Acid Rain Monitoring Project

FY12 End of Fiscal Year Report
DRAFT

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Introduction

This report covers the period July 1, 2011 to June 30, 2012, the eleventh year of Phase IV of the Acid Rain Monitoring Project. Phase I began in 1983 when about one thousand citizen volunteers were recruited to collect and help analyze samples from nearly half the state's surface waters. In 1985, Phase II aimed to do the same for the rest of the streams and ponds[1] in Massachusetts. The third phase spanned the years 1986-1993 and concentrated on a subsample of streams and ponds to document the effects of acid deposition to surface waters in the state. Over 800 sites were followed in Phase III, with 300 citizen volunteers collecting samples and doing pH and ANC analyses. In 2001, the project was resumed on a smaller scale: about 50 volunteers are now involved to collect samples from approximately 150 sites, 26 of which are long-term sites with ion and color data dating back to Phase I. In the first years of Phase IV (2001-2003), 161 ponds were monitored for 3 years. Between Fall 2003 and Spring 2010, the project monitored 151 sites twice a year, mostly streams, except for the 26 long-terms sites that are predominantly ponds. Since 2011, reduced funding eliminated our October sampling and monitoring now occurs in April only. In 2011, we also stopped monitoring some of the streams in order to add and revisit ponds that were monitored in 2001-2003. This year is the second year of monitoring for those newly added ponds.

Goals

The goals of this project are to determine the overall trend of sensitivity to acidification in Massachusetts surface waters and whether the 1990 Clean Air Act Amendment has resulted in improved water quality.

Methods

The sampling design was changed in 2011 to monitor both streams and ponds, and that design was continued in 2012. In 2001-2003 mostly ponds were monitored. In Fall 2003 the sampling scheme switched to streams to evaluate their response to air pollution reductions. In 2011 the site list was modified to include both ponds and streams. Half of the streams monitored since 2003 were kept, and half of the ponds monitored in 2001-2003 were added back. The streams that were removed were chosen randomly within each county. Ponds that were reinstated on the sampling list were chosen at random within those counties, by ease of accessibility, to replace the removed streams. Because those sites were not chosen with a preconceived plan, they can be considered picked at random.

One collection took place this year, on April 15, 2012.

Methods were unchanged from previous years: Volunteer collectors were contacted six weeks before the collection to confirm participation. Clean sample bottles were sent to them in the mail, along with sampling directions, a field sheet/chain of custody form, and directions including GPS coordinates and maps to the sampling sites. Volunteers collected a surface water sample at their sampling sites either from the bank or wading a short distance into the water body. They collected water one foot below the surface, upstream of their body, after rinsing their sample bottle three times with pond or stream water. If collecting by a bridge, they collected upstream of the bridge unless safety and access do not allow it. They filled in their field data sheet with date, time, and site code information, placed their samples on ice in a cooler and delivered the samples to their local laboratory right away. They were instructed to collect their samples as close to the lab analysis time as possible. In a few cases, samples were collected the day prior to analysis because the lab is not open on traditional "ARM Sunday." Previous studies by our research team have established that pH does not change significantly when the samples are refrigerated and stored in the dark.

Volunteer labs were sent any needed supplies (sulfuric acid titrating cartridge, electrode, buffers), two quality control (QC) samples, aliquot containers for long-term site samples, and a lab sheet one week to ten days before the collection. They analyzed the first QC sample (an unknown) in the week prior to the collection and called in their results to the Statewide Coordinator. If QC results were not acceptable, the volunteer analyst discussed possible reasons with the Statewide Coordinator and made modifications until the QC sample analysis gave acceptable results. The Statewide Coordinator also made visits to two of the labs with newer analysts to go over procedures and quality control. On collection day or the day after, volunteer labs analyzed the second QC sample before and after the regular samples, and reported the results on their lab sheet along with the regular samples. Analyses were done on their pH-meters

[1] Note: The term stream in this report refers to lotic waters (from creeks to rivers) and the term ponds refers to lentic waters (lakes and ponds, but not marshes)

with KCl-filled combination pH electrodes. Acid neutralizing capacity (ANC) was measured with a double end-point titration to pH 4.5 and 4.2. Most labs used a Hach digital titrator for the ANC determination, but some used traditional pipette titration equipment. Aliquots were taken from the 26 long-term sites to fill two 60mL bottles and one 50mL tube per site for later analysis of ions and color. These aliquots were kept refrigerated until retrieval by UMass staff.

