THE EFFECT OF A LOCAL SOURCE ON THE COMPOSITION OF PRECIPITATION IN SOUTH-CENTRAL MAINE

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ABSTRACT

Bulk precipitation samples were collected from ten sites in south-central Maine during the period 18 June to 30 September 1974. Data from the chemical analyses of the precipitation were used to determine regional deposition patterns of the ionic constituents. Acidic pH values ranging from 3.8 to 5.0 are characteristic of the region, but relatively alkaline pH values of 5.5 to 7.0 were observed in the precipitation from one collection site. Systematic increases in sulphate and sodium deposition in the samples from this site suggest a local source.

The observations of the bulk precipitation analysis lead to a study of the chemical composition of precipitation near a kraft paper mill. Samples were collected during single precipitation events. The results indicate that this source can affect background levels of composition up to a distance of at least 20 km and that considerable care must be taken in the selection of sites for sampling background precipitation.

INTRODUCTION

Long-range transport of anthropogenic sulfur dioxide and sulfate aerosols from industrial emissions in Great Britain and Northern Europe has been shown to significantly influence the chemical composition of precipitation over regions of Scandinavia (Rodhe et al. 1972). The State of Maine represents a situation which in some respects is similar to that of southern Scandinavia. During periods of prevailing southerly and southwesterly winds common in May through September (Court 1974), Maine lies downwind of major industrial development.

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Little intensive precipitation monitoring has been initiated in New England, except the work at Hubbard Brook in New Hampshire by Likens et al. (1975). Two collection sites established in Maine by the United States Geological Survey comprised a small component of a large-scale northeastern regional study by Pearson and Fisher (1971).

In the present study, a network of collection sites was developed in south-central Maine for the sampling and analysis of bulk precipitation. Analyses included conductivity, pH, sulfate, nitrate, sodium, and calcium determinations. Data from this phase of the investigation provides preliminary information on the relationship between acidity and the chemical composition of the precipitation and to some extent distinguished the contributions of rainfall and dry deposition.

The results of this brief regional study are shown to be unexpectedly conditioned by local sources, and a more detailed study was undertaken in the vicinity of a large kraft-process pulpmill.

EXPERIMENTAL PROCEDURES

COLLECTION OF PRECIPITATION SAMPLES

Ten sites in south-central Maine were selected for sampling bulk precipitation during the summer of 1974 (fig. 1). The locations for the collectors were chosen to provide a representative picture of regional variations in precipitation chemistry. A wide variety of terrain was included: coastal, urban, and inland rural areas. Collectors were placed well away from heavily traveled roads, buildings, and trees. Each collector was exposed for 2 or 4 week intervals during the period 18 June to 30 September 1974. Sampling periods included 2 week intervals between 18 June and 12 August and a 4 week span from 12 August to 10 September. Insufficient volumes of precipitation were obtained during a 2 week dry spell from 31 July to 12 August, so data for this interval have been omitted.

Two-liter plastic milk bottles were used as collection containers. A 15-cm diameter polyethylene funnel was inserted into the bottle, creating an effective sampling surface of about 175 cm^2. The funnels were placed 0.4 to 1.0 m above ground level. Packaged presterilized bottles were cleansed thoroughly with a brush and detergent and then rinsed several times with distilled water. The rinse water from several containers had no measurable levels of the ions studied here.

After collection, the samples were subjected to crude filtration, using glass wool to remove odd bits of organic matter. The filtration step was included in the treatment of the blank. Subsequent analysis indicated that use of this collection procedure did not contaminate the precipitation samples.

