

**Vermont Precipitation Monitoring Program**

**Data Summary Report 1980-1997**



Vermont Agency of Natural Resources  
Department of Environmental Conservation

**Biomonitoring and Aquatic Studies Section**

BASS #1999-01

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Data Summary Report 1980-1997**

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**May, 1999**

## Acknowledgments

The "Acid Rain" volunteers created and sustained this program. Over the past 17 years they have provided energy and countless hours to monitor Vermont's environment. When acid rain became a major issue, this program sprang up and has continually provided quality data. We gratefully acknowledge all past and present monitors.

Monitors who have provided data and observations for this report include the following: Sumner Williams, Joanne Cummings and Mim Pendleton (Proctor Maple Research Center, Underhill); Andy Fisher (St. Johnsbury); Don Spooner (Holland); Phil Sweetser (Hyde Park); Mike Rainey and Bob Rickner (WCAX TV, Mt. Mansfield); Captain Harry Wiseman (National Weather Service, South Lincoln); Ed Salvas, Donald Ward, Larry Miller, and Mike Cochran (Morrisville Wastewater Treatment Facility); Andy Fisher and Tom Smith (Concord High School, Concord); Sylvie Carrier, Mark Lienau, Fred Cowan and Roy Liard (Canaan), Nancy Martin (Vermont Institute of Natural Science, Woodstock); Frank Mastrianni and Bob Chaperon (Swanton); Tom Hopkins (Burr and Burton Seminary, Manchester); Staff of the West Dover Wastewater Treatment Facility (West Dover).

Individuals at the State of Vermont have provided oversight to this program over the years. Jim Kellogg has been a constant in the acid rain program tracking Vermont's precipitation in addition to lake acidification. Both Jim Kellogg and Doug Burnham have provided review and support. Rich Poirot has provided technical review as well as his dedication to monitoring air quality in the region.

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## Introduction

Acid rain has been a prominent international issue since it first gained attention in the 1970s. The destruction of marble statues and limestone buildings, the decline of the Black Forest in Germany, hazy skies, and the weakened state of many ecosystems sounded the alarm. In the United States, the 1970 Clean Air Act (CAA) mandated the improvement of air quality in the vicinity of midwestern and southeastern fossil fuel burning plants. These plants built higher smoke stacks to improve local air quality. However, this resulted in the long distance transport of pollutants (primarily sulfur and nitrogen oxides) along dominant frontal patterns, increasing acid precipitation throughout the Northeast. The pH of lakes and streams began to decline to the point where aquatic biota were affected. As a result, many acid precipitation studies were undertaken in the United States and abroad.

Vermont responded by establishing the Volunteer Acid Precipitation Monitoring Program (VAPMP) and, in cooperation with the US Environmental Protection Agency, started chemical monitoring of highly sensitive lakes. The VAPMP was initiated in 1980 to monitor the pH of bulk precipitation on an event basis through volunteer monitors located throughout Vermont.

The purpose of this report is to address the following goals of the Vermont Acid Precipitation Monitoring Program:

1. To describe the pH range of bulk precipitation in Vermont.
2. To evaluate seasonal trends in bulk precipitation pH.
3. To evaluate spatial differences in pH in relation to elevation and site location.

In 1990, amendments were passed to the Clean Air Act which required reductions in atmospheric pollutants. Title IV of the amendments required sulfur dioxide (SO<sub>2</sub>) emissions to be cut 10 million tons in the United States by the year 2000. These reductions were implemented in two phases: Phase I, effective January 1, 1995, required the largest fossil fuel-fired plants to reduce emissions; Phase II, effective in the year 2000, includes the smaller fossil-fuel burning plants and the large coal-burning power plants. With these reductions in atmospheric pollutants being implemented, the VAPMP has added an additional goal:

4. To evaluate temporal trends in bulk precipitation pH in Vermont.

This report analyzes and reviews 17 years of data, from 1980 through 1997. It builds upon previous VAPMP reports by Kellogg (1982), Scott (1987) and Schamaun (1994). The program currently has a total of five monitoring sites at Mount Mansfield, Underhill, Hyde Park, Holland, and St. Johnsbury. We welcome three new monitors to the Program: Mim Pendleton, who replaces Joanne Cummings at the Underhill Proctor Maple Research Center; Don Spooner in Holland; and Phil Sweetser in Hyde Park who replaces the Morrisville station run by Don Ward.

## Summary

### Frequency Distribution

Precipitation in Vermont is clearly acidic. The overwhelming majority of precipitation events have a pH less than 5.6, the theoretical pH of unpolluted rain. The most acidic precipitation occurs with low volume events, and conversely, the more neutral precipitation occurs with larger storm events. Average annual pH appears to fluctuate with the annual volume of precipitation. As volume increases, so does pH. (Lynch, Bowersox & Grimm 1996). In addition, there is a tendency for more acidic events to occur when storms originate from the southwest, the more industrialized area of the eastern United States. This corresponds with past conclusions that the majority of sulfate particulates arriving in Vermont originate from a southwesterly direction (Poirot, Wishinski, Schichtel and Girton 1998).

### Seasonal Variation

In Vermont, a significant seasonal difference has been observed at only one station, West Dover ( $p=0.015$ ). All other stations show no significant difference between summer and winter mean pH ( $p>0.05$ ). In the northeastern United States, seasonal differences decrease as one moves north. Vermont may be at the northern extent of the range where seasonal differences exist (Scott 1987).

Monthly differences were also examined at two sites, Underhill and Morrisville. At the Morrisville site, January was significantly different from May, June, and September ( $p<0.05$ ). While May and September are not "summer" months, they do receive more hours of sunlight and higher temperatures, supporting the theory of seasonal variation in precipitation pH. February was also significantly different from August and September at Morrisville, while April vs September also differed ( $p<0.05$ ).

In contrast, at the Underhill site, February was significantly different from all the fall months, September, October and November ( $p<0.05$ ). These results weakly indicate that winter differs significantly from fall. However, February differed significantly from March and July; November was significantly different from January, December and August.

Overall, these results indicate that there is no true seasonal variability in the pH of bulk precipitation in Vermont.

### Spatial Variation

In comparing Mt. Mansfield (3,800 feet) with Underhill (1,300 feet) and Morrisville (700 feet) there appears to be a pattern of decreasing pH with increasing elevation. Underhill, on the west side of the Green Mountains, has a lower annual volume-weighted pH than does Morrisville, located on the east side of Mt. Mansfield. Mount Mansfield has a lower annual volume weighted pH than either site. As storm systems arrive in Vermont from a southwesterly direction, those sites located to the west of the Green Mountains receive an initial flush of atmospheric pollutants. Thus, they would also receive more acidic precipitation than the eastern sites.

