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ACID PRECIPITATION AND ITS EFFECTS ON WATER QUALITY OF SMALL RIVER BASINS IN RHODE ISLAND*

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ABSTRACT

The effects of acid precipitation on the water acidity, alkalinity, and pH of three small rivers in Rhode Island rural areas were studied. Satellite pictures, radar scans, and pressure maps were used to trace storm paths. In general more acidity was found in storms coming from the west-southwest direction. Rainfall pH as low as 3.81 and another rainfall with strong acid components at a concentration of 1.59×10^{-4} N were recorded. The degree of impact on river water quality depended on storm acidity, storm size, amount of dry deposition prior to the storm, river flow prior to the storm, and land use pattern in the watershed. It was found that a drop of half a pH unit in a river could take place in one-half day. The largest pH drop recorded was 2.15 units and the largest increase of acidity was eleven fold. The impact on water quality could last longer than five days from the onset of the maximum impact, which generally coincided with that of the peak flow, to the time of recovery of the pre-storm water acidity, alkalinity, and pH.

INTRODUCTION

A great concern over the acidification of freshwater ecosystems, reduction in visibility, nutrient and toxic metal leaching from soil, effects on human health, and damage to materials, has been expressed in the final draft of the joint US/Canadian report on Acid Precipitation and the Long Range Transport of Air

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Pollutants in Eastern Canada and New England [1]. Calculations of sulfate deposits for the months of January and August 1977 using the EURMAP model showed that one-quarter of the deposition occurring in New York and New Jersey region originated in Pennsylvania, Virginia, and West Virginia; another quarter originated in Ohio, Indiana, Illinois, Mississippi, Wisconsin [2]. Other Studies also reported that high sulfate depositions were associated with emissions of SO_4 to the south and southwest of New York state, i.e., Ohio River Valley origin [3-5].

While many studies tend to indicate most sulfate deposits originate from the midwestern states, one study also showed in calculations that one-quarter of the sulfate deposition occurring in New York and New Jersey originated in regions north and south of the New York-New Jersey area [2]. Another study suggested that acid deposition in the Adirondack Mountains might come from Ontario [6]. Statistical analyses of precipitation data showed little change in pH from 1965-78 within New York State as a whole, but the pH of bulk precipitation has decreased in the western part of the state by 0.2 pH units since 1965 and increased in the eastern part by a similar amount [7]. Also, stream water analyses of the same study showed that sulfate concentrations decreased an average of 1 to 4 percent per year.

In the New England states a statistical analysis of air quality and meteorological data in Connecticut showed that as much as 70 percent of the atmospheric particulates, of which 25 percent by mass were sulfates and nitrates, were attributable to sources outside the state [8,9]. Recently, data on peak sulfate loadings in Maine and Vermont were compared and they were almost identical [10]. Similarly, a report indicated a relatively uniform spread of SO_4 from west to east across the state of Massachusetts in precipitation events [11]. These findings suggest that outside sources associated with the prevailing air trajectory from west to east account for much of the sulfate deposition in the New England area. However, hard evidence of the midwest originated sources of sulfate depositions and their quantification are difficult to obtain. In fact, there is a general weather pattern of a south-southwesterly depression track that often guides storms from the south moving along the Atlantic seacoast up north to the New England states. Sulfates from the Atlantic coast states can therefore be another outside source of acidic deposition. On the basis of a tracer study Rahn suggested that the Midwest states may be responsible for different proportions of the pollution at different sites in the Northwest, but that sources more to the south including the oceanic sources may make the largest contribution of this pollutant in coastal areas of the Northeast [12]. Also sources of sulfate from the north are possible. The first objective of this study was to collect precipitation data in the southern part of Rhode Island over an eight-month period in order to determine if there is a recognizable pattern of the relative amount of acidity associated with groups of storms coming from various directions.

Water quality data are routinely collected for major rivers as a part of the nationwide water resources data informational program conducted by U.S. Geological Survey. However, the majority of the data is collected for downstream sections near population centers. Normally the water in these locations is not very sensitive to acidic deposition as it is already contaminated with chemicals from sewage effluents. The headwaters usually are of high quality but are very sensitive to acidic deposition if they contain a low buffering capacity. This is normally the case for the northeastern states. Another objective of this study was to monitor the buffering capacity of the headwaters in southern Rhode Island. These rivers are in the upwind direction of the prevailing storms away from the Providence-Cranston-Warwick urban center so that the local acid precipitation effects are usually negligible. By monitoring the water quality before, during, and after each storm, the final goal was to determine the short term effects of acid precipitations on some aspects of the water quality of these small rural rivers.

