Acid Rain Monitoring Project

FY18 Annual Report

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Bureau of Waste Prevention

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Introduction

This report covers the period January 1, 2018 to June 30, 2018, the seventeenth 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 monitored 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 60 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 seventh year of monitoring for those 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 continues to date. 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 and by ease of accessibility to replace the removed streams. Because those sites were chosen without a preconceived plan, they can be considered picked at random.

One collection took place this year, on **April 8, 2018**.

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 latitude and longitude coordinates along with 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 did 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 in 24 hours 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. 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 with KCl-filled combination pH electrodes. Acid neutralizing capacity (ANC) was measured with a double end-point

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[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)

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 24 long-term sites to fill two 50mL bottles and one 50mL tube per site for later analysis of ions and color. These aliquots were kept refrigerated until retrieved by UMass staff.

Note that two of our 26 long-term sites were not sampled (Lake Lorraine in Springfield and Great Pond in Wellfleet) this year. Also note that it was discovered this year that Great Pond was accidentally dropped from the long-term list and replaced with Hatches Creek in Eastham in 2014. We will not include results for Hatches Creek with the long term sites analyses, as it was not selected to be a long term site in 2001 and does not satisfy the criteria to be put on that list. We plan to re-instate Great Pond to the long-term sites list in 2019.

Aliquots, empty bottles, and results were collected by the ARM Statewide Coordinator between one and three days after the collection.

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 proofread by another. Data were entered in a MS excel spreadsheet and uploaded into the web-based database at http://63.135.115.71/acidrainmonitoring/. Data were also posted on the ARM web page at http://wrrc.umass.edu/research/acid-rain-monitoring-project.

Water Resources Research Center's Travis Drury, with the help of sophomore student Haena Jung, managed 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 color analysis for the long-term site samples. The UMass Extension Soils Laboratory analyzed the samples from the long-term sites for cations, and University of New Hampshire's Water Quality Analysis Laboratory, under the direction of Jody Potter, analyzed the samples from the long-term sites for anions.

Aliquots for 24 long-term sites were analyzed for color on a spectrophotometer within one day; anions within two months on an Ion Chromatograph; and cations within one month on an ICP at the UMass Extension Soils Laboratory on the UMass Amherst campus. The available data was sent via MS Excel spreadsheet to the Statewide Coordinator who uploaded it into the web-based database.

The Project Principal Investigator plotted the data to check for data inconsistencies and gaps. She then analyzed the available April data from 1983 through 2018, using the statistical software JMP (http://www.jmp.com/software/) to run bivariate analyses of pH, ANC, and ions against date. This yielded trends analyses with a fitted X Y line, using a 95% confidence interval.

Results

1. There were 149 sites to be monitored, 76 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 138 sites (72 ponds and 66 streams) including 24 of our long-term sites.

3. There were no quality control problem this year, so that all sites sampled yielded results for pH and ANC.

4. For the ion analyses, both UNH and UMass analyzed the 24 long term site samples for Mg, Ca, Na, and K. Because the UMass lab had a positive blank for K, we decided to use the UNH data for these 4 ions. The other ions (Mn, Fe, Al, Cu) were analyzed by UMass only and UMass results were uploaded to the database. We noticed that one known 2017 outlier for K was included in the dataset, so we corrected that and included the corrected value in our analysis. Note that neither lab provides analyses for Si, so that parameter is no longer included in the analysis.

5. 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 listserv. Over 60 volunteers participated in this year's collection. Several new volunteer collectors were recruited to replace ill or retiring volunteers via Volunteermatch.org, a press release which was picked up by at least two Massachusetts newspapers, 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). As the Cape Cod National Seashore lab was not available this year, their samples were analyzed by the Bristol County Community College lab.