However, the Northeast Kingdom (Canaan, St. Johnsbury, and Concord) receives some of the state's most acidic precipitation. This portion of the state may be influenced by more industrialized areas to the north and northwest. In addition, Swanton, located on Lake Champlain west of the Green Mountains has the highest mean pH. This may be due in part to the "buffered" local soils. These soils contain large amounts of calcium and other base cations which counteract the effects of acid rain.

### Temporal Variation

Recent reports suggest that precipitation has become less acidic (decreased hydrogen ions) in the eastern United States (Lynch, Bowersox & Grimm 1996; Lynch, Bowersox & Simmons 1995). However, Vermont has not seen an overall improvement in pH of bulk deposition over time. Two stations appear to have a insignificant decreasing trend in pH (St. Johnsbury and Canaan), while others appear to have a insignificant increasing trend in pH (South Lincoln, Swanton, Underhill).

## Methods

### Sites

The VAPMP began in the summer of 1980 with five stations staffed by trained volunteer monitors. At first, these volunteers only recorded pH from the summer months; presently, they monitor year round. During the past 17 years, there have been up to 13 sites monitored under the auspices of this program. Presently, five sites are operating, with new stations being added periodically. Holland was added in the spring of 1997, and Hyde Park was added in the spring of 1998. All VAPMP sites, both past and present, are shown in **Figure 1**.

### Sampling Methods

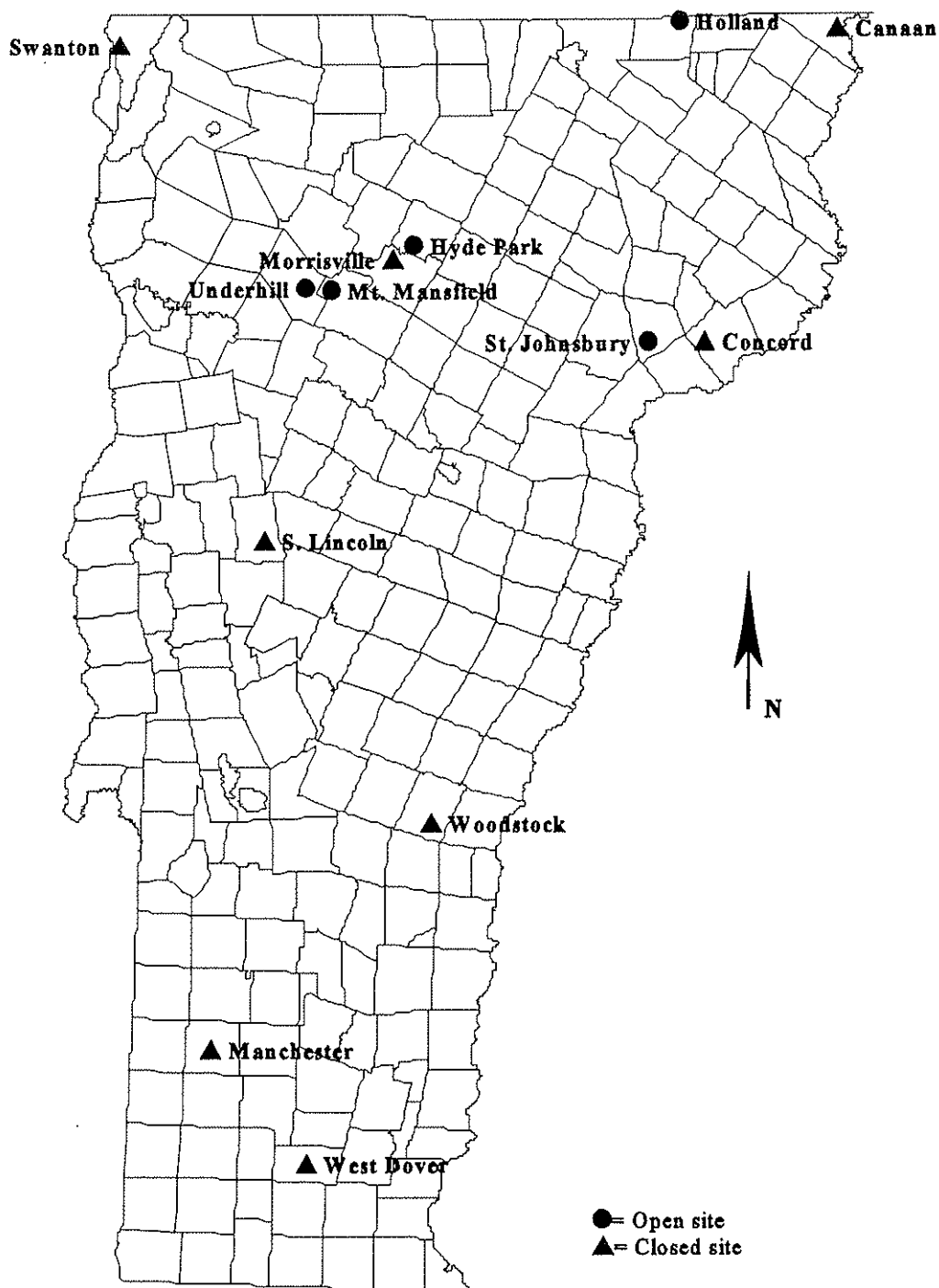
Precipitation is collected in bulk collectors on an event basis with the pH and precipitation amount measured for each event. The pH is determined by either a Cole Parmer digital pH meter model 5987 or an ATI Orion digital pH meter model 310 and a Cole Parmer combination electrode with calomel reference.

Rainfall is intercepted by a funnel with a polyethylene screen (1241 micron mesh) at its vortex, passed through a length of tygon tubing until it reaches and collects in a one gallon polyethylene jug. The entire apparatus is housed in a wooden box, one foot in width and four feet in height. Snow is collected in a five-gallon polyethylene bucket and brought indoors to completely melt into liquid form before the pH is measured.

The collectors are located in flat open areas, away from roads, point sources, urbanized areas and agricultural areas, trees, and overhead wires. See **Appendix A** for complete details on the revised methods of sampling for the Vermont Acid Precipitation Monitoring Program.



Figure 1. Map of VAPMP Sites, 1980-1997



## Quality Assurance/Quality Control

All monitors were trained by the Department of Environmental Conservation (DEC). The monitors methods are observed twice per year. The low turnover of monitors has contributed to the consistency in the data collection.