SITE OF STUDY AND METHODOLOGY

This study was conducted in southwestern Rhode Island with three streams being the subject of analysis. All three streams are considered class A high quality water in Rhode Island with great biological and recreational value. The areas of study as outlined in Figure 1 are generally rural, with open land and forests, individual housing, and agricultural land. The center of the general area of study is approximately (35 km) southwest of Providence, Rhode Island, (114 km) northeast of New Haven, Connecticut, and (217 km) northeast of New York City. Soils throughout the area range from strongly acidic to very strongly acidic and most local waters in the area are slightly acidic with low alkalinity. The characteristics of the study areas are described in Table 1.

River water samples were collected from each of the three sampling stations before, during, and after each precipitation event. Sampling before the storm established a baseline set of data, while the subsequent samples indicated any changes in water quality due to the event and the time period needed to recover from the changes. Samples were collected from midstream using a Kahlsico Van Dorm bottle, model #135 WA103, modified to hold one liter of sample and to trigger the closure mechanism with a trip wire instead of the usual messenger. This allowed the bottle to be used horizontally in shallow streams with water depths varying from one to two feet at low flow periods. Samples were stored in one liter polyurethane bottles at 4°C for laboratory analysis. Each bottle was filled leaving no air space, eliminating possible changes in water chemistry due to air effects. Field measurements were taken at the site after pouring water collected with the Van Dorm bottle into a plastic bucket.

Field analyses included measurements of temperature, specific conductivity, and pH. Specific conductivity and temperature were measured using a YSI