Table 1: Volunteer Laboratories

Analyst Name	Affiliation	Town
Joseph Ciccotelli	Ipswich Water Treatment Department	Ipswich
Amy Johnston	UMass Boston	Boston
Mark Putnam	MDC Quabbin Lab	Belchertown
Dave Bennett	Cushing Academy	Ashburnham
Kimberly Newton and Mary Rapien	Bristol Community College	Fall River
Bob Bentley	Analytical Balance Corp	Middleborough
Dave Christensen	Westfield State University	Westfield
Denise Prouty	Upper Blackstone Water Pollution Abatement District	Millbury
Carmen DeFillippo	Pepperell Waste Water Treatment Plant	Pepperell
Cathy Wilkins	Greenfield High School	Greenfield
Travis Drury	UMass Amherst Environmental Analysis Lab	Amherst

6. The ARM web site and searchable database were maintained and updated. 2018 pH, ANC, color, and ion 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. We discussed needed improvements to the data upload utility and database for future improvement of data downloads, and plan to hire our database consultant next year to add these improvements.

7. The data collected was analyzed for trends in pH and ANC in April months (138 sites) and for color and ions (24 sites), using the JMP® Statistical Discovery Software (http://www.jmp.com/software/). Trend analyses (scatter plots, regression, and correlation) were run on pH, ANC, color, and each ion separately for each site, predicting concentration vs. time.

Data Analysis Results

pH and ANC

Table 2 displays the number of sites 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 2018 (Number of sites)

	All Sites		Ponds		Streams	
	pH	ANC	pH	ANC	pH	ANC
Increased	42	45	21	29	21	16
Decreased	6	0	1	0	5	0
No Change	90	93	50	43	40	50
Total	138	138	72	72	66	66

Those results are graphed as percentages of all sites in Figure 1.

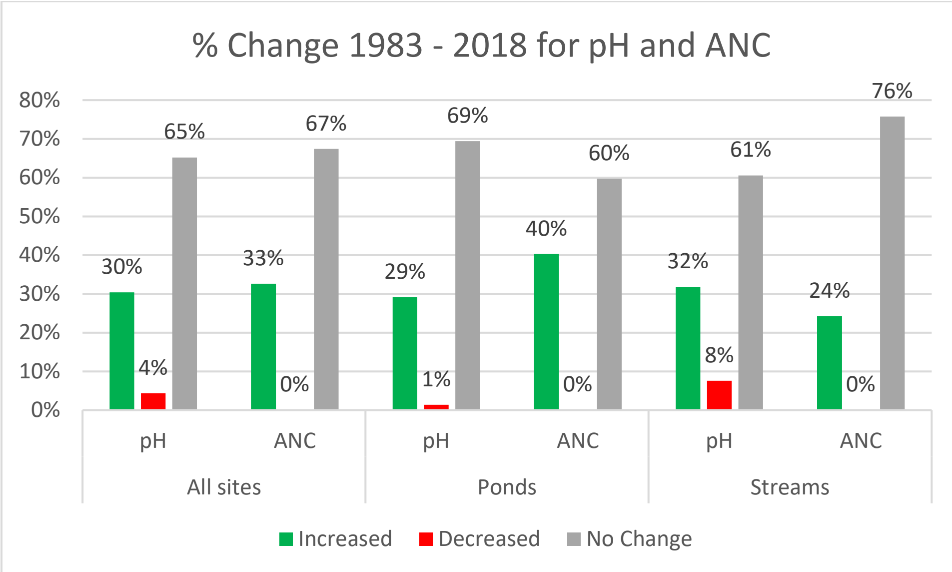

Figure 1. Percent change in number of sites for pH and ANC, from trend analysis, April 1983-2018

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, many more show an increase than a decrease in value: 30% of the sites saw an increase in pH and 33% had an increase in ANC.

While in general the picture does not vary much from year to year, this year a much higher percentage of ponds exhibited an increase in ANC compared to streams (40% vs. 24%), while more streams had a higher pH than in the past than ponds (32% vs. 29%). More streams saw a drop in pH (8%) than ponds (1%), while neither ponds nor streams saw any decrease in ANC.