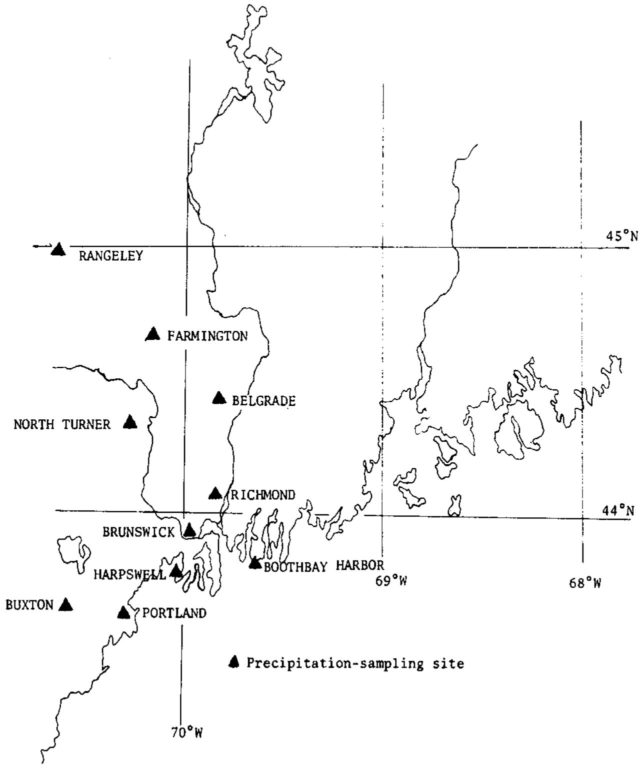

Figure 1. Locations of bulk precipitation sampling sites in Maine.

A slight modification of the sampling procedure was required during the second phase of the study. Twenty-five-centimeter glass funnels were used to increase the effective collection surface to about 500 cm^2. These collectors were placed at 10 locations around the pulpmill in Jay, Maine, as illustrated in figure 2. The glass funnels were washed and rinsed in the manner described previously and covered with a sheet of polyethylene until time of sampling. This prevented contamination of the collector by dry deposition prior to the precipitation events. Samples were capped and transported immediately following termination of the rainfall. Precipitation was collected in this manner on 13 and 15 November. Control experiments demonstrated that leaching of sodium from the glass funnels did not introduce significant levels of contamination.

Snow samples associated with the precipitation of 13 January and 5 February 1975 were also obtained. The snow was collected in the immediate proximity of the rain collectors. Sites were selected at a distance greater than 50 meters from roadways to avoid contamination from salting and sanding operations. After removal of the top 3 to 4 cm of snow, samples were taken from an area of about 1 m^2 to a depth of 6 to 8 cm. Forland and Gjessing (1970) demonstrated that constituents arising from dry deposition and absorption of gases contaminate only the

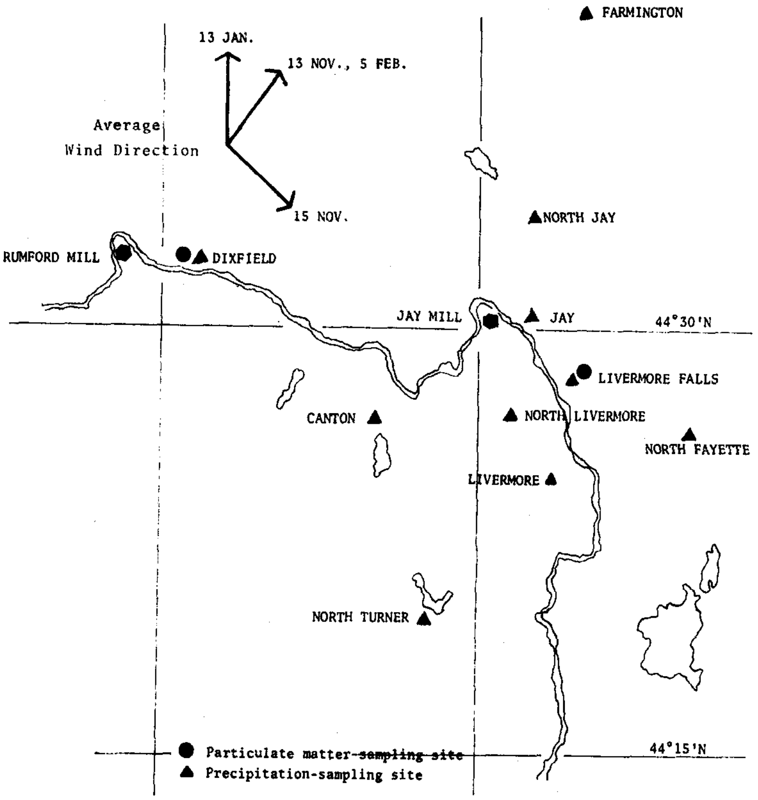

Figure 2. Locations of rain and snowfall sampling sites around the kraft paper mill at Jay, Maine.

upper 2 to 3 cm of snowfall. Samples were collected with a clean plastic shovel, stored in polyethylene bags, and allowed to melt prior to analysis.

