ACID RAIN ON THE WOODENS RIVER WATERSHED

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by
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INTRODUCTION. Over the years there has been considerable concern over the acidity of the lakes in the Woodens River Watershed. In a study conducted for WRWEO by the author in 2000, the acidity of 8 lakes in the watershed (Cranberry, Black Point, Frederick, Sheldrake, Five Island, Birch Hill, Hubley and Long) ranged from 8-55 μM (pH 4.9-5.1).

In a study by Stantec Consulting in the fall of 2009, the acidity ranged from 3-21 μM (pH 4.68-5.57). The lowest acidity (3 μM) was found in Ben Miller Lake (feeds Long Lake), which we had not studied. Stantec reported that Fleck Brook, which feeds Hubley from Birch Hill, had an acidity of 0.5 μM (pH 6.3). Several active trout redds were observed in Fleck Brook, but their development was not followed. Five Island Run, which connects Five Island Lake to Hubley, had an acidity of 0.3 μM. These acidities are conducive to trout development. It is very unfortunate the development of the redds in Fleck Brook were not followed. WRWEO should consider undertaking a suitable study.

The Stantec report concludes, among many other things: "The water quality of the Woodens River watershed exhibits patterns that should be the cause for concern with respect to acidity…..".

This conclusion is based on a small number of samples taken in the fall of one year. As a first step in understanding the effect of acid rain on our watershed better, we have measured the acidity of each rain fall from November 5, 2010 to October 30. 2011. At the same time, the effect of the acid rain on Black Point Lake was measured.

This report summarizes the results of that study.

ACIDITY. Although acidity is usually expressed as pH, it is defined as the molar concentration, M, of hydrogen ions ($[H^+]$). $pH = 10^{-pH}$. The pH scale is useful for covering a very broad range of acidities. Unfortunately, the pH scale is the inverse of acidity and is based on powers of ten. For the range of acidities we find in our lakes and streams, the micromolar concentration, μM ($\mu M = M \times 10^{-6}$), is much more useful than pH because there is a direct 1 to 1 relationship between acidity and μM.

A neutral solution is 0.1 μM (pH 7.0). Trout have prospered in our watershed with acidities as high as 16 μM (pH 4.8).

EXPERIMENTAL PROCEDURE. A rain gauge (33mm I.D.) was located about 20 meters from Black Point Lake. Starting on November 2, 2010 a rain sample was collected after each rain storm. In two cases, snow was collected. The following day the acidity of the rain sample was measured with a YSI multiprobe meter[1] standardized just before use with pH 4.01

[1] We are indebted to Mr. David Bryson and the Three Brooks Corporation for funds to purchase this meter and to carry out several water quality studies on the watershed.

and 7.00 buffers. The meter measures $[H^+]$ in mvolts and converts the data to pH. We converted pH back to μM $[H^+]$ using μM $[H^+] = 10^{-pH}$. Snow samples were melted and allowed to warm up before measuring the acidity.

At the time the rain sample was measured, a sample was taken from Black Point Lake near the shore and the acidity was measured.

The results were plotted using the computer program Kleidagraph. The data points were connected with a Cubic Spline curve fit.

RESULTS and DISCUSSION.

Table 1 shows the raw data.

Table 1. Acid Rain at Black Point Lake

Sample #	Date	Guage, mm	pH, rain	pH, lake	Comments
1	11/5/10	20	4.81	-	
2	11/6/10	30	4.69	-	
3	11/7/10	60	4.81	-	
4	11/17/10	30	4.68	-	
5	12/4/10	40	4.68	-	
6	1/13/11		6.40	-	melted snow
7	2/2/11		5.98	-	melted snow
8	4/2/11		4.80	-	snow & rain
9	4/6/11		4.34	-	
10	4/12/11		4.25	-	
11	4/10/11	11	4.74	-	
12	4/19/11	15	4.20	-	
13	4/26/11	10	4.45	-	
14	4/28/11	22	4.90	4.91	
15	4/29/11	10	4.37	-	
16	5/4/11	8	4.21	-	
17	5/6/11	15	4.46	5.54	
18	5/8/11	20	4.44	5.14	
19	5/9/11	32	4.31	5.38	GW[1] pH 6.55
20	5/10/11	25	4.28	5.37	
21	5/16/11	10	4.17	5.06	
22	6/2/11	18	3.80	5.04	TS[2]
23	6/14/11	13	4.51	6.11	
24	6/15/11	51	4.74	5.39	
25	6/16/11	23	4.58	5.01	
26	6/19/11	20	4.25	5.20	TS
27	7/9/11	25	4.84	5.49	
28	7/22/11	8	4.70[3]	5.37	TS
29	7/26/11	18	4.51	5.47	
30	7/31/11	20	4.43	5.43	
31	8/8/11	20	5.61	5.26	
32	8/16/11	5	5.21	5.39	
33	9/7/11	10	4.79	5.50	
34	9/15/11	18	4.65	5.04	
35	9/23/11	26	4.55	5.78	
36	9/24/11	20	4.80	6.87[4]	
37	10/2/11	30	5.52	5.97	
38	10/3/11	20	4.73	5.56	
39	10/5/11	70	4.62	5.35	
40	10/15/11	50	4.30	5.25	
41	10/21/11	105	4.30	5.43	
42	10/30/11	55	4.80	5.57	