Last year, when there was snow on the ground in early April, we observed a small change to more acidic conditions. This year the picture looks similar overall, though fewer ponds showed a decrease in pH and alkalinity, and more streams showed such a decrease. This year there was no snow on the ground on sampling day, though it snowed 2 days prior. Over the whole winter, 2018 had similar total snow amounts as 2017, but March was much snowier this year than last. We purposely sample in early April to catch any large snowmelt events, but this year the snow melted early and we evidently missed the big snowmelt event.

Ions and color

Trend analyses were run for 24 long-term sites that were analyzed for eleven ions and for color. Results are shown in Table 3 and Figure 2. Note that the trends period is 1985-2018 rather than 1983-2018 because we do not have ion analyses for 1983 and 1984 for the long-term sites.

Table 3: Trends for number of sites with increases or decreases in ion concentration and color April 1985 – April 2018

	Increased	Decreased	No Change
Color	19	0	5
Cl	17	0	7
NO3_N	11	1	12
SO4	0	22	2
Mg	5	0	19
Mn	0	5	19
Fe	0	6	18
Cu	2	0	22
Al	2	3	19
Ca	5	0	19
Na	13	0	11
K	8	0	16

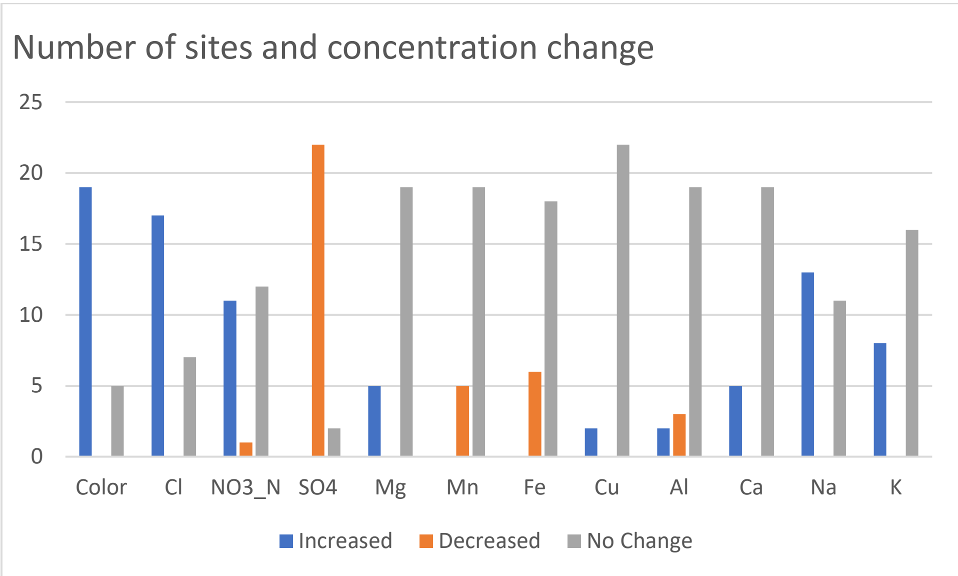

Figure 2: Results of trend analysis for ions and color at 24 long-term sites, April 1985-2018 Shown is how many sites showed an increase (blue), decrease (orange), or no significant change (yellow) over the period 1985 – 2018

Results are similar to last year. While there are still more sites that show no significant change either up or down, more cations display an increase than a decrease over the years. Sodium is now again the ion with the most increases, with iron showing the most decreases. This year we had another opportunity to compare analytical results for four cations (Mg, Ca, Na, and K) between the UNH and the UMass lab, and because of a positive blank at UMass, we used the UNH results for those 4 cations. As we noted last year, the UMass lab results are often higher than the UNH lab, and indeed this year we are seeing fewer statistically significant increases, particularly for Potassium.

For anions, we continue to see a very significant downward trend in Sulfate (again 22 sites). Nitrates, on the other hand, continue to show more increases than decreases, and it is unknown at this time whether it is due to increasing vehicular emissions, or a result of climate change – smaller and less persistent snowpacks result in fine root damage and reduced microbial activity. This can result in losses of nutrient elements, most notably Nitrogen in the form of NO_3^-.