COLLECTION OF PARTICULATE MATTER SAMPLES

Samples of suspended particulate matter were collected from areas near the pulpmill during each precipitation period. In addition to the principal source under investigation, a second kraft-process mill is located in Rumford, about 30 km west of Jay. Two high-volume air samplers were used to collect particulate matter associated with both sources. One sampler was placed at Livermore Falls, 5 km south of the Jay facility. The second was placed in Dixfield, about 15 km northwest of Jay and between the two sources. Precipitation collectors were placed next to the high-volume samplers at each location.

Each high-volume filter was cut into quarters, and the soluble matter was extracted with 300 ml of distilled water for a 24 hour period, using a Soxhlet extractor. Extraction thimbles were not used due to the high concentrations of sodium found to result from their use. To determine the contribution of ions from the glass fiber filters, the extraction from several clean filters was used as a blank.

METEOROLOGICAL MEASUREMENTS

Meteorological data for the precipitation of 13 and 15 November were obtained with a portable recording instrument. Wind speed, direction, and temperature were recorded from the summit of a hill located about 5 km south of the Jay mill. Due to servicing of the equipment, hourly observations 13 January and 5 February 1975 were obtained from the Brunswick Naval Air Station, located about 60 km south of the Jay mill.

CHEMICAL ANALYSES

The pH and electrical conductivity of the samples were determined at the time of filtration. Conductivity was measured with an Industrial Instruments Model 16B1 Wheatstone Bridge. The pH was measured with a London Instruments Model PHM Research pH Meter. Nitrate ion was determined, using the cadmium reduction method described by Gleason (1973). Sulfate was determined by the barium sulfate turbidity method outlined in *Standard Methods for the Examination of Water and Wastewater* (Amer. Public Health Assoc., 1971). To achieve the desired sensitivity for sulfate, the samples were concentrated by evaporation by a factor of 10 before analysis. Metal analyses were performed with a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer.

DATA

EMISSION DATA

There are two sources of sulfur dioxide and particulate matter in the rain-collection area: the kraft-process mill at Jay, Maine and a second, similar mill located about 30 km to the west in Rumford. The emission data were based on 1973 figures obtained from the Bureau of Air Quality Control of the Maine Department of Environmental Protection. The pulpmill at Jay emits an average of 1570 kg h^{-1} of sulfur dioxide and 665 kg h^{-1} of particulate matter. The Rumford facility emits about 880 kg h^{-1} of sulfur dioxide and 442 kg h^{-1} of particulate matter. Particulate emissions from the Jay mill include significant amounts of sodium sulfate and other sodium salts.

METEOROLOGICAL DATA

A prevailing northeasterly wind accompanied the precipitation of 13 November 1974 and 5 February 1975. The rainfall of 14 and 15 November was associated with surface winds from the south and southeast, while northerly winds occurred during the snowfall of 13 January 1975.

PARTICULATE MATTER ANALYSES

Results of the chemical analyses of total suspended particulate matter for each sampling period are shown in Table I. A significant decrease in concentration for the Livermore Falls sample of 15 November reflects the upwind location of this site. The high particulate matter concentration at Dixfield on 5 February very likely results from the consistent easterly wind between 1600 and 2400 hours on that date, which placed this site downwind from the Jay mill.