[1]Ground Water running into lake. [2]Thunder storm. [3]Slight greenish cast. [4]Rechecked standardization of meter.

It is clear that the lake is significantly less acidic than the rain after each storm. Figure 1 show a plot of the acidities:

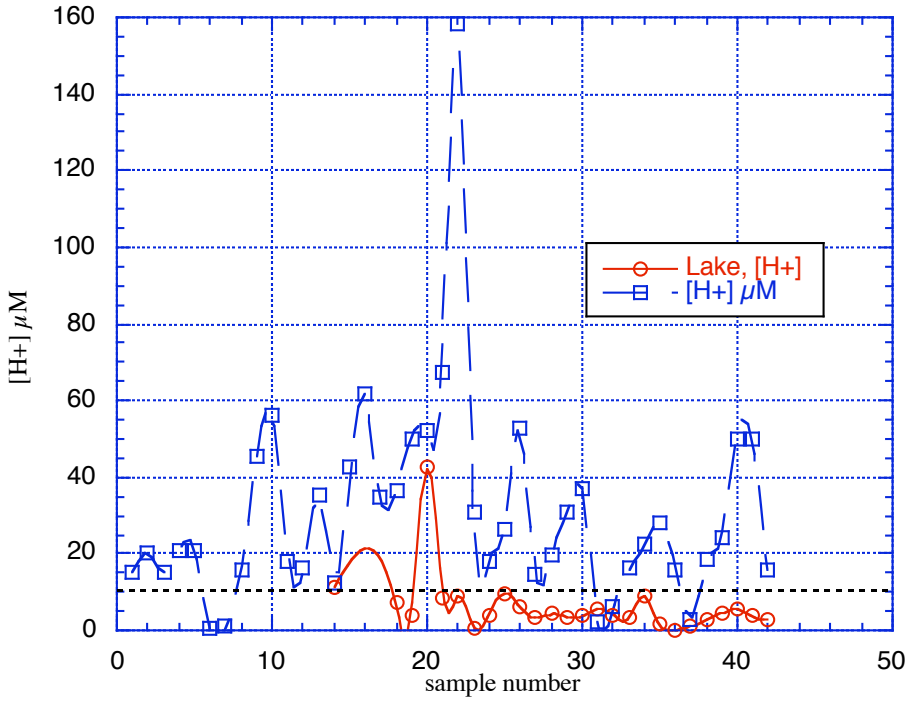

Figure 1. Acidity of the rain and Black Point Lake after each storm. Data from Table 1. Acidity calculated from the pH data.

There are several important conclusions. First, the acidity varies in unpredictable ways. Clearly, one cannot reach any reliable conclusions from one or two random samples. Most of the rain samples had acidities between 10 and 60 μM. However, Figure 1 shows an outlier that occurred on June 2, 2011. This was after a large thunder storm, and one might suppose that the high acidity was due to electric discharge. However, measurements after two later thunderstorms failed to confirm this hypothesis. The cause of the outlier is not clear. Even ignoring the outlier, it is clear that a systematic study is necessary before any reliable conclusions can be reached.

The lake also showed variability, but it did not track that of the rain exactly. For example, the outlier for the lake on May 10 (sample 20) did not correspond to the outlier for the rain, which occurred on June 2 (sample 22). The acidity of the rain increased from 14.5 to 37 μM in

samples 27-30, but the acidity of the lake increase only slightly from 3.2 to 3.7 μM. Clearly, one cannot draw any reliable conclusions about the lake from rain acidity alone.