Color is still increasing in most of our sites, which is consistent with a recovery of natural alkalinity.

Discussion

The continued trend in decreasing sulfate confirms that the Clean Air Amendment of 1990 is having a positive effect in the quality of the Commonwealth's surface water quality. Road salting in the winter continues to affect the concentration of sodium and calcium in the water bodies. Continued monitoring will help tease out whether nitrate pollution is countering the beneficial effect of decreased sulfates.

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.

Cover photo: PI Marie-Françoise Hatte takes a sample from Eagleville Pond in Orange, MA on April 8, 20187. Photo by C. Walk.

Appendix

Table A-1: April 8, 2018 pH and Alkalinity data

Name	Palsite	pH	Alkalinity
Shingle Island Brook	188	5.38	1.05
Beagle Club Pond	371	6.21	3.80
Cheshire Res North	11002	7.72	64.20
Belmont Reservoir	21010	6.72	25.70
Lake Garfield	21040	7.19	40.20
Long Pond	21062	7.53	81.40
Trout Pond 2	31042	5.91	2.10
Upper Spectacle Pond	31044	5.86	5.80
Cobble Mtn Reservoir	32018	6.33	5.00
Ashfield Pond	33001	7.37	36.70
Bog Pond	33003	5.76	2.60
Plainfield Pond	33017	6.05	1.50
Brass Mill Pond	34011	7.00	9.30
Fiske Pond	34023	5.20	0.10
Hawley Reservoir	34031	6.12	1.57
Scarboro Pond	34080	5.95	1.70
Lake Wyola	34103	6.22	1.70
Bassett Pond	35002	5.79	0.80
Cowee Pond	35013	5.18	0.20
Greenwood Pond	35026	4.63	-1.00
Moores Pond	35048	5.82	1.40
Stump Pond	35085	4.75	-0.80
Tully Pond	35089	6.35	2.30
Upper Naukeag Lake	35090	6.00	1.80
Lake Watatic	35095	6.34	3.80
Lake Rohunta	35107	5.90	1.80
Bickford Pond	36015	6.30	2.60
Cloverdale Street Pond	36036	6.63	5.30
Crystal Lake	36043	6.11	0.88
Quabbin Reservoir	36129	6.85	4.48
Thompsons Pond	36155	6.41	4.90
Nipmuck Pond	42039	5.42	0.70
Coes Reservoir	51024	6.94	14.00
Holden Reservoir 1	51063	6.25	2.80
Lynde Brook Reservoir	51090	6.74	9.70
Wallis Reservoir	51179	6.50	4.20
Plain Street Pond	52032	6.35	8.70
North Watuppa Lake	61004	5.25	0.30

Table A-1: April 8, 2018 pH and Alkalinity data (continued)			
Deep Pond	62058	6.32	7.20
Johnson Pond	62097	6.20	3.05
Winnecunnet Pond	62213	6.71	7.90
Upper Mystic Lake	71043	7.68	36.80
Farm Pond	72039	6.62	5.40
Notch Pond	72088	4.88	-0.20
Lake Pearl	72092	6.81	21.40
Pleasant Reservoir	72095	6.42	16.60
Stony Brook Pond	72113	6.39	16.00
Storrow Pond	72115	6.36	2.00
Blue Hills Reservoir	73004	7.45	15.10
Ashby Reservoir	81001	6.31	2.70
Grove Pond	81053	6.80	16.60
Heald Pond	81056	7.40	15.20
Phoenix Pond	81100	6.90	21.60
Robbins Pond	81111	6.85	15.80
Sandy Pond	81117	6.70	8.70
Lake Wampanoag	81151	5.33	0.20
Wright Pond	81160	6.10	1.70
Whitehall Reservoir	82120	6.03	3.40
Mystic Pond	84043	6.89	18.80
Upper Attitash Pond	84072	7.23	16.60
Duck Pond	84083	6.35	5.90
Hedges Pond	94065	6.22	2.50
Indian Pond	94072	6.23	8.20
College Pond	95030	6.64	2.50
Ezekiel Pond	95051	6.63	3.10
Little Sandy Pond	95092	6.46	1.60
New Long Pond	95112	6.18	1.80
Spectacle Pond	95142	6.70	5.20
Turner Pond	95151	4.86	-0.60
Noquockoke Lake	95170	6.20	3.40
Great Pond	96117	5.81	0.60
Kinnacum Pond	96163	5.07	0.15
Round Pond	96264	4.97	-0.20
Soda Creek	2103725	6.58	20.60
Williams River	2104100	7.77	110.60
Sleepy Hollow Brook	2104200	8.06	161.00
Barton Brook	2105350	6.88	26.60
Anthony Brook	2105425	6.42	6.80