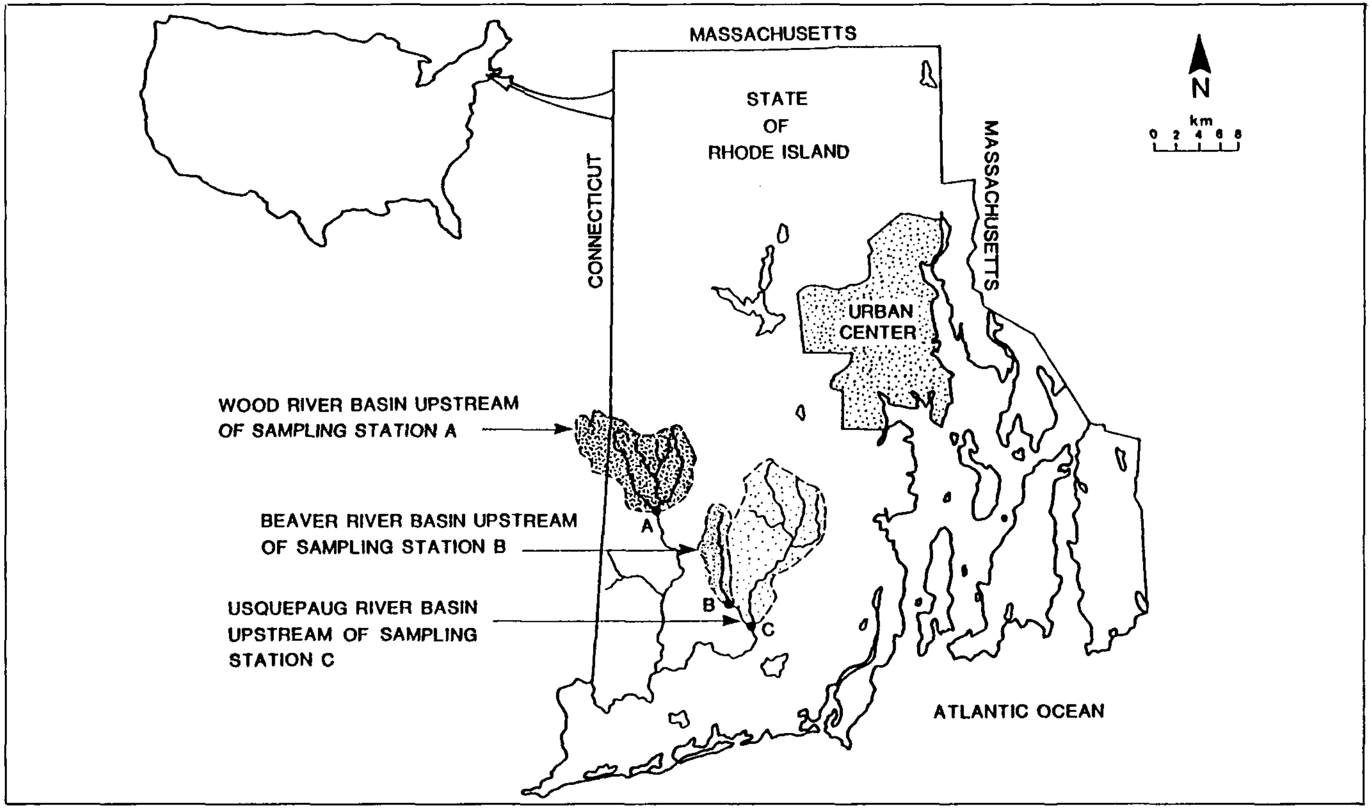

Figure 1. Sampling locations on the Rivers Wood, Beaver, and Usquepaug.

Table 1. Summary of the Characteristics of the Study Area (Headwaters of the Wood, Beaver and Usquepaug River Basins)

Characteristics	*Wood River Basin Upstream of Sampling Station A*	*Beaver River Basin Upstream of Sampling Station B*	*Usquepaug River Basin Upstream of Sampling Station C*
Location of river Sampling Station	Bridge on Ten Rod Road, Route 165, Exeter	Beaver River Bridge Route 138, Richmond	Heaton Orchard Bridge, Route 2, South Kingston
Size of Study Area	91 km^2 (18.6 km^2 within the State of Connecticut)	23 km^2	93.5 km^2
Distance from Providence Metropolitan Area	37 km	37 km	33 km
Land Use:			
Open land forest and public land	93.4%	81.2%	84.1%
Agricultural	4.5%	11.4%	9.0%
Residential	2.1%	4.5%	1.3%
Others	0	2.9%	5.6%
Soil Type	Canton-Charlton -Sutton Series and Hinckley-Merrimack Series from Strongly to Very Strongly Acidic.	Canton-Charlton -Sutton Series and Narragansett -Bridgehampton -Wapping Series from Strongly Acidic to Very Strongly Acidic.	Same as in Beaver River and Some Enfield-Bridgehampton-Agawan Series.

salinity, conductance, and temperature meter, model 33. A Cole-Palmer Digisense digital pH meter, model #5986, was used to measure the pH in the field.

Laboratory analysis was performed with the samples at room temperature. If the samples could not be analyzed immediately after collection, they were refrigerated (at 4°C) and then allowed to warm to room temperature immediately prior to analysis. Laboratory analyses included the measurements of pH, alkalinity and acidity. A Cole-Palmer Digital Chemcadet pH meter, model #5984-00, was used in the laboratory for pH determination. Alkalinity was determined using the low alkalinity method described in Standard methods [13]. Acidity was also determined according to Standard Methods.

Precipitation samples were collected at the East Farm Agricultural station at the University of Rhode Island. The sampler was approximately 19, 10 and 7 km away from the study areas respective to river sampling stations A, B, and C. The sampler consisted of a plastic bucket fitted with a 20-cm diameter funnel.

Rubber tubing allowed precipitation to drain from the funnel into the bucket without water loss due to evaporation. During snow storms, the funnel was removed to allow direct fallout into the bucket. This apparatus was held in place and maintained at a height of 1.2m by a wooden frame, located in an open field on the East Farm. The sampler was covered during dry periods and manually opened just before a precipitation event occurred. The sample was manually collected after the storm was over and brought back to the laboratory for analysis.

A titration curve was constructed using a 100 ml volume of sample and 0.02N NaOH solution as the titrant, and in a nitrogen atmosphere. A sample was titrated to an endpoint of pH 10. pH was recorded with each addition of NaOH and the titration curve was constructed. This curve was used to obtain the concentrations of strong acids, as well as H_2CO_3, NH_4^+ and HCO_3^- which constitute the acidity in the precipitation. The acid concentrations were calculated using the modified Gran Plot method described by Seymour et al. [14].