Aliquots, empty bottles, and results were collected by the ARM Statewide Coordinator between one and three days after the collection. The Cape Cod National Seashore lab mailed those in, with aliquot samples refrigerated in a cooler with dry ice. Unfortunately they sent the samples too late and cation analysis could not be done on those samples due to sample holding time violation.

The Statewide Coordinator reviewed the QC results for all labs and flagged data for any lab results that did not pass Data Quality Objectives (within 0.3 units for pH and within 3mg/L for ANC). pH and ANC data were entered by one ARM staff and proofed by another. Data were entered in a MS excel spreadsheet and uploaded into the web-based database at http://umatei.tei.umass.edu/ColdFusionProjects/AcidRainMonitoring. Data were also posted on the ARM web page at http://www.umass.edu/tei/wrrc/arm/.

Water Resources Research Center’s Elizabeth Finn ran the Environmental Analysis Lab (EAL) and provided the QC samples for pH and ANC to all of the volunteer labs. EAL also provided analysis for pH and ANC for samples from Hampshire and Franklin Counties, and color analysis for the long-term site samples. UMass Chemistry Department’s Dr. Julian Tyson and his laboratory team of graduate students analyzed the samples from the long-term sites for anions and cations.

Aliquots for 26 long-term sites were analyzed for color on a spectrophotometer within one day; anions within one month on an Ion Chromatograph; and cations within two months on an ICP at the Environmental Analysis Lab (EAL) on the UMass Amherst campus. The data was sent via MS Excel spreadsheet to the Statewide Coordinator who uploaded it into the web-based database.

The Statewide Coordinator and the Project Principal Investigator plotted the data to check for data inconsistencies and gaps. They then analyzed the April data from 1983 through 2012, using the statistical software JMP (http://www.jmp.com/software/) to run bivariate analyses of pH, ANC, ions, and color against date. This yielded trends analyses with a fitted X Y line, using a 95% confidence interval.

Results

1. There were 150 sites to be monitored, 77 ponds and 73 streams. Of those, 19 ponds and 7 streams are “long-term” sites that are sampled every year and analyzed for color and a suite of ions in addition to pH and ANC.

2. Sampling was completed for 143 sites (72 ponds and 71 streams) including 25 of our long-term sites. Two of our long-term sites were not analyzed for anions due to unmet holding times, and in the cation analysis, the lab was unable to analyze for K due to equipment failure.

3. The only quality control problem this year was the UMass Boston laboratory not passing our quality control samples, so we picked up all of their samples and analyzed them at EAL.

4. The network of volunteers was maintained and kept well informed on the condition of Massachusetts surface waters so that they would be able to participate effectively in the public debate. This was accomplished by e-mail and telephone communications, as well as through updates via an internet list-serv. 54 volunteers participated in this year’s collection. Several new volunteer collectors were recruited to replace ill or retiring volunteers via several internet listservs and by word of mouth. There were 10 volunteer labs across the state, in addition to the EAL at UMass Amherst, in charge of pH and ANC analyses (Table 1).

Table 1: Volunteer Laboratories

Analyst Name	Affiliation	Town
Joseph Ciccotelli	Ipswich Water Treatment Dept	Ipswich
Nicole Henderson	UMass Boston Environmental Studies Program	Boston
Sherrie Sunter	MDC Quabbin Lab	Belchertown
Dave Bennett	Cushing Academy	Ashburnham
Holly Bayley	Cape Cod National Seashore	South Wellfleet
Robert Caron	Bristol Community College	Fall River
Bob Bentley	Analytical Balance Labs	Carver
David Christensen	Biology Dept. Wilson Hall WSC	Westfield
Jim Bonofiglio	City of Worcester Water Lab	Holden
Carmen DeFillippo	Pepperell Waste Water Treatment Plant	Pepperell
Beckie Finn, Marie_Françoise Hatte	University of Massachusetts Environmental Analysis Lab	Amherst

5. The ARM web site and searchable database were maintained and updated. 2012 pH, ANC, ions and color data that met data quality objectives were added to the web database via the uploading tool created in previous years. The database was evaluated for quality control and uploading errors were corrected. Note that our website is migrating to a new address (www.wrrc.umass.edu).