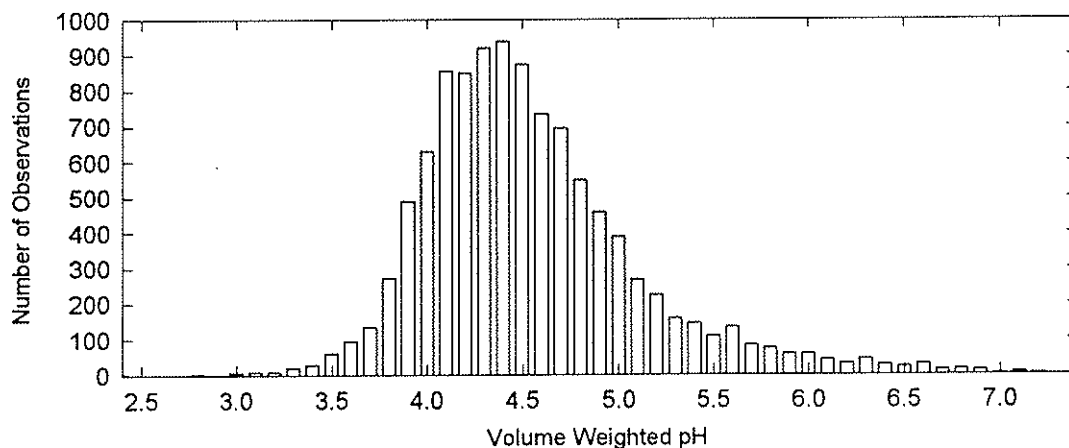
The pH meters are calibrated with buffers 4.00 and 7.00 prior to use. In addition, the monitors are supplied with a check sample of pH 4.70 +/- 0.10 at 25°C to ensure the electrodes are working properly. The pH meters are professionally calibrated yearly and electrodes replaced when they show signs of slow response or failure. The pH and amount of precipitation are recorded on monthly report sheets along with comments about duration of event, type of precipitation, time and date of analysis, use of pH check sample and presence of visible contaminants in the sample. Several of the sites report local wind direction (Concord, S. Lincoln, Underhill, St. Johnsbury) as well as specific conductance (Underhill). The bulk collector jugs and snow buckets are rinsed with distilled water three times after each precipitation event.

## Discussion

### pH Range

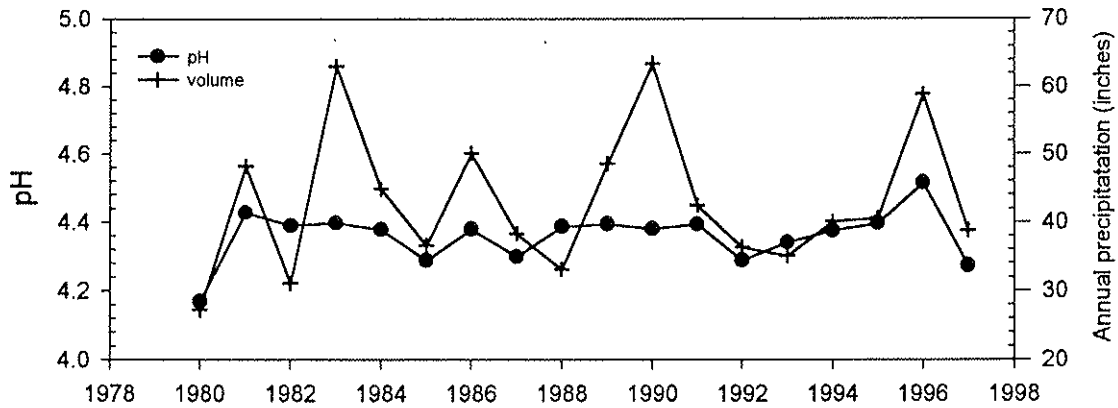
**Figure 2** presents the frequency distribution of bulk precipitation pH observations. Ninety-four percent of all precipitation events have a pH of less than 5.60, the theoretical pH of unpolluted rain. Forty-three percent of all events occur between the pH of 4.10- 4.60. The mean pH is 4.54. The most extreme pH events, both high and low, occur with low volume events. The highest recorded pH since 1980 was 7.41 at Concord on June 3, 1991. The lowest recorded pH was 2.44 at Canaan on November 2, 1987.

**Figure 2.** VAPMP frequency distribution for all stations, 1980-1997. 10,545 observations



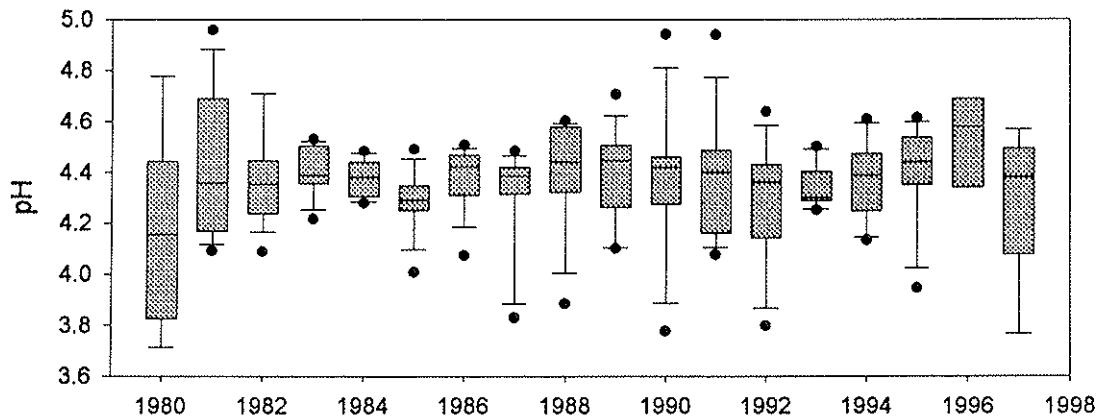
Annual volume weighted pH is positively correlated to volume of precipitation (**Figure 3**). During “wet” years, pH tends to increase, due to a lower concentration of acids in solution. While during “dry” years, pH tends to decrease due to lower concentration of acids in solution (Spearman Rank Order Correlation Coefficient= 0.602,  $p < 0.01$ ).