Table A-1: April 8, 2018 pH and Alkalinity data (continued)			
Kilburn Brook	2105700	6.74	8.40
Cady Brook	2105725	6.78	13.80
Bilodeau Brook	2105750	6.68	19.60
Fox Brook	3106825	6.24	2.40
Babcock Brook	3107625	5.74	0.90
Valley Brook	3107700	6.01	2.90
Walker Brook	3210300	6.56	10.20
Hinsdale Brook	3313175	7.71	53.30
Shingle Brook	3313850	7.56	59.00
North River	3314100	6.94	19.00
Kinsman Brook	3314450	6.98	14.70
Vincent Brook	3314550	7.27	14.00
Underwood Brook	3314650	6.52	2.80
Bozrah Brook	3315325	6.95	15.00
Mill River	3419825	7.28	31.50
Black Brook	3522675	6.12	1.80
Kenny Brook	3523750	5.97	1.20
Beaman Brook	3523825	5.66	1.20
Wilder Brook	3523950	5.37	0.00
Baker Brook	3524050	5.67	1.50
Towne Brook	3524200	5.48	0.30
Robbins Brook	3524250	5.46	-0.10
Sucker Brook	3625975	6.31	3.50
Maynard Brook	3626475	5.40	0.50
Cadwell Creek	3626575	5.98	0.97
West Branch Swift River	3626800	5.48	0.10
Hop Brook	3627000	6.54	3.90
East Branch Swift River	3627200	6.41	2.28
Flat Brook	3627500	6.67	6.50
West Branch Ware River	3628175	6.06	1.80
French River	4230075	6.57	8.40
Wellington Brook	4230325	6.36	15.20
Round Meadow Brook	5131275	6.04	2.50
Aldrich Brook	5131425	6.10	3.70
Sewall Brook	5132600	6.88	16.30
Cronin Brook	5132625	6.54	7.40
Dorothy Brook	5132700	6.61	16.40
Bungay River	5233750	6.75	16.00
Torrey Creek	5334075	7.05	31.30
Rocky Run	5334100	6.43	7.10

Table A-1: April 8, 2018 pH and Alkalinity data (continued)			
Clear Run Brook	5334150	6.37	12.90
Kickamuit River	6134500	6.75	8.15
Blossom Brook	6134700	4.66	-1.70
King Phillip Brook	6134725	4.54	-2.15
Rattlesnake Brook	6235125	5.01	-0.15
Mulberry Meadow	6235775	6.67	6.70
Beaver Brook	6235800	6.63	10.80
Bassett Brook	6236100	6.24	3.80
Godfrey Brook	7240375	6.94	21.10
Gulf Brook	8143675	6.90	14.25
Robinson Brook	8143825	7.15	29.90
Mcgovern Brook	8144725	6.95	15.60
Bartlett Pond Brook	8146000	5.30	0.10
Millham Brook	8247475	6.81	21.20
Ipswich River	9253500	7.00	19.90
Black Brook	9253700	6.74	16.40
Boston Brook	9253925	6.78	14.50
Angeline Brook	9560000	5.73	1.40
Bread And Cheese Brook	9560150	6.21	2.90
Hatches Creek	9661525	6.07	6.25