The information on the origin of each storm and its subsequent route to Rhode Island area was important in determining the probable source of the acidity associated with the storm. Storm track was determined using meteorological weather maps supplied by a major television station in Providence. Satellite photos, radar scans, and pressure maps were the main sources of information used to follow the storm paths.

RESULTS AND DATA ANALYSIS

Precipitation

All together, seventeen storm events were monitored with the first one occurring on October 12, 1983 and the last one on May 23, 1984. They were grouped according to their origin and storm path as they approached Rhode Island. Three categories of storms were developed; those approaching Rhode Island from a west or west-southwest direction, those from a south or south-southwest direction, and those approaching from a west-northwest direction. The precipitation data from each of the storm groups were then analyzed and recorded in Table 2.

Data in Table 2 show that precipitations associated with storms from the west-southwest direction had the lowest pH values. This was the only group to have rainfall pH less than 4, with the lowest recorded value being 3.81. No precipitation events from this group had a pH above 5.00. Precipitation associated with storms originated in the south had pH values above 5.0 possibly due to marine contribution of alkaline materials and there were no values less than 4.30. Both storms from west-northwest had pH values near 4.5.

Acidity values for the three storm categories closely followed the pattern of pH values. Precipitations associated with storms from west, west-southwest had

Table 2. Storm Data

Storm Origin	*Date*	*Amount of Precipitation cm of water*	*Duration Hours*	*pH*	*Acidity mg/1 as*	*Calculated Mass Flux of Acidity kg/km²-h*
west southwest	11-4-83	1.7 Rain	29.0	3.81	11.17	6.55
	1-10-84	1.0 Snow	12.0	4.11	4.05	3.38
	1-24-84	2.2 Rain	12.0	4.64	4.05	7.43
	2-3-84	4.8 Rain	20.0	4.58	3.02	7.25
	2-28-84	5.1 Rain	11.5	4.92	2.54	11.26
	3-22-84	0.7 Rain	2.5	4.42	4.00	11.20
	4-4-84	4.1 Rain	24.0	4.01	5.50	9.40
	5-3-84	2.5 Rain	25.0	4.81	3.84	3.84
south southwest	10-12-83	2.7 Rain	15.0	5.10	5.60	10.10
	11-15-83	9.0 Rain	15.5	5.10	1.94	11.26
	1-18-84	0.6 Snow	23.5	4.30	5.67	1.45
	4-24-84	2.8 Rain	20.5	4.70	4.84	6.61
west northwest	11-28-83	3.6 Rain	23.0	4.51	3.21	5.03
	5-23-84	0.4 Rain	2.0	4.48	3.07	6.15
Unknown	10-24-83	6.0 Rain	21.0	5.35	2.96	8.46
northwest and south-southwest	12-28-83	2.3 Rain	9.0	4.51	3.87	9.89
west and south-southwest	1-30-84	2.2 Rain Snow	34.0	4.32	5.57	3.60

a wide range of values, with a maximum value of 11.17 mg/1. This value was almost twice as high as the maximum for either of the other two groups. The lowest value recorded was 1.94 mg/1 for a storm from the south, southwest.

The values of mass flux of acidity of storms in kg/km^2-h were calculated and were used to compare the relative potential of the storm's effect on river chemistry. The calculated values are also recorded in Table 2.