**Figure 3.** Annual volume weighted pH vs inches of annual precipitation.



**Figure 4** demonstrates the variability of pH within and among different years. No overall increasing or decreasing trend appears in Vermont precipitation. In addition, for all sites but one,

**Figure 4.** Annual volume-weighted mean pH for all sites combined by year, 1980-1997.

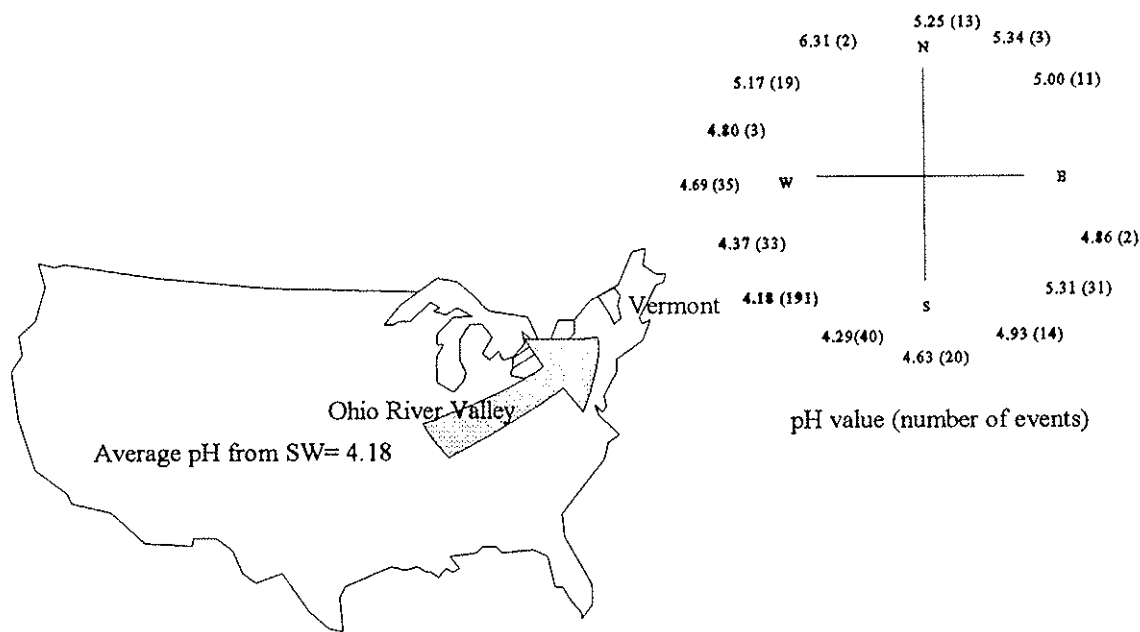


annual volume weighted pH are normally distributed.

In addition to precipitation pH and volume, the St. Johnsbury station records wind direction. A five-year analysis (1992-1997) of St. Johnsbury wind patterns vs. pH supports work by Poirot, Wishinski, Schichtel and Girton 1998.

The overwhelming majority (46%) of storms that reach St. Johnsbury, Vermont originate from the southwest (SW). Sixty-three percent of precipitation events in St. Johnsbury are associated with winds from the south-southwest (SSW), the southwest or the west-southwest. These storms have a lower mean pH than from any other direction. Using the Mann-Whitney Rank Sum Analysis, pH readings from the SW differ significantly from all other directions except the SSW (p values range from <math><0.001 - 0.038</math>). **Figure 5** demonstrates this tendency. Thus, storms which originate from the SW produce the lowest pH and are the most frequent storm events in Vermont. As storms move farther away from the SW region, the mean pH rises (p=0.03).

Figure 5. St. Johnsbury, Vt. mean precipitation pH by wind direction



## Seasonal Variation

Summer pH values are expected to be lower due to increased sunlight, temperature, humidity, and photochemical oxidants which enhance the chemical transformation from emitted pollutants to sulfuric and nitric acids. As a result, sulfuric acids exist in higher concentration in the summer months than the winter. (Allan and Mueller 1985; Bowersox and Stensland 1985). Months are grouped into the following seasons: winter includes December, January, February; spring includes March, April, May; summer includes June, July, and August; fall includes September, October, and November.

Using a Mann-Whitney Rank Sum, a non-parametric analysis, Vermont's pH has not differentiated significantly on a seasonal basis ( $p > 0.05$ ). **Table 1** compares the summer and winter means of 11 stations. T-tests were used to compare the individual stations. Only one station, West Dover, demonstrated a significantly lower pH in the summer than in the winter (power of 0.669,  $p = 0.015$ ). Manchester, Mt. Mansfield, South Lincoln, Swanton, Woodstock, and St. Johnsbury all had summer volume weighted means which were lower in the summer than in winter, but not significantly. Canaan, Concord, and Morrisville had volume weighted means which were higher in the summer than the winter, but again, the differences were not significant. This could be due to the cleansing affect as less and more dilute precipitation is expected to fall east of the Green Mountains.

Two sites, Morrisville and Underhill, were examined for monthly comparisons of volume weighted pH. These sites were the longest continuously-operating sites in the network and therefore the best candidates for month to month comparisons. Using a Mann-Whitney Rank Sum Analysis, Morrisville's pH data was examined from 1984-1997. January's volume weighted mean pH was significantly lower than the following months: May, June and September. February was significantly higher from August and lower than September. April was significantly lower than September. Overall, lower pH values occurred in the winter instead of the summer as predicted.

Monthly mean pH data was examined at Underhill from 1984-1997. February pH was significantly lower than March, July, September, October and November ( $p < 0.05$ ). November was significantly higher than December, January, August.

No true pattern of seasonal difference emerges from these comparisons.

Table 1. Winter vs. Summer Volume Weighted pH

Site	Winter		Summer	
	Number of Observations	Mean Volume Weighted pH	Number of Observations	Mean Volume Weighted pH
Canaan	8	4.24	11	4.33
Concord	13	4.42	12	4.47
Manchester	7	4.44	5	4.36
Morrisville	14	4.47	17	4.60
Mt. Mansfield	16	4.30	17	4.28
South Lincoln	13	4.45	13	4.43
Swanton	11	4.60	12	4.47
Underhill	14	4.33	15	4.35
<b>West Dover</b>	9	<b>4.39</b>	12	<b>3.99</b>
Woodstock	9	4.46	10	4.37
St. Johnsbury	6	4.33	6	4.18

\***bold** indicates a significant difference between winter and summer means

#### Spatial Variation

Consistent with previous VAPMP reports, two spatial relationships are supported in this report: 1) There is a decrease in pH with increasing elevation due to increasing acidic fog at higher elevations; 2) A lower pH is expected to occur in precipitation at sites west of the Green Mountains as a result of storm fronts moving west to east over the Green Mountains and depositing more acidic and concentrated pollutants as they rise and pass over the mountains (VAEC 1984; Scherbatskoy and Bliss 1983).