TABLE I. Data Summary for Particulate Matter Samples ($\mu g\ m^{-3}$)

Sample	Date	Total Mass. Conc.	$[Na^+]$	$[Ca^{2+}]$	$[SO_4^{2-}]$	$[NO_3^-]$
Livermore Falls	11/13	39	5.42	<0.05	3.19	0.92
Livermore Falls	11/15	14	3.33	<0.05	8.80	1.55
Livermore Falls	1/13	50	4.16	0.05	24.57	3.80
Livermore Falls	2/5	43	3.35	0.22	11.09	1.79
Dixfield	11/13	43	2.00	<0.05	5.15	0.10
Dixfield	11/15	41	1.60	0.22	11.50	0.74
Dixfield	1/13	87	0.67	0.42	12.43	0.36
Dixfield	2/5	57	10.22	0.51	21.07	0.42

PRECIPITATION ANALYSES

Expression of chemical composition of precipitation in terms of concentration is not always the most useful parameter for a discussion of regional variations. Ionic concentrations in precipitation are subject to changes resulting from evaporation during sampling, which can become particularly significant over a 2 week sampling period. Losses due to sample evaporation may vary from site to site. These losses have not been evaluated in this study; thus only the deposition of ions for the period 18 June to 31 July are presented in table II.

TABLE II. Total Deposition in Bulk Precipitation (Mg m^{-2})

Sample	Na^+	Ca^{2+}	SO_4^{2-}	NO_3^-	Rainfall (cm)	$[H^+]$ [b]
Boothbay Harbor	146	49	156	198	10.0	6.73
Harpswell	76	30	109	155	8.7	3.26
Portland	82	61	175	177	10.1	3.99
Brunswick	49	45	139	146	7.4	2.83
Richmond [a]	13	17	67	93	4.1	3.59
Buxton [a]	7	9	71	89	3.6	6.62
North Turner	79	46	185	220	12.3	1.75
Belgrade	103	54	152	248	14.8	1.65
Farmington	165	151	295	315	21.7	0.14
Rangeley	66	27	122	61	14.2	2.62

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[a] Deposition based on Two Sampling periods.

[b] Evaluated from pH = $-\log [H^+]$

RESULTS AND DISCUSSION

Sodium deposition shows a sharp gradient with increasing distance from the ocean. Such a distribution is clearly attributable to sea salt aerosols which become incorporated into coastal precipitation. Sulfate, nitrate, and calcium content is fairly constant over much of the sampling network. This uniformity seems to suggest that most of these ions originate from distant or natural sources.

Unusually high sodium deposition values were evident in precipitation samples from each site during 18 June to 2 July. The ion loads for this period constitute between 55 and 90% of the six week total even though rainfall amounts were of equal magnitude to those during other bi-weekly periods. Examination of synoptic surface weather charts reveals the passage of a series of low pressure troughs off the Maine coast during 22 to 27 June. Constant east to northeasterly winds associated with these systems produced an influx of marine air into the region, resulting in a prolonged period of rain and fog. A network average pH of 5.8 was observed during this two week period. For the rest of the six week sampling period, precipitation originated mainly from convective showers associated with frequent frontal passages through the region. The pH values for these periods ranged from 4.0

to 5.0.

Total depositions of Na^+, Ca^{2+}, $SO_4^=$, and NO_3^- are plotted as a function of precipitation amount in order to examine the origin of each constituent (Figures 3 and 4). Pearson and Fisher (1971) note that dry

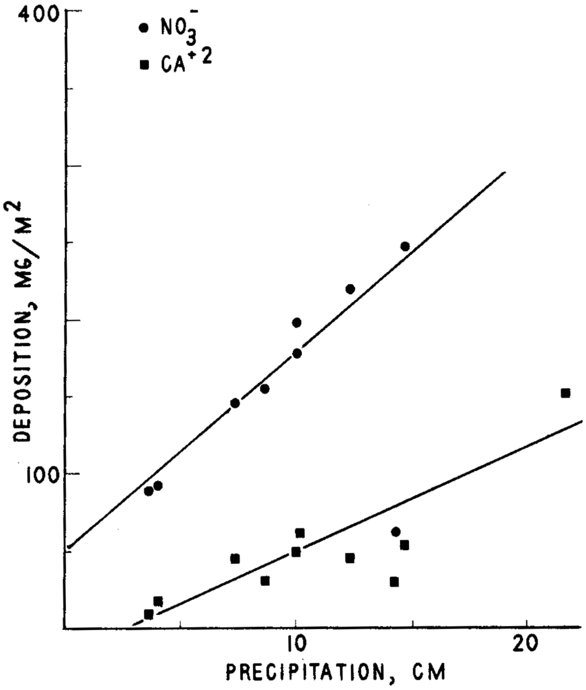

Figure 3. Deposition of nitrate and calcium versus precipitation amount for the period of 18 June to 31 July, 1974.