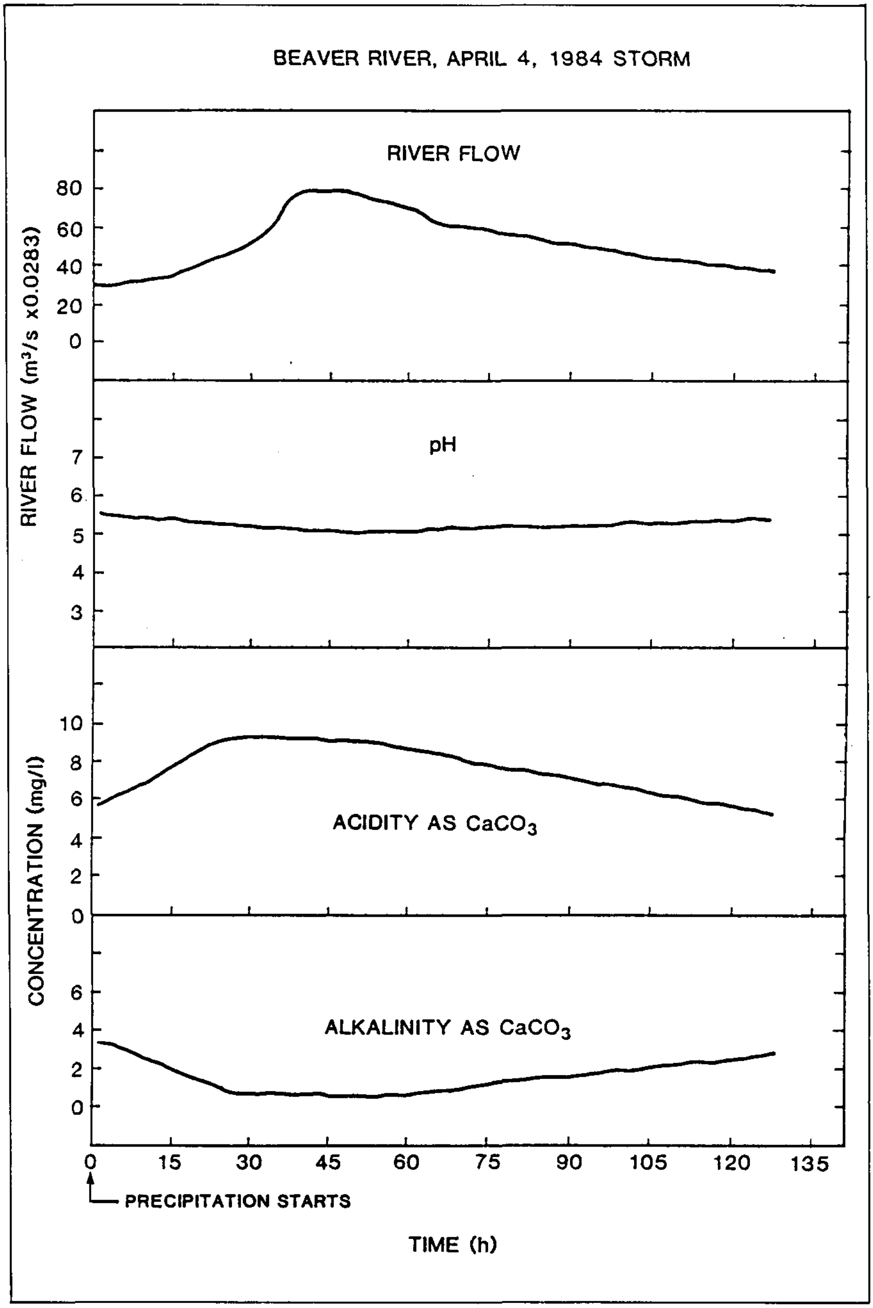

Figure 2. Impact of April 4, 1984 Storm on Beaver River.

Mass Flux of Acidity

Each precipitation event was responsible for changing some parameter of river chemistry. The precipitation and its associated runoff caused changes in pH, alkalinity, and acidity of each of the rivers to some extent. The three rivers all showed the same trend in response to a particular storm, but differed in the magnitude of the effects due to differences in stream flow, watershed size, and water quality before the precipitation event.

All factors being equal, the magnitude of the impact of precipitation upon river water quality increased linearly with the increase of the mass flux of acidity. Table 2 shows six storms with their mass flux of acidity much higher than that of other storms within the study period, three from the west-southwest direction (2/28/84, 3/22/84 and 4/4/84), two from the south-southwest direction (10/12/83 and 11/15/83) and one from the northwest and south-southwest directions (12/28/83).