6. The data collected was analyzed for trends in pH and ANC in April months only for 143 sites and for color and ions for 25 sites, using the JMP® Statistical Discovery Software (http://www.jmp.com/software/). Trend analyses (scatter plots, regression, and correlation) were run on pH, ANC, each ion except K, and color separately, predicting concentration vs. time.

Data Analysis Results

pH and ANC

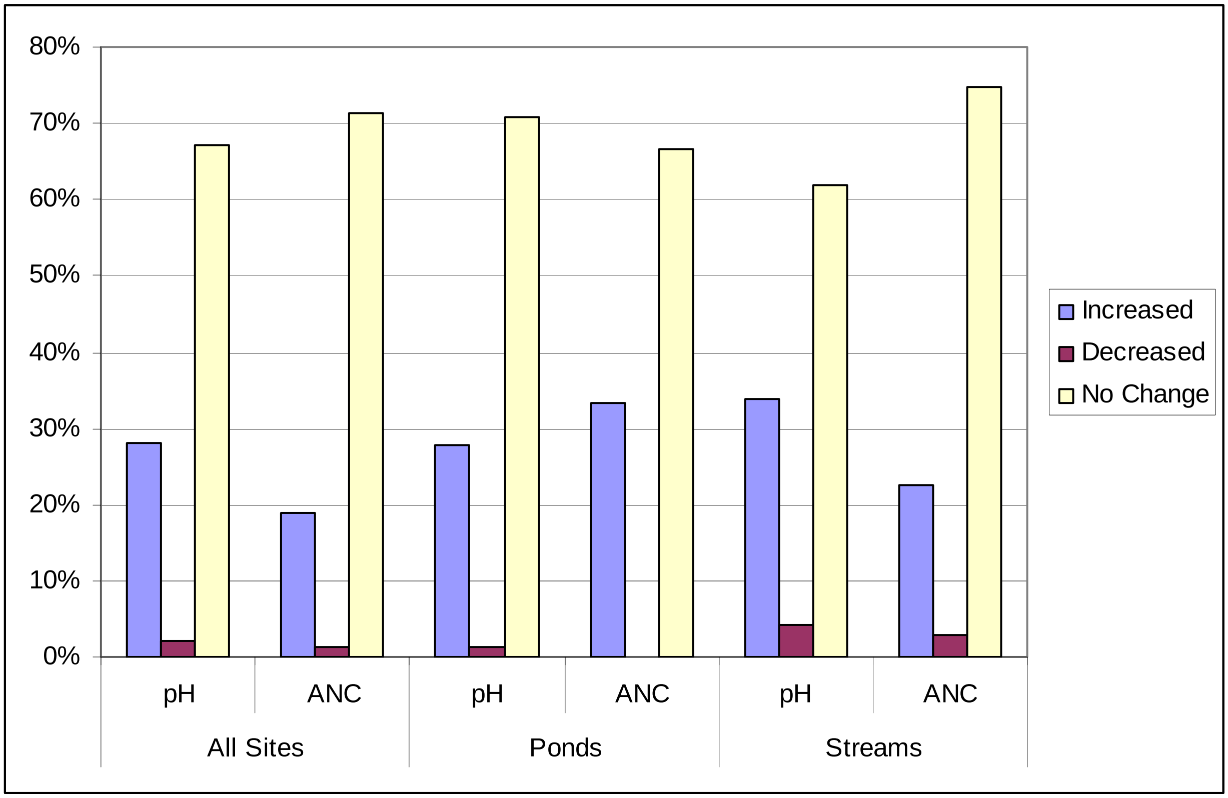
Trend analysis for pH and ANC
Table 2 displays the number of sites out of a maximum of 143 that show a significant change over time for pH or ANC. If the difference was not statistically significant ($p>0.05$), the sites are tabulated in the 'No Change' category.

Table 2: Trend analysis results for pH and ANC, April 1983 – April 2012

	All Sites		Ponds		Streams	
	pH	**ANC**	**pH**	**ANC**	**pH**	**ANC**
Increased	40	27	20	24	24	16
Decreased	3	2	1	0	3	2
No Change	96	102	51	48	44	53
Total	143	143	72	72	71	71

Those results are also graphed in Figure 1.