Three sites were chosen to evaluate the relationship between elevation and pH, and to compare the pH east and west of the Green Mountains. Underhill, at 1300 feet just west of Mt. Mansfield, Mt. Mansfield at 3800 feet and Morrisville, at 700 feet just east of Mt. Mansfield (see **Figure 1** for locations). These sites continuously operated from 1984-1995.

The three sites differentiated from lowest elevation to highest elevation according to pH. The lowest site, Morrisville had the highest annual volume weighted pH, while Mt. Mansfield, the highest site, had the lowest pH. The Underhill site on the east side of the Green Mountains, had a lower annual volume weighted pH than Morrisville on the west side. Annual volume weighted pH was significantly different between Morrisville and Underhill

( $p = < 0.001$ ), and Morrisville and Mt. Mansfield ( $p = 0.002$ ). There was no significant difference between Mt. Mansfield and Underhill (Table 2).

Table 2. Elevation vs pH at 3 sites from 1984-1995.

Site	Elevation (ft)	AVW pH*	Location
Underhill	1300	4.37	West of Mt. Mansfield
Mt. Mansfield	3800	4.24	Highest point along the Green Mountain Chain
Morrisville	700	4.49	East of Mt. Mansfield

\* annual volume-weighted pH

#### Temporal Variation

All sites were analyzed for significant trends over time (Figures 6-16). Only continuously operating sites were plotted. All sites that had at least eight months of data per year with no two consecutive months of missing data were considered "continuously operating".

Using simple linear regression, no significant relationships between pH and time were demonstrated. Overall, pH has neither increased or decreased significantly over time. However, individual sites suggest weak non-significant trends.

Canaan (Figure 6) had a tendency for pH to decrease over time ( $p = 0.011$ ,  $r^2 = 0.556$ ). South Lincoln (Figure 11) had a tendency for pH to increase over time ( $p = 0.377$ ,  $r^2 = 0.372$ ). Swanton (Figure 12) had a tendency for pH to increase over time ( $p = 0.686$ ,  $r^2 = 0.622$ ). Underhill (Figure 13) also suggested a weak trend towards increasing pH ( $p = 0.098$ ,  $r^2 = 0.216$ ). St. Johnsbury (Figure 14), with only 5 years of data ( $p = 0.448$ ), has shown a tendency towards decreasing pH ( $r^2 = 0.760$ ). All of these tendencies should be interpreted cautiously, without the necessary high degree of confidence to indicate a trend. As these stations continue to operate, the degree of confidence should increase.

Variable results throughout the state may be due to local effects. Local effects include the following: level of exposure to atmospheric pollutants from localized sources (industrial and private); local soils influences (which tend to buffer bulk precipitation samples); variable amounts of precipitation between regions; wind direction; and origin of storms.

St. Johnsbury and Canaan are the only two stations with an apparent tendency towards decreasing pH. Canaan, a town on the United States-Canadian border, may be affected by more populated and industrialized areas to the north and north-west, such as Sherbrooke and Montreal. The St. Johnsbury station has been in operation for 7 years, a relatively brief period of time to establish a long-term trend. However, it has received less precipitation than any other continuously operating station from 1993-1997. As has been previously stated, low precipitation

volume correlates with low pH values.

Other stations have shown apparent trends over 5-8 year periods of time and then become erratic, such as Mount Mansfield (**Figure 10**). Underhill has much less variation than the other stations and there appears to be a weak tendency for pH to increase over time (**Figure 13**). Some stations demonstrate an increasing tendency in pH, then turn downward, such as West Dover (**Figure 15**) and Woodstock (**Figure 16**).

Swanton (**Figure 12**) had the strongest tendency for pH to increase over time. This may be due in part to the station's proximity to Lake Champlain with its seemingly infinite buffering capacity and the area's well buffered soils. Lake Champlain can affect pH by local evaporation and precipitation. Area soils can influence pH as airborne dust particles will be deposited in the VAPMP bulk collection container.

### Conclusions

Bulk collection of Vermont's precipitation is unquestionably acidic. Ninety-four percent of all storm events result in a pH less than 5.6, the theoretical pH of unpolluted precipitation. The most extreme pH events, both high and low, occur with low volume events. Volume of precipitation is positively correlated to annual volume weighted pH. Only one site has shown significant seasonal differences, but overall, Vermont has shown no significant difference between summer and winter mean pHs. Sites on the east side of the Green Mountains seem to have higher summer pHs potentially due to the cleansing effect of moving from west to east over the mountains. Precipitation is more acidic when a storm originates from a south-westerly direction. Overall, Vermont bulk precipitation, as measured by the VAPMP, has shown no improvement in pH over time (1980-1997).