The April 4, 1984 storm of the three west-southwest storms with a high mass flux of acidity, produced 4.1 cm of rain with the following acid components: 7.59×10^{-5} N strong acids (H_2SO_4 and HNO_3); 1.11×10^{-4} N H_2CO_3; no NH_4^+; and 3.53×10^{-4} N HCO_3^-. A four-day dry period preceded the storm. Figure 2 shows the impact of the storm on the chemistry of Beaver River. The peak flow occurred thirty-six hours after the storm's arrival, with a discharge increasing from 0.85 to 2.15 m^3/s. Alkalinity in the river water was reduced from 3.86 to 0.62 mg/1, or a 84 percent decrease, and pH dropped from 5.90 to 5.02. Acidity rose to a high of 9.45 mg/1, or 84 percent increase from 5.13 mg/1 before the storm. The other two rivers, Wood and Usquepaug, followed the same pattern. In every case, the maximum drop of pH and alkalinity, as well as the maximum increase of acidity occurred almost at the same time the river flow peaked. All rivers recovered in eighty-eight hours after the flow peaked, with the pH, acidity, and alkalinity returned to the pre-storm values. The two other storms with high mass flux of acidity (2/28/84 and 3/22/84) from the west-southwest direction had slightly lesser impacts on these three rivers. It is possible that some other factors such as dry depositions and the amount of river flow before the storm also influence the river chemistry at the same time.

Two storms approached Rhode Island from the west-northwest direction. The storm of May 23, 1984 had little or no effect on the rivers due to its small rainfall of 0.4 cm containing 3.96×10^{-5} N strong acids. No noticeable flow increase was detected in all three rivers. Wood and Usquepaug Rivers showed no changes in pH, alkalinity and acidity. The Beaver River, being the smallest river basin, did show a decrease in alkalinity (21%), and a small increase in acidity (8%) while pH remained constant. It appears that even small amounts of precipitation can cause a change in river water quality in a very small river.

Out of the four storms coming from the south-southwest direction, two of them, (10/12/83 and 11/15/83) brought in respectively a heavy mass flux of acidity of 10.00 and 11.26 kg/km^2-h. Each of these two storms brought about the most significant changes in river water alkalinity, acidity, and pH in all three rivers for the entire period of this study. The 11/15/83 storm increased the river flows from 1.05, 0.085, and 1.19 m^3/s to 6.46, 0.99 and 4.48 m^3/s respectively for Wood, Beaver, and Usquepaug Rivers. Analyses of the river waters showed acidity increased by 15 percent (6.24 to 7.18) and 37 percent (9.26 to 12.66) in the Wood and Usquepaug Rivers, and by a striking 120 percent (4.54 to 10.02) in the Beaver River. This significant increase of acidity was parallel to the 11.6 times increase of river flow caused by the storm.

The storm of 10/12/83 from the south-southwest direction produced some unique changes of water chemistry in all three rivers. This storm gave 2.7 cm of rainfall. No strong acid component was found in the rainfall. Despite its moderate size, the rainfall brought significant changes of pH, acidity, as well as alkalinity in Wood River and Beaver River. The Wood River alkalinity decreased from 11.84 mg/l to 0.2 mg/l and acidity changed from 2.22 to 21.09 mg/l representing almost a ten-fold increase. The pH decreased from 6.44 to 4.29, which was the most significant pH drop in the entire period of study. Similarly a significant decrease of alkalinity from 11.08 to 3.44 mg/l and an increase of acidity from 1.11 to 12.21 mg/l (11-fold increase) were observed for the Beaver River although the pH drop from 6.45 to 6.31 was less drastic. The drastic changes of water quality in these two rivers were unexpected from the moderate size and acidity of the storm. The study area and the state of Rhode Island as a whole had experienced a long drought period prior to the October 12 storm. There were five months of very dry weather from May through September. One storm on October 2 produced 0.68 cm of rainfall, with no data taken. The October 12 storm was the first one in this study. The very long drought period resulted in extremely low flows in all three rivers. The October 12 storm washed out significant amounts of dry acid deposition accumulated on the watersheds and possibly some acid accumulated in the swampy areas upstream as well. This was a unique situation, producing drastic changes in alkalinity and acidity not to be witnessed again throughout the entire study period. Figure 3 shows the response of Beaver River to the storm in the first forty-eight hours.

The response of the Usquepaug River water to the October 12 storm, however, was quite different. The river water acidity increased from 1.11 to 12.21 mg/l and yet experienced only a slight decrease of alkalinity (from 19 to 13.18 mg/l) and pH (from 6.45 to 6.31). Through contact with the owner of the Hollis Tucker Turff farm, it was learned that lime was applied in an amount of 1 1/2 to 2 tons/acre in late July 1983. The turf farm is located immediately upstream from the sampling station of the Usquepaug River. The possible inclusion of lime in the runoff or groundwater connecting to Usquepaug River could explain why the alkalinity remained relatively high while the same storm reduced significantly the alkalinity of the two other rivers.