Figure 1. Percentage of site changes in pH and ANC, from trend analysis, April 1983-2012



This trend analysis indicates that for most sites, neither pH nor ANC changed significantly over time. However, for those sites that show a significant change, more show an increase than a decrease in value: about a quarter of the sites saw an increase in pH and ANC, more so for pH than ANC over all. However, we see a difference between ponds and streams. More ponds saw an increase in ANC (33%) than in pH (28%), but for streams, more saw an increase in pH (34%) than in ANC (23%). Compared with last year's results, these results are consistent for streams, but for ponds we notice a definite increase in number of sites with increased pH and ANC. This is not consistent with last year's results, but as we have only two years of new data for ponds, it will be interesting to see what the trend looks like in future years.

Ions and Color

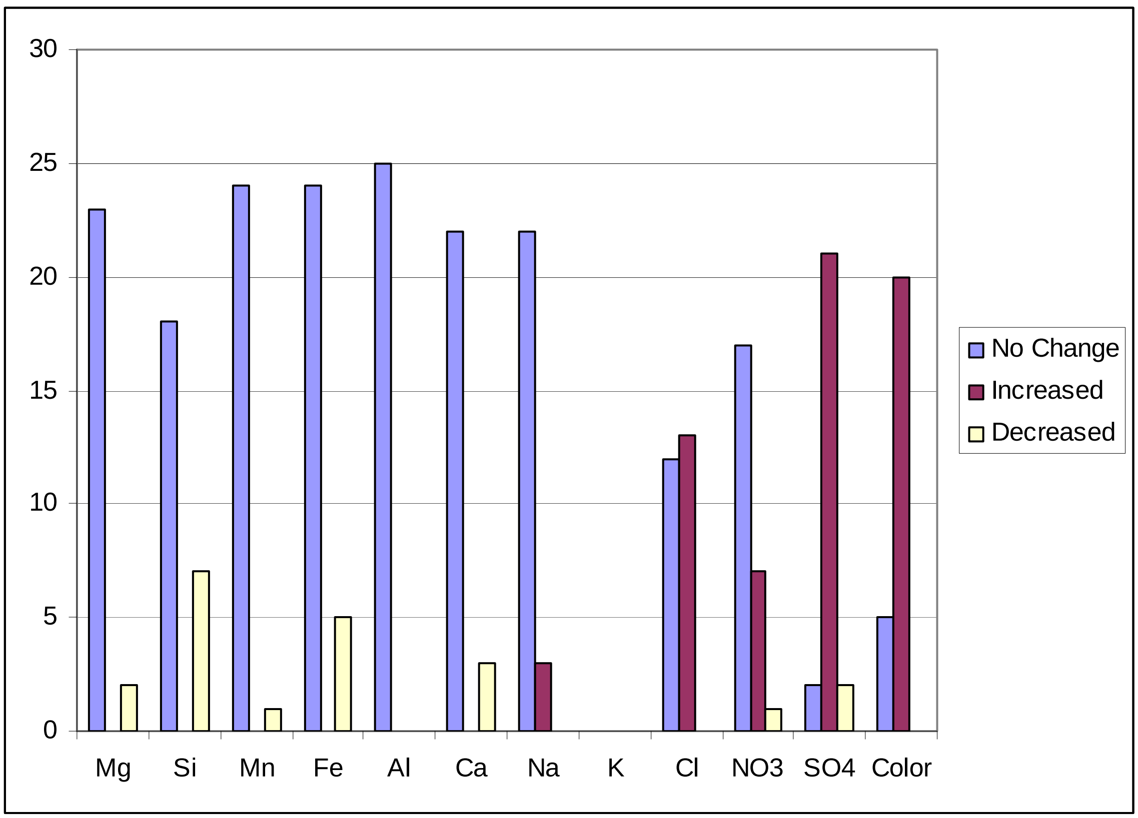
Trend analyses were run for the 25 long-term sites that are analyzed for ten ions and color.

Table 3 and Figure 3 show the results of the trend analysis for all parameters.

Table 3: Trend analysis results for ions and color

	April 1983 - April 2012		
	No Change	Increased	Decreased
Mg	23	0	2
Si	18	0	7
Mn	24	0	1
Fe	24	0	5
Al	25	0	0
Ca	22	0	3
Na	22	3	0
K	n/a	n/a	n/a
Cl	12	13	0
NO3	17	7	1
SO4	2	21	2
Color	5	20	0

Figure 3: Results of trend analysis for ions and color for 25 long-term sites, April 1983-2012



This year the results look different than in previous years. The only consistent result is that color has decreased at almost all sites. Most cations show no significant change over time for the 25 sites we are following. The exception, as in the past, is for sodium, but this year it increased in only three sites.