Figure 6. Canaan, Vt. ; Annual volume weighted pH, 1981-1991

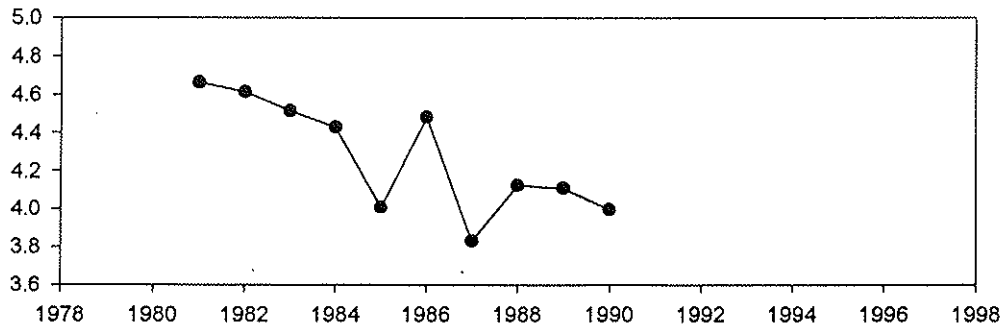


Figure 7. Concord, Vt. ; Annual volume weighted pH, 1983-1995

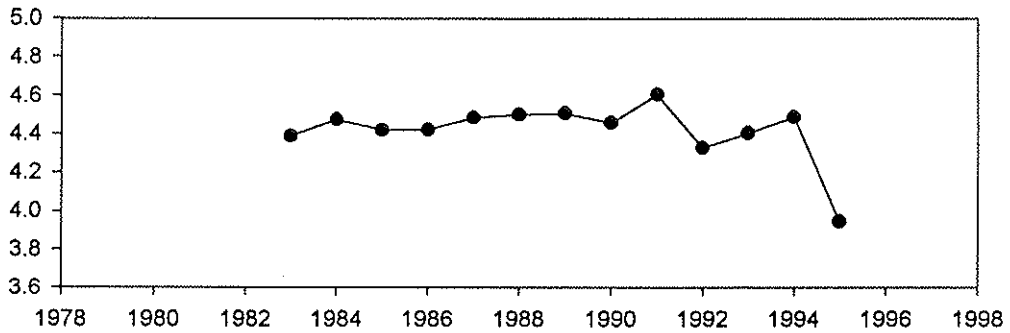


Figure 8. Manchester, Vt. ; Annual volume weighted pH, 1983-1987

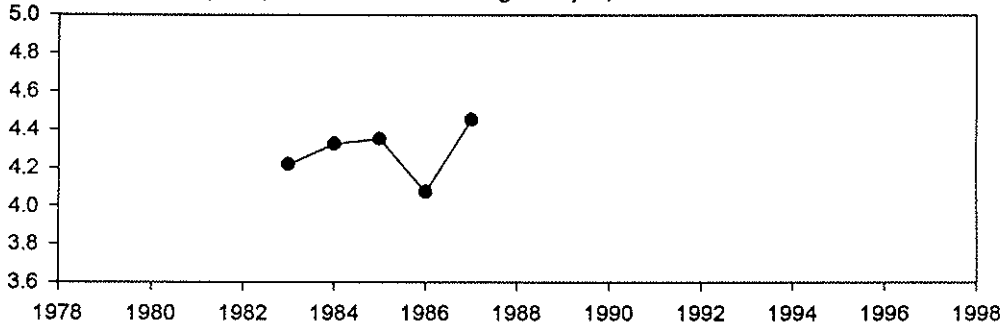


Figure 9. Morrisville, Vt. ; Annual volume weighted pH, 1984-1997

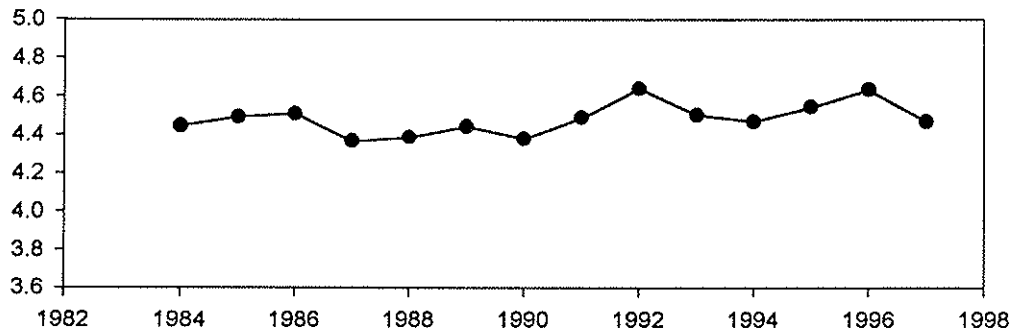


Figure 10. Mount Mansfield, Vt. ; Annual volume weighted pH, 1981-1995

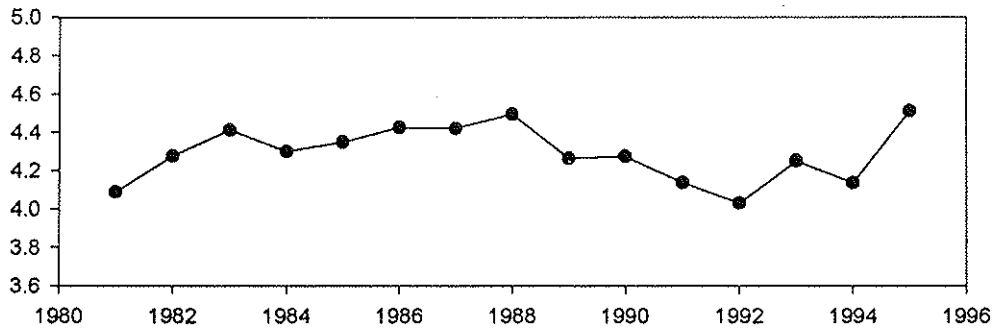


Figure 11. South Lincoln, Vt. ; Annual volume weighted pH, 1983-1996

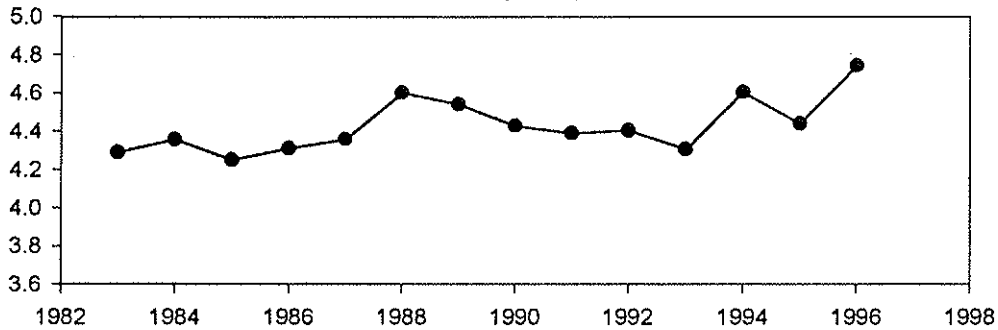


Figure 12. Swanton, Vt. ; Annual volume weighted pH, 1982-1991

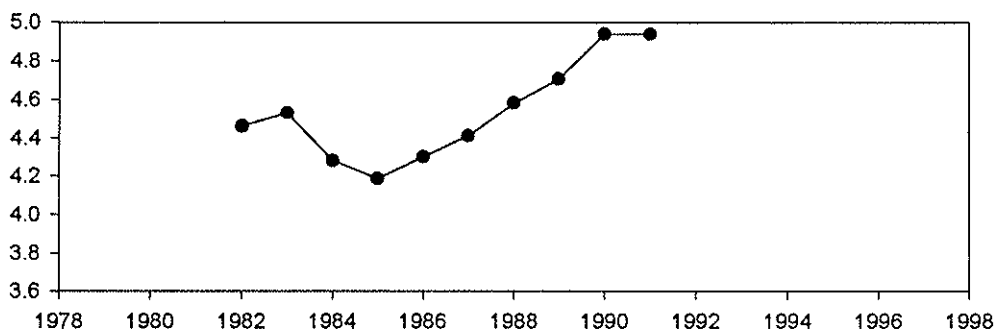


Figure 13. Underhill, Vt. ; Annual volume weighted pH, 1984-1997

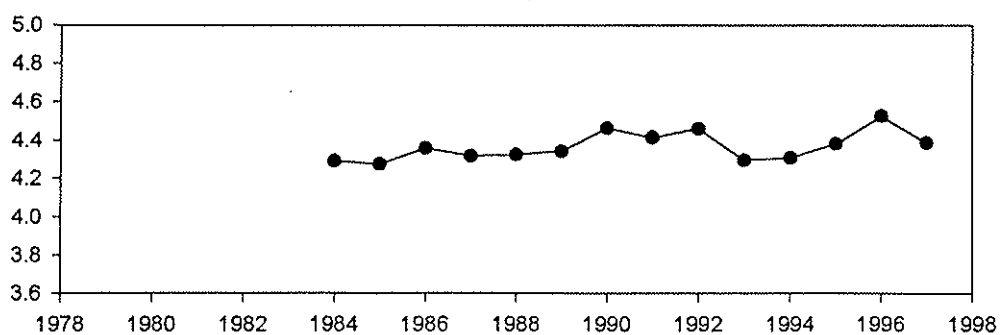


Figure 14. St. Johnsbury,; Annual volume weighted pH, 1991-1997

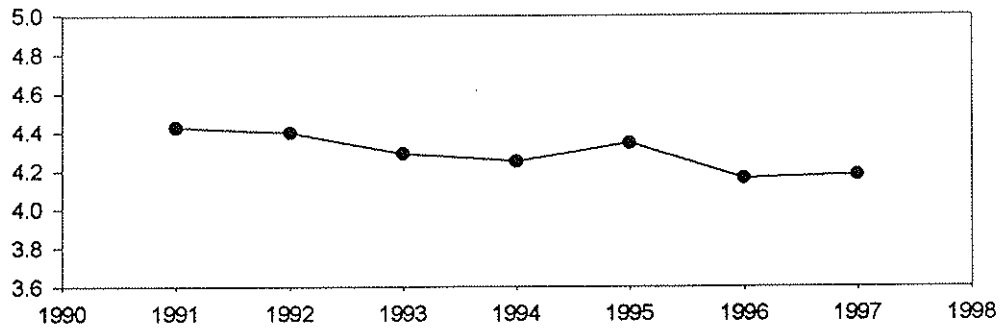


Figure 15. West Dover, Vt.; Annual Volume weighted pH, 1981-1986, 1988-1989

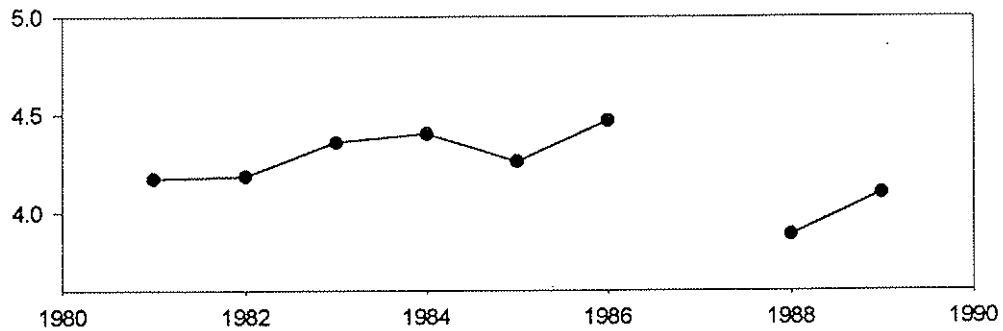
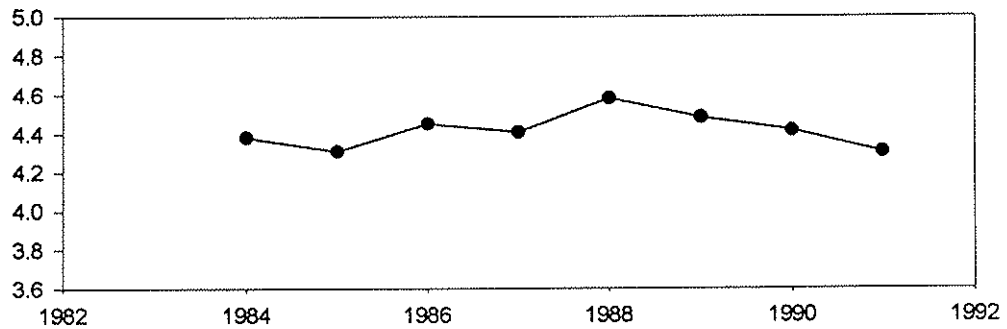


Figure 16. Woodstock, Vt.; Annual volume weighted pH, 1984-1991



## Recommendations

Phase I of the 1990 Clean Air Act Amendments implemented reductions in key acid precipitation-causing pollutants on January 1, 1995. The act mandated the reduction of SO<sub>2</sub> emissions by 10 million tons below 1980 levels. Nationwide, sulfur dioxide emissions were reduced by 40 percent below the required level for 1995. The Act