Table A-2: April 8, 2018 color and ion concentration for 24 long term sites. Ion concentrations are in mg/L, color in PCU

PALSITE	NAME	Mg	Mn	Fe	Cu	Al	Ca	Na	K	Cl	NO_3_N	SO_4	Color
188	Shingle Island Brook	1.10	0.045	0.2338	0.004	0.302	3.03	11.37	1.27	17.64	0.16	2.25	258
21010	Belmont Reservoir	3.41	0.000	0.0165	0.004	0.050	8.83	0.74	0.38	2.03	0.09	1.34	26
32018	Cobble Mtn. Res.	1.23	0.000	0.0165	0.004	0.069	3.51	12.19	0.63	19.18	0.06	1.23	46
34031	Hawley Reservoir	0.67	0.004	0.0165	0.004	0.125	3.36	11.12	0.45	18.13	0.07	1.98	42
34103	Lake Wyola	0.46	0.000	0.0284	0.004	0.078	2.27	6.16	0.50	8.71	0.04	1.32	45
35090	Upper Naukeag Lake	0.36	0.000	0.0165	0.004	0.097	1.47	10.56	0.37	15.14	0.01	0.92	44
36043	Crystal Lake	0.32	0.000	0.0165	0.004	0.041	0.94	0.93	0.35	2.62	0.01	0.38	39
36129	Quabbin Reservoir	0.62	0.000	0.0165	0.004	0.041	3.10	6.55	0.59	9.62	0.01	1.57	21
42039	Nipmuck Pond	0.37	0.000	0.0165	0.004	0.191	1.79	7.29	0.28	10.53	0.01	1.71	27
61004	N. Watuppa Lake	0.66	0.085	0.0775	0.004	0.201	1.87	10.75	0.51	16.44	0.01	1.64	149
81001	Ashby Reservoir	0.63	0.000	0.0789	0.004	0.131	3.09	16.98	0.68	26.14	0.05	1.29	53
81160	Wright Pond	0.41	0.000	0.1341	0.004	0.088	1.85	10.69	0.46	15.2	0.01	0.87	69
82120	Whitehall Reservoir	1.16	0.000	0.0165	0.004	0.043	4.97	22.91	1.16	42.1	0.01	1.52	47
94065	Hedges Pond	1.26	0.000	0.0165	0.004	0.084	1.13	8.49	0.66	14.47	0.01	1.4	39
95030	College Pond	0.87	0.000	0.0165	0.004	0.053	1.19	4.47	0.30	6.85	0.01	1.11	20
95051	Ezekiel Pond	1.28	0.000	0.0165	0.004	0.042	2.61	18.78	0.97	31.16	0.1	1.48	34
95092	Little Sandy Pond	1.23	0.000	0.0165	0.004	0.049	1.86	16.01	1.02	25.52	0.4	1.73	43
96163	Kinnacum Pond	1.65	0.014	0.0186	0.004	0.104	0.67	12.98	0.83	22.23	0.01	0.94	87
3626575	Cadwell Creek	0.56	0.005	0.0165	0.004	0.152	2.32	8.43	0.21	13.15	0.01	1.71	36
3626800	West Br Swift River	0.35	0.002	0.0165	0.004	0.149	1.61	3.60	0.36	5.4	0.01	1.36	46
3627200	East Br Swift River	0.57	0.000	0.0279	0.004	0.109	2.82	7.04	0.65	11.11	0	1.37	80
6235125	Rattlesnake Brook	0.70	0.016	0.1357	0.004	0.284	2.05	8.34	0.54	11.71	0.04	2.43	176
9560000	Angeline Brook	1.39	0.000	0.144	0.053	0.560	3.21	9.51	1.29	15.55	0.32	1.65	254
9560150	Bread & Cheese Br.	1.66	0.015	0.212	0.004	0.276	5.62	35.92	1.54	60.43	0.63	2.23	269