All anions show significant changes. Chloride still never decreases with time, and increases for more than half of the sites. Nitrate's change is less definite, but it clearly increases for about a third of the sites and decreases for only one site. Sulfate shows the most unexpected change, a significant increase for 22 sites, vs. a strong decrease for 85% of the sites last year.

Discussion

While last year saw a heavy and late-melting snow cover, this year we had no snow cover to speak of in the winter, and by monitoring day on April 15, most of Massachusetts was under drought conditions. Some water bodies were extremely low, and we saw “dirty” samples because there was so little water to sample from that some of the stream or pond bottom had to be scraped with the sample bottle. While this might be the reason for the unexpected changes we are seeing in this year’s data, we will examine the raw data more thoroughly in the coming months to ensure that the proper sites were sampled and lab reports are accurate.

Acknowledgements

Thank you to all of the project’s volunteers who make this project possible by collecting samples all over the state under any weather conditions, and who spend many hours in the lab analyzing samples.

Appendix

Table 4: April 2012 ARM Color and Ion Data

Name	Palsite	MG	SI	MN	FE	CU	AL	Ca	NA	K	CL	NO3_N	SO4	Color
Shingle Island Brook	188	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	NS
Belmont Reservoir	21010	0.75	0.18	0.043	0.20	0.010	0.14	2.5	0.25		1	0.009	3.46	50.71
Cobble Mt. Reservoir	32018	0.94	0.24	0.007	0.10	0.0072	0.016	2.2	2.3		11	0.020	3.39	34.29
Hawley Reservoir	34031	0.66	0.44	0.020	0.11	0.010	0.029	2.9	2.1		10	0.029	5.99	36.43
Wyola Dam	34103	0.40	0.19	0.0035	0.034	0.0072	ND	1.6	1.4		5	0.006	4.51	24.29
Upper Naukeag Lake	35090	0.28	0.16	0.0083	0.044	0.0049	0.026	0.85	2.3		11	0.006	2.79	3.57
Crystal Lake	36043	0.23	0.0029	0.013	0.016	0.0093	ND	0.44	0.22		1	0.006	2.09	66.43
Lake Lorraine	36084	0.76	0.013	0.0047	0.041	0.0094	ND	3.9	5.8		28	0.006	4.54	2.14
Quabbin Station	36129	0.61	0.13	0.0014	0.0083	0.0029	ND	2.3	1.5		7	0.009	4.17	11.43
Nipmuck Pond	42039	0.40	0.29	0.0062	0.015	0.0021	0.051	1.7	2.2		9	0.006	5.66	16.43
N. Watuppa Lake	61004	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	NS
Ashby Reservoir	81001	0.64	0.24	0.053	0.46	0.012	0.039	2.4	2.8		12	0.012	4.30	33.57
Wright Pond	81160	0.38	0.22	0.026	0.29	0.0086	0.092	1.2	1.7		6	0.009	2.83	90.71
Whitehall Reservoir	82120	1.04	0.0082	0.0064	0.11	0.011	ND	3.7	4.3		22	0.006	4.82	
Hedges Pond	94065	1.3	0.093	0.0036	0.041	0.0081	0.059	1.0	2.3		13	0.006	4.03	41.43
College Pond	95030	0.73	0.016	0.0014	0.012	0.0067	ND	0.70	1.2		6	0.006	3.55	52.14
Ezekiel Pond	95051	1.2	0.0092	0.0045	0.082	0.0047	ND	2.1	5.3		28	0.006	4.73	14.29
Little Sandy Pond	95092	0.99	0.014	0.018	0.083	0.0049	ND	1.1	4.1		21	0.096	3.07	60.71
Great Pond	96117	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	NS
Kinnacum Pond	96163	1	0.0022	0.024	0.060	0.0021	0.017	0.30	3.8		NS	NS	NS	37.14
Caldwell Creek	3626575	0.58	0.42	0.010	0.093	0.010	0.053	1.8	1.5		6	0.009	5.35	55.71
W. Branch Swift River	3626800	0.37	0.22	0.0063	0.053	0.0011	0.024	1.5	0.85		3	0.006	5.04	18.57
E. Branch Swift River	3627200	0.65	0.19	0.0053	0.16	0.012	0.0081	2.6	1.9		9	0.012	4.78	84.29
Rattlesnake Brook	6235125	0.57	0.18	0.034	0.29	0.0034	0.23	1.2	1.9		8	0.006	4.53	185.00
Angeline Brook	9560000	1.3	0.37	0.013	0.25	0.0076	0.38	2.1	2.7		15	0.023	4.18	200.00
Bread & Cheese Brook	9560150	2.1	0.19	0.019	0.40	0.0071	0.14	6.2	9.7		52	0.301	6.29	213.57