mandates that nitrous oxide emissions be reduced by 2 million tons by the year 2000. Phase II will be implemented in the year 2000, further reducing pollutants from large coal-burning power plants. Previous authors have expressed the opinion that acid rain will continue to be a problem until major reductions in nitrous oxides are achieved; this report concurs. An unexpected result of reduced sulfur emissions has been the accompanying declines in base cations, most notably calcium. This has offset improvements in pH throughout New England. (Likens et al. 1996)

The largest source of anthropogenic emission of nitrous oxides is energy use. Energy use encompasses transportation; cars, trucks, buses, motorcycles; two-cycles engines such as outboard motors, snowmobiles, jet skis and lawnmowers; and electric utilities. Mobile sources (vehicles) have accounted for 33 percent of all nitrous oxide emissions in the United States. Fertilizer use is the second highest contributor to emissions, however it has been declining in recent years [Emissions of Greenhouse Gases in the United States 1996, DOE/EIA-0573(96)]. Therefore, in order to reduce acid rain, we must limit our energy consumption.

The National Atmospheric Deposition Program (NADP) operates two sites to monitor precipitation chemistry in Vermont. Due to cuts in federal funding, the operation of these sites has been in jeopardy. Although VAPMP has up to 17 years of data for several sites, continued monitoring will be essential to track long-term changes and trends in the pH of bulk precipitation.