The acidity of the lake is usually 5-10 times less acidic than the rain. There are two reasons for this. The first is dilution. Think of the lake as a tub of water. Now dump a cup of red dye (hydrogens ions) into the tub (lake). You see an intense red spot where you dumped the dye. When you come back some time later, you no longer see the dye, but the dye molecules are still there. They have defused throughout the water in the tub. Let's assume that the tub has 100 times more water than the cup. If you take a random cupful of water from the tub, you will find that there are 100 times fewer red dye molecules than there were in the initial cupful. The same thing happens to hydrogen ions from acid rain when they fall into the lake. Since μM is based on molecules/liter, the acidity of the lake will be less than the rain after diffusion has occurred. In addition, some hydrogen ions are running out of the lake continuously so the acidity of the lake is going to decrease slowly unless additional hydrogen ions are added. In general, the acidity of the lake will resemble that of the rain, but have a lower value.

Second, acid rain falls on the soil around the lake and, eventually, runs off into the lake. The acidity of the runoff will depend on the nature of the soil. We measured this in one of the samples: Rain, 50 μM; lake, 4.2 μM; ground water close to lake, 0.3 μM. Clearly, much of the acidity of the rain was neutralized by bases (lime?) in the soil. Measurement of soil samples around a lake are important is accessing its acidity, and we have limited data in this study.

Ideally, we would like the acidity of a lake to be neutral (0.1 μM = pH 7). Sporadic measurements by the author in the early 80's when there were abundant trout and Mayfly populations in Black Point Lake gave pH values around pH 5. It seems likely that acidity less than 10 μM (>pH 5) is probably acceptable for most organisms in this watershed. All but one of the values for the lake in Table 1 meet this criterion. The average pH is 5.475, which corresponds to an acidity of 3.3 μM. However, the lake samples were taken close to shore where runoff may have produced biased results.

CONCLUSIONS. This study doesn't tell us much we didn't know. We do have acid rain, and it is not going to go away anytime soon. Lakes in the watershed are acidic, and have been so for a long time. Our lakes deal with this acidity by dilution and flushing and, in some cases (Ben Miller ?) by surrounding alkaline soil. The most important point is that you cannot draw valid conclusions from single measurements. It is important to take samples at different times of year in different lakes and at different places on a given lake. We have done this in our previous studies. The current study shows how the acidity of rain varies on our watershed over a year period and how that affects one of the lakes.

SOME THOUGHTS ON ACID RAIN AND THE WOODENS RIVER WARERSHED

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Water with a hydrogen ion concentration of 0.1 micromoles/liter (0.1 μM) is defined as "neutral". Most organisms can exist at acidities between 0.1 μM and 10 μM. Some may adapt to higher acidities. In fact, some bacteria live with an acidity as high as 1 M (10^6 μM). Trout can exist between 0.3 and 10 μM[1]. However, trout eggs fail to hatch at 10 μM[1] .

The acid rain falling on the Woodens River watershed from November 5, 2010 to October 30, 2011 averaged 21.4 μM. The acidity of Black Point Lake during that same period averaged 3.3 μM, which is well within the levels tolerated by trout. However, the lake samples were taken near the shore where runoff may have biased the values. In fact, the acidity of Black Point Lake measured at the deepest part of the lake in November of 2000 was 15.8 μM. A further study in which samples are taken from several sampling stations in the lake during a year of rain fall is necessary to address this question.

A study of 10 lakes in the watershed in the fall of 2000 gave acidities that ranged from 10 μM to 15.8 μM. The average was 12.6 μM (S.D. 2.5 μM). This is above the threshold for trout egg development. However, this usually takes place in connecting streams. The acidity of Fleck Brook near an observed trout redd was 0.5 μM, which is well within the tolerated limits.

There is no question that acid rain is undesirable, but the problem in the Woodens River Watershed may not be as bad as some would have us believe. Clearly, additional studies over an extended period of time (e.g. 1 year) need to be done. They should include observing the development of the trout redds in Fleck Brook. This waterway feeds Hubley Lake, which was a major trout lake until the late 1980's.

[1]U.S. Environmental Protection Agency Web Site ,"Effects of Acid Rain"