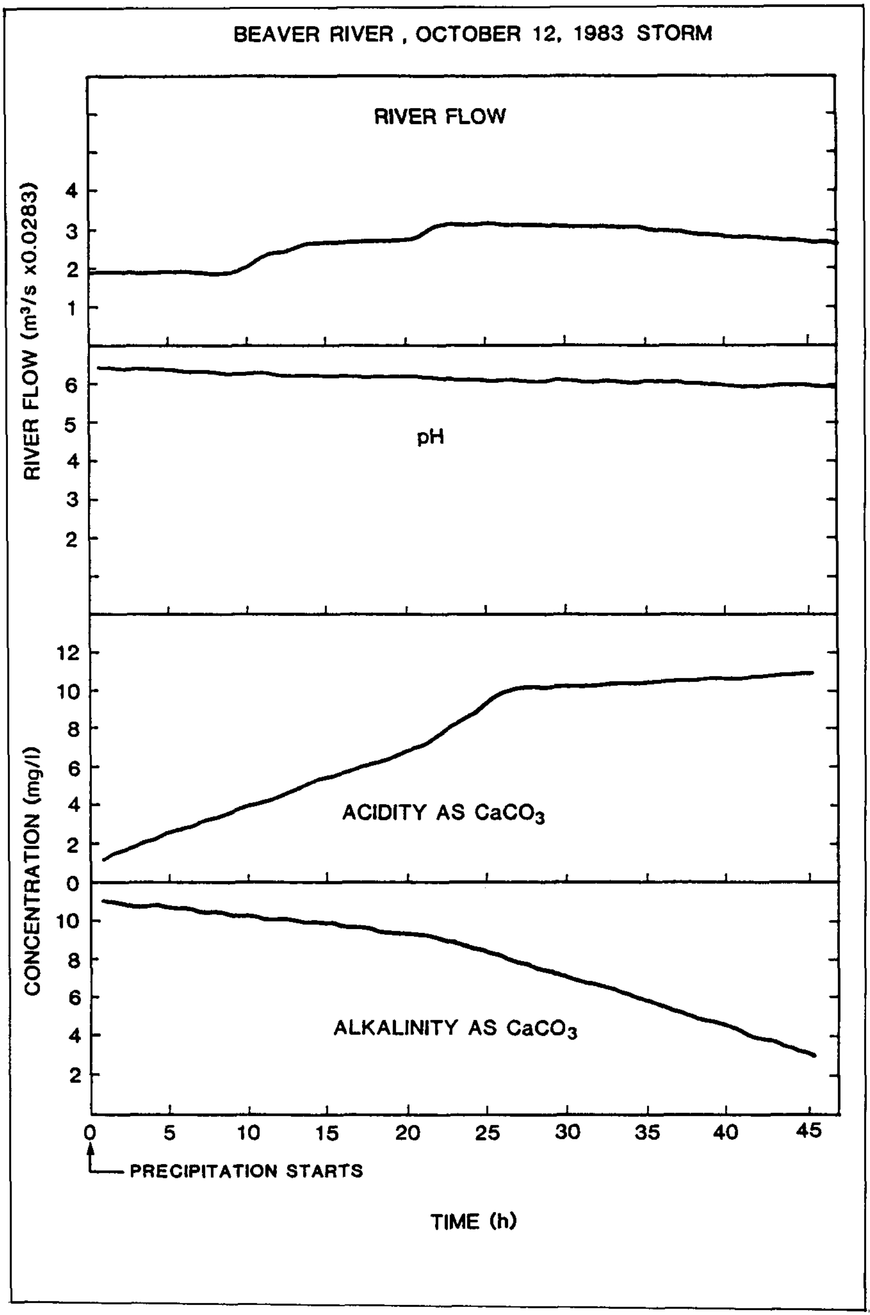

Figure 3. Impact of October 12, 1983 Storm on Beaver River.