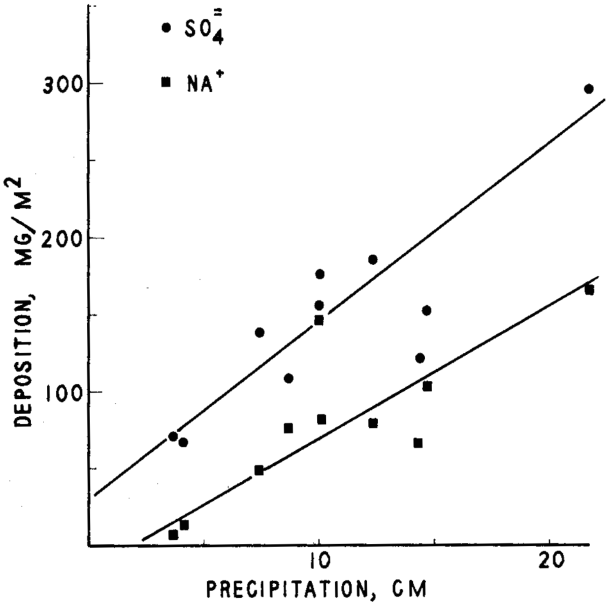

Figure 4. Deposition of sulphate and sodium versus precipitation amount for the period of 18 June to 31 July, 1974.

fallout should be deposited in amounts independent of the amount of rainfall, whereas those substances dissolved in precipitation should have loads that vary with precipitation amount. The data used in the plots are drawn from Table II. The data for Rangeley was not considered in drawing any of the least square lines. In addition, the Boothbay Harbor data, representing a marine source, and the Farmington data, greatly influenced by a local source, were not taken into account for the sodium correlation. The results for nitrate, sulfate and sodium suggest that these ions are mainly incorporated through precipitation processes. Low yields of these three ions in the Rangeley samples reflects the "unpolluted" rural atmosphere of this area. Excess sodium in the Boothbay Harbor precipitation very likely arises from dry deposition of sea salt aerosols. Calcium varies somewhat irregularly with precipitation amount, suggesting that soil dust and particulate matter entering as dry deposition may be important sources.

A great deal of the acidity and sulfate found in precipitation has been found to arise from the oxidation of sulfur dioxide and, perhaps, nitrogen oxides. In the absence of alkaline materials, the simple model projected by Scott and Hobbs (1967) predicts a decrease in pH with increasing quantities of sulfate ion. This relationship was observed in many of the bulk precipitation samples. In contrast, however, the Farmington and Belgrade samples were relatively alkaline (pH between 5.7 and 7.1). Corresponding increases in sulfate, nitrate, sodium, and calcium were also observed. Two factors appear to reduce the predicted acidity. The first involves the presence of large amounts of basic substances, as reflected by the sodium and calcium levels. Second, the large depositions of sulfate may not arise from the oxidation of sulfur dioxide, but rather from the presences of sulfate salts emmitted form a local source.

Rainout, or removal by cloud processes, has a high overall efficiency for the removal of gaseous pollutants such as sulfur dioxide, which become widely dispersed in the atmosphere during long range transport. Sulfate and nitrate contained in bulk precipitation was shown to arise primarily from rainout/washout. Because emissions from a point source must travel a great distance before intersecting the cloud layer, washout is expected to dominate as the primary mechanism in the vicinity of the source. This assumption serves as the basis for comparisons of the composition of particulate matter and precipitation.