NS= Not Sampled ND= Not Detected

Table 5: pH and ANC, all sampling sites, April 2012

PALSITE	NAME	April 2012 PH	April 2012 ALK
188	Shingle Island Brook	6.36	3.4
371	Beagle Club Pond	7.18	8.8
11002	Cheshire Res. North	8.37	85.1
21010	Belmont Res;Steam Sawmi	6.52	6
21040	Lake Garfield	8.46	16
21062	Long Pond	7.9	67.2
31042	Trout Pd 2; Demming Pd	6.23	2.6
31044	Upper Spectacle Pond	6.86	6.8
32012	Buck Pond	8.64	16.2
32018	Cobble Mtn. Reservoir	6.64	3.8
33001	Ashfield Pd;Ashfield L;	7.69	40.1
33003	Bog Pond; Anthony Pond	6.17	1.4
33017	Plainfield Pond	6.81	4.8
34011	Brass Mill Pond	6.95	17.1
34023	Fiske Pond	5.62	0.6
34031	Hawley Reservoir	6.49	NA
34080	Scarboro Pond	6.71	5.5
34103	Lake Wyola; Locks Pond	6.51	2.1
35002	Bassett Pond	5.67	0.6
35013	Cowee Pd;Marm Johns Pd	5.47	0.4
35017	Lake Denison	6.54	3.3
35026	Greenwood Pond	5.49	0.5
35048	Moores Pond; Lake Moore	6.56	1.9
35085	Stump Pond	5.8	1.4
35089	Tully Pond	6.7	3.4
35090	Upper Naukeag Lake	6.1	0.7
35095	Lake Watatic	7.03	4.9
35107	L Rohunta; South Basin	6.58	3.4
36015	Bickford Pd;Ropers Res	6.54	2
36036	Cloverdale Street Pond	6.8	14
36043	Crystal Lake	5.67	0.3
36084	Lake Lorraine	6.83	7.2
36129	Quabbin Res.Station 202	6.73	3.8
36155	Thompsons Pond	7.05	11
41014	East Brimfield Res	NS	NS
42039	Nipmuck Pond	5.87	2.6
51024	Coes Reservoir	7.39	19.8
51063	Holden Res 1;Upper Hold	7.01	8.3
51090	Lynde Brook Reservoir	7.45	12.3
51179	Wallis Res	6.09	2.7
52032	Plain Street Pond	NS	NS
61004	North Watuppa Lake	6	0.8
62048	County Road Pond	6.91	12
62058	Deep Pond	7.1	4.5
62097	Johnson Pd; Factory Pd	6.83	5.9