In the period between early January and early February, 1984, there were five individual precipitation events in the study area. The first two of these storms (Jan. 10 and 18, 1984) were snow storms with subfreezing temperatures throughout the period. The third storm (Jan. 24) brought rain, but some snow remained on the ground. The fourth storm (Jan. 30) was a mixture of rain and snow which contributed more snow to that on the ground. The last storm (Feb. 3) was a heavy rainfall which washed away all of the snowpack. This combination of precipitation events made the impacts of each storm upon water chemistry individually indistinguishable. Consequently, this group of storms was treated as one event, even though the amount of precipitation resulting from each storm was recorded. Of the five storms, three were from the west, west-southwest group, one was from the south, and one was a combination of a storm from the west and a storm from the south. The acidity of the precipitation did not show a strong correlation with the direction the storm travelled. The type of precipitation appears to be important. The three storm events which produced snow all had a consistently large strong acid component ranging between 5.49×10^{-5} N and 5.58×10^{-5} N. Both of the rainstorms had strong acid components of only 2.20×10^{-5} N and 2.87×10^{-5} N. The pH of the precipitation was consistent with this pattern, with snowstorms ranging 4.10 to 4.32 and rainstorms 4.60 to 4.65. Acidity ranges were 5.59 to 6.05 mg/l in snow and 3.02 to 4.05 mg/l for the rain. This would suggest that either the snow was a more efficient scavenger of acidic precursors from the atomosphere than the rainfall or that more acid was in the atmosphere in deep winter due to house heating and more electricity use.

The impacts of the combined storms caused changes in river chemistry which fluctuated with the runoff associated with a particular event. Water quality parameters changed little throughout the first two snow storms and subfreezing temperatures, as most of the acidic precipitation was tied up in the snowpack. After the passing of the third storm, causing some of this snowpack to melt and runoff to the rivers increased, changes in river chemistry were observed.

The Wood River had maintained a high alkalinity of 6.38 mg/l until the rainstorm of January 24 arrived and the combined runoff reduced alkalinity by 33 percent to 4.25 mg/l. Acidity increased by 7 percent to 5.40 mg/l. The pH showed little change, rising slightly from 5.80 to 5.86. The river began to recover after this storm and did not appear to be adversely affected by the rain/snow combination of January 30. The final rainfall of February 3 and the total combined runoff did cause significant impacts. Alkalinity dropped from 7.76 mg/l before this storm to 2.03 mg/l three days after the storm, or a decrease of 74 percent. pH decreased from 6.60 to 5.91 during this period while acidity actually decreased by 39 percent from 6.75 to 4.10 mg/l. By February 10 the river quality had recovered to values near that before the storm series began. Both the Usquepaug and Beaver Rivers showed a pattern similar to that of Wood River.

CONCLUSIONS

1. In general, storms coming to Rhode Island from the west-southwest direction carried more acid and the precipitations had the lowest pH. Storms from south-southwest were the least acidic and storms from west-northwest were in between. Rainfall pH as low as 3.81 and a strong acid component as high as 1.59×10^{-4} N were recorded in storms from the west-southwest direction.
2. Rhode Island has fresh waters very low alkalinity. Many storms with high acidity have temporarily reduced the river water alkalinity to less than 1 mg/1. The acidity in the river water increased by as much as eleven-fold. The lowest pH recorded for Wood River during one storm was 4.29.
3. Other than the mass flux of acidity of the storm, there are other important factors that impact the river water quality. These include: the accumulated amount of dry acid deposition on land prior to the storm event; the river flow prior to the storm event; and the land use patterns in the area. A very acidic precipitation from a small storm may not impact the river water quality as much as a large storm with only moderate amounts of acidity. A long drought period or several snow storms in subfreezing weather preceding a rainfall may result in a significant impact of water quality because of the large accumulation of dry or wet acidic deposition in the area. A high pre-storm river flow may dilute the acidic rain runoff, thus minimizing the impact. Agricultural use of lime in the area may significantly neutralize the impact also.
4. A drop of half of a pH unit could take place in approximately one-half a day. Depending on the amount of acid and other factors presented previously, the impact on river water quality may last longer than five days from onset of the maximum impact to the time of a recovery of the pre-storm water quality.

As an observation in this study, it is felt that future studies of the effects of acid precipitation on river water quality should include the characterization of groundwater contributing to the river flow and seasonal variations of impounded surface water quality in the upstream area including reservoirs, bogs, and swamps.

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