	1.37	57
10.0-19.9	0.48	0.20	0.02	0.99	62
20.0-29.9	0.43	0.21	0.21	1.00	18
NH ₄ ⁺ (μeq/l)					
<0.0	0.59	0.23	0.22	1.01	18
0.0-9.9	0.71	0.32	0.16	1.75	61
10.0-19.9	0.66	0.29	0.14	1.59	67
20.0-29.9	0.69	0.30	0.25	1.42	18
Cl ⁻ (μeq/l)					
<0.0	0.55	0.27	0.20	1.15	14
0.0-9.9	0.63	0.33	0.07	1.53	47
10.0-19.9	0.59	0.27	0.08	1.15	50
20.0-29.9	0.75	0.43	0.22	1.74	11
Na ⁺ (μeq/l)					
<0.0	0.73	0.38	0.27	1.68	14
0.0-9.9	0.83	0.39	0.13	1.77	56
10.0-19.9	0.77	0.38	0.10	1.89	56
20.0-29.9	0.77	0.62	0.17	2.44	13