62213	Winnecunnet Pd;Winnecon	7.23	13.1
71043	Upper Mystic Lake	NS	NS
72039	Farm Pond		0
72088	Notch Pond	5.21	0.1
72092	Lake Pearl; Whitings Pd	7.63	24.3
72095	Pleasant St. Pd;Frankli	5.89	11.8
72113	Stony Brook Pond	6.96	25.3
72115	Storrow Pond	NS	NS
73004	Blue Hills Reservoir	7.24	26
81001	Ashby Reservoir	6.61	4.1
81053	Grove Pond	7.05	29
81056	Heald Pond	7.25	16.5
81100	Phoenix Pond; Double Pd	7.35	22.5
81111	Robbins Pond	7.65	61.4
81117	Sandy Pond	7.2	8.5
81151	L Wampanoag; Nashua Res	5.83	0.3
81160	Wright Pd; Upper Wright	6.4	2.3
82120	Whitehall Reservoir	6.7	4.2
84043	Mystic Pond	NS	NS
84072	Upper Attitash Pond	7.04	20.8
84083	Duck Pond	6.63	23.8
94065	Hedges Pond	6.13	1.1
94072	Indian Pond	7.12	16.2
95030	College Pond	6.41	1.6
95051	Ezekiel Pond	6.74	2.6
95092	Little Sandy Pond	6.08	1.5
95112	New Long Pond	6.33	1.6
95142	Spectacle Pond	6.95	3
95151	Turner Pd;Turners Mill	5.55	0.3
95170	Noquockoke L;South Basi	6.74	4.4
96117	Great Pond	5.88	0.6
96163	Kinnacum Pond	5.11	-0.2
96264	Round Pond	6.03	0.8
2103725	Soda Creek	7.35	45
2104100	Williams River	8.12	138.5
2104200	Sleepy Hollow Brook	8	181.6
2105350	Barton Brook	7.34	30.2
2105425	Anthony Brook	6.63	6
2105700	Kilburn Brook	7.06	14.3
2105725	Cady Brook	6.78	19.2
2105750	Bilodeau Brook	7.2	29.3
3106825	Fox Brook	6.32	3
3107375	Benton Brook	6.33	5.5
3107625	Babcock Brook	5.91	1.3
3107700	Valley Brook	6.2	4.4
3208725	Little River	6.68	13.3
3210300	Walker Brook	6.9	17.4

3313175	Hinsdale Brook	8.07	66.9
3313850	Shingle Brook	7.6	68.6
3314100	North River	8.35	35.4
3314450	Kinsman Brook	7.36	15.9
3314550	Vincent Brook	7.49	20.7
3314650	Underwood Brook	7.11	10.1
3314925	East Oxbow Brook	6.9	9
3315075	Hartwell Brook	7.76	28.1
3315325	Bozrah Brook	7.56	21
3316050	Todd Brook	6.88	5.3
3316550	Lord Brook	7.01	5.4
3417750	Bagg Brook	8.36	94.7
3419825	Mill River	7.86	61.6
3522675	Black Brook	6.35	2.5
3523750	Kenny Brook	6.6	9.4
3523825	Beaman Brook	5.95	1.7
3523950	Wilder Brook	5.75	1.5
3524050	Baker Brook	5.99	4
3524200	Towne Brook	6.11	1.9
3524250	Robbins Brook	5.75	0.4
3625975	Sucker Brook	6.72	9.5
3626475	Maynard Brook	5.98	4.2
3626575	Cadwell Creek	6.48	NA
3626800	West Br Swift River	6.13	0.5
3627000	Hop Brook	6.85	6.8
3627200	East Br Swift River	6.69	3.9
3627500	Flat Brook	6.9	NA
3628175	West Br Ware River	6.65	3.3
4230075	French River	6.93	22.4
4230325	Wellington Brook	6.42	25.3
5131275	Round Meadow Brook	6.48	8.5
5131425	Aldrich Brook	6.46	9.3
5132600	Sewall Brook	7.48	27.5
5132625	Cronin Brook	6.86	17.4
5132700	Dorothy Brook	6.69	27.7
5233750	Bungay River	7.01	16.9
5334075	Torrey Creek	6.56	13.2
5334100	Rocky Run	6.63	10.1
5334150	Clear Run Brook	7.13	37
6134500	Kickamuit River	6.78	11.1
6134700	Blossom Brook	4.63	-1.6
6134725	King Phillip Brook	4.5	-1.5
6235125	Rattlesnake Brook	5.07	-0.7
6235775	Mulberry Meadow	6.92	13
6235800	Beaver Brook	6.96	15.1
6236100	Bassett Brook	6.54	7.4
7240375	Godfrey Brook	NS	NS

8143675	Gulf Brook	7.22	13.3
8143825	Robinson Brook	7.6	28.3
8144725	Mcgovern Brook	7.29	25.9
8146000	Bartlett Pond Brook	5.77	3.8
8247475	Millham Brook	7.29	26.2
9253500	Ipswich River	7.1	32.8
9253700	Black Brook	6.7	29.3
9253925	Boston Brook	6.85	24.8
9560000	Angeline Brook	5.04	-0.3
9560150	Bread And Cheese Brook	6.55	3.6
9661525	Hatches Creek	6.4	7.6