Results of the chemical analyses of the rain and snow samples collected in the vicinity of the Jay mill are reported in Table III. The concentrations of the 15 November samples are significantly greater than those collected during the other precipitation events. Comparatively small amounts of precipitation (the network average was 0.3 cm) were deposited by a series of brief showers. This is in sharp contrast to samples collected from a twenty-four hour continuous rainfall on 13 November which deposited an average of 2.9 cm of rain. Gambell and Fisher (1964) report that small amounts of rainfall are subject to large changes in constituent concentration due to evaporation and other

TABLE III. Ion Concentrations in Rain and Snow Samples (mg ℓ^{-1})

Sample	Date	$[Na^+]$	$[Ca^{2+}]$	$[SO_4^{2-}]$	$[NO_3^-]$	pH
Farmington	11/13	0.32	0.17	1.24	1.12	4.99
	11/15	3.96	1.20	--	12.80	4.02
	1/13	4.24	0.40	0.52	1.70	4.72
	2/5	0.88	0.10	0.16	0.80	--
North Jay	11/13	0.55	0.10	0.80	0.58	5.38
	11/15	2.08	1.55	--	11.50	4.77
	1/13	0.12	0.15	0.20	1.60	4.89
	2/5	0.25	0.18	0.18	1.00	--
Jay	11/13	0.34	0.15	0.40	0.75	5.41
	11/15	1.92	4.55	--	11.20	6.61
	1/13	1.00	0.85	3.84	1.40	5.95
	2/5	1.09	0.90	3.76	0.90	--
Livermore Falls	11/13	0.12	<0.05	0.36	0.83	5.01
	11/15	1.64	1.20	--	9.50	3.97
	1/13	0.10	0.15	0.14	1.30	4.71
	2/5	0.59	0.35	1.80	0.75	--
North Fayette	11/13	0.15	<0.05	0.57	1.42	5.16
	11/15	1.04	0.45	--	9.30	4.00
	1/13	0.11	0.15	0.26	1.15	4.82
	2/5	0.23	0.10	0.79	0.85	--
Livermore	11/13	0.36	<0.05	0.67	0.80	5.93
	11/15	1.00	0.40	--	9.50	4.04
	1/13	0.12	0.12	0.29	0.90	4.78
	2/5	0.20	<0.05	0.26	0.97	--
North Turner	11/13	0.11	<0.05	0.56	0.20	4.96
	11/15	0.95	0.60	--	3.50	3.96
	1/13	0.11	0.15	0.56	1.30	4.75
	2/5	0.22	0.05	0.38	0.35	--
North Livermore	11/13	1.52	0.20	2.82	1.05	5.62
	11/15	0.98	0.85	--	9.00	4.06
	1/13	2.06	0.85	7.50	1.65	4.91
	2/5	0.81	0.42	2.92	0.77	--
Dixfield	11/13	0.32	0.17	1.24	1.12	6.36
	11/15	4.12	1.50	--	10.30	4.29
	1/13	0.27	0.10	0.44	1.70	4.70
	2/5	1.92	0.20	0.32	1.15	--
Canton	2/5	0.88	0.10	0.16	0.80	--

processes.

The concentrations of all ions vary considerably from site to site in the vicinity of the Jay mill. With a prevailing northeasterly wind, the North Livermore and Dixfield sites are downwind from the source and had sulphate concentrations of 300% and 90% above the network background. Increases of a similar magnitude are seen in snow collected downwind from the source on 13 January and 5 February. Similar variations are seen in the sodium concentration. The concentration of 1.52 mg ℓ^{-1} sodium collected downwind from the source on 13 November is more than five times the background concentration for that date. The pH of samples ranged from 3.97 to 6.36. Higher pH values were characteristic of rain and snow collected downwind from the mill.

In the particulate matter, sodium and sulfate comprise the major constituents of the ions analyzed. The correlation between wind direction and the chemical composition of particulate matter and precipitation permits a qualitative observation on the effects of the Jay mill.

CONCLUSIONS

While the results of this brief regional bulk precipitation study are tentative, two factors make the results from the individual precipitation events particularly interesting. Firstly, the kraft mill appears to contribute a buffering influence on rain and snow, balancing the acidic character of the regional precipitation. Most previous studies have been concerned with the increased acidity produced by point sources of sulfur dioxide and other pollutants. Secondly, the results show that this effect can be observed at considerable distances downwind from the source. While the magnitude of the increases in deposition of ions from these sources may not be significant for large scale regional considerations, the influence of an individual facility may extend to greater distances from the source than would be observed in an urban background. With the large number of pulp mills in Maine, the data stresses the importance of considering their influence on precipitation chemistry in establishing a regional precipitation network.

ACKNOWLEDGMENT

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