Acid Rain continues to impact Vermont, but with current and future EPA mandated reductions in acid precipitation-causing pollutants, pH may improve. The VAPMP will continue to monitor any changes in Vermont's precipitation.

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## Appendix A

## **I. SAMPLE COLLECTION**

### **A. For rain and rainfall amount:**

#### **As soon as possible following each rain event**

- 1) Remove the collection jug from the collection box.
- 2) Simultaneously, record rainfall amount which is in the inner cylinder of the rain gauge to the nearest hundredth, under the "inches rain/snow column".
- 3) Record next to amount of precipitation the type of precipitation. For example, rain, sleet, hail etc.
- 4) Check the screen located in the funnel for insects, pollen or other particles. Remove any contaminants.
- 5) Rain may be used to rinse rain gauge and screen, otherwise, empty the rain gauge and replace.
- 6) Once inside, thoroughly rinse a 250 ml beaker to be used for pH analysis with distilled water.
- 7) Pour approximately 100 ml of rain sample into beaker.

### **B. Snow and snowfall amount:**

#### **As soon as possible following each snow event**

- 1) Rinse extra polyethylene bucket with distilled water.
- 2) Replace used sample bucket with the just rinsed extra bucket to the sample site.
- 3) In addition, replace the outer 4" cylinder of the rain gauge with the spare cylinder.
- 4) Cover sample bucket and cylinder and bring inside, allowing snow to melt at room temperature.
- 5) As soon as sample has thoroughly melted, pour approximately 100 mls into a 250 ml beaker which has been rinsed by distilled water.
- 6) After the snow located in the outside of 4" cylinder of the rain gauge has melted, pour it into the inner graduated cylinder.
- 7) Record the melted amount under the "inches rain/snow" column of the data sheet.
- 8) Record the type of precipitation next to the amount.

## **II. BUFFER PREPARATION, PH METER CALIBRATION AND USE OF PH CHECK SAMPLE**

### **A. Buffer Preparation:**

Prepare the buffer solution for pH 4 and 7 weekly. For capsules, use a 100 ml graduated cylinder, pour 100 ml of distilled water into a plastic bottle which has been thoroughly rinsed with distilled water. Empty the contents of a pH 4 powder capsule into the bottle and shake vigorously until all powder has dissolved. Repeat procedure for the pH 7 buffer. For prepared solution, pour the provided buffer from the bottles into your weekly sample container.

### B. pH Meter Calibration:

Before the pH of the sample can be determined, the Cole/Parmer digital pH meter model 5987 and the Orion 310 need to be calibrated with buffer 4 and 7 using the two point standardization procedure:

#### **For the Cole/Parmer pH meter**

- 1) Set mode switch on meter to Standby/Temperature. Install and connect the electrode (Cole Parmer model C-5992-10) and turn on power switch which is located on the back of meter.
- 2) For an accurate pH test to occur, the buffer solutions should be close in temperature to the precipitation sample. Take the temperature of the buffers using a mercury thermometer (-20° to 100°C). Set the temperature control to that temperature.
- 3) Lower rubber sleeve on the electrode and immerse probe tip into the pH 4 buffer solution.
- 4) Turn Mode switch to pH. Adjust standardize control until display reads 0.00.
- 5) Set Mode switch to Standby/Temperature and remove electrode from pH 4 buffer solution. Rinse electrode tip thoroughly with distilled water and blot dry with kim wipe.
- 6) Immerse electrode in pH 7 buffer solution. Set Mode switch to pH and rotate Slope % Set Control until it reads pH 3.00 which is the difference between pH 4 and 7.
- 7) With electrode still in the pH 7 buffer solution, rotate Standardize Control clockwise until display reads 7.00.
- 8) Remove electrode from pH 7 buffer solution and rinse thoroughly with distilled water, then blot dry with kim wipe.

#### **For the Orion pH meter**

- 1) Install and connect the electrode (Cole Parmer model C-5992-10) and plug in the meter. (Turns the meter on, there is no ON/OFF switch)
- 2) For an accurate pH test to occur, the buffer solutions should be at 25°C or approximately room temperature. Take the temperature of the buffers using a mercury thermometer (-20° to 100°C). Use a warm water bath if necessary to heat the sample.
- 3) Once the meter is On, wait a few seconds for the self test to complete then press CAL key to initiate calibration sequence. Press YES key to accept the last calibration range (7-4). The pH 7 buffer indicator will light up.

4) Rinse electrode tip thoroughly with distilled water and blot dry with kim wipe. Immerse electrode in pH 7 buffer. When READY light comes on, press the YES key to accept.

5) The pH 4 buffer indicator now will light up. Remove electrode from 7 buffer, rinse electrode tip thoroughly with distilled water and blot dry with kim wipe. Immerse electrode in the 4 buffer. When the READY light comes on, press the YES key to accept.

6) SLP will be displayed while the calculated slope is displayed. The slope should be between 95-100%. Meter will automatically go into MEASURE mode. The READY light will come on to indicate electrode stability.

### C. USE OF pH CHECK SAMPLE

Once a week, the pH check sample must be used to check the electrode and meter for accuracy and sensitivity. It requires greater sensitivity of the electrode and meter to determine the correct pH and check sample (both are low ionic strength solutions) than to determine the pH of buffers 4 and 7 (both high-ionic strength solutions).

Please contact Jim Kellogg when you are running low on a check sample.

The Department of Environmental Conservation Biomonitoring laboratory, 103 S. Main St, Waterbury, VT 05671-0459.

#### **Use check sample after steps in SECTION B have been completed.**

1) Remove provided check sample out of the refrigerator and pour a small amount into a clean beaker. This simulated "acid rain" check sample has a pH of 4.70 +/- .10 pH units at 25°.

2) Warm up the check sample in a warm water bath to 25°.

3) Place electrode into the check sample and for Cole Parmer meters, adjust temperature control to 25°. If using an Orion meter, record pH displayed then skip to step 5.

4) Turn Mode switch to pH and record pH on the data sheet under the "check sample" column.

5) Retape the bottle and refrigerate.

### D. TROUBLE WITH THE CHECK SAMPLE

If reading is not within 0.10 pH units of the 4.70 at 25°, there may be a problem with the meter, electrode or the check sample may be contaminated. Often, simply repeating the steps in Section C takes care of the problem. If repeated calibration with buffer solutions fails to correct the problem, the problem in most cases exists in the probe and can be fixed.

1) Disconnect the electrode and gently shake out the internal KCL solution. If the KCL has crystallized in the electrode tip, a small amount of distilled water added directly to the











