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Comparing and assessing acid rain-sensitive ponds

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Abstract

Changes in pH and temperature were monitored in two freshwater ponds in Southeastern Massachusetts from 1990 to 1993 using a remote-sensing system that collected data on a continuous basis. The sensing system included a combination electrode, pH meter and portable computer powered by a marine battery. Temperature and pH information from the pH meter were acquired every 10 min and stored in the computer. The two ponds, located within 2 km of one another, have a different average pH and sensitivity to acid precipitation. Maquan Pond has an average pH of 6.0 and an alkalinity of 7.4 mg/l, while Furnace Pond has an average pH of 6.9 and alkalinity of 14.9 mg/l. The pH of both ponds varied seasonally and showed diel changes due to the photosynthetic and respiratory activity of aquatic organisms. Precipitation events did not change the pH of Furnace Pond. Maquan Pond on the other hand, did exhibit changes in surface water pH due to specific acidic precipitation events. During certain rainstorms, the pH of Maquan surface waters dropped to values as low as pH 4. In addition to the transient changes in pH, the acid-sensitive pond also exhibited differences in planktonic distribution patterns.

Keywords: Sensing system; pH; Temperature; Plankton; Acid rain

1. Introduction

Freshwater ponds, lakes, rivers, and streams are exposed to a multitude of anthropogenic inputs, which may alter their chemical composition. Most ponds and lakes have a natural buffering capacity that prevents large changes in pH on a short or long term basis. Freshwater systems with low buffering capacity are most sensitive to acidic inputs, making them susceptible to changes in pH, which can subsequently affect their biota. In freshwater systems with low alkalinity, pH changes are observed in association

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with specific acidic precipitation events [1]. Most inputs of acidity into these systems are the result of fossil fuel combustion, which emits sulfur dioxides and nitrogen oxides into the atmosphere. When these substances are oxidized, they enter freshwater systems as sulfuric and nitric acids. In acid-sensitive ponds and lakes, acidic storms can lower the pH of surface waters. Low alkalinity ponds are the most susceptible to transient changes in pH due to acidic precipitation.

The effects of anthropogenic inputs into freshwater ponds, lakes, rivers, and streams have been studied for the past century. Most analyses have focused on water systems with chronic problems [2–4]. Acid precipitation events have been studied on an ongoing basis since the mid 1970s. Publications by Schindler [5] and Schindler and Turner [6] summarize many of the experimental measurements and monitoring that was performed. This long term monitoring built data bases on aquatic systems and how they were being continually damaged by acidic precipitation events. Water systems were also deliberately treated with excess acid in order to examine the damage/recovery of aquatic life [7–11]. All of these studies laid the groundwork for the intense monitoring, which took place in the late 1980s and early 1990s, setting the stage for emissions penalties and incentives for controlling sulfur dioxides in particular.

During the past 10 years, monitoring investigations have included experiments, which examine the short-term effects of acid precipitation on water systems and their biota. Episodic acidification of water systems from precipitation events may change the chemistry and biota of a water body depending on the magnitude and duration. In a 2-year study supported by the United States Environmental Protection Agency (EPA), investigators monitored 13 sensitive streams draining forested watersheds in the Adirondack and Catskill Mountains in New York and the Northern Appalachian Plateau of Pennsylvania. This Episodic Response Project, which extended from the fall of 1988 to the spring of 1990, obtained information on the effects of acidic precipitation on a range of chemistry and fish populations in streams [12–15].

In acid-sensitive ponds and lakes, acidic precipitation, depending on the magnitude and duration of the event, can cause transient decreases in the pH of surface waters. These pH changes are temporary and the pH of the pond returns to previous values after a brief period of time. It is important to be able to obtain a chemical profile of these ponds in a timely and accurate fashion and to predict harmful effects. We have assembled an environmental monitoring system that collects and stores water quality data such as pH and temperature with a high degree of temporal resolution. We have used this system to study the effects of transient acidification events on the pH and biota of Maquan and Furnace Ponds. Effects of low pH pulses on fish species and their early life history are not measurable unless the pH depressions coincide with hatching and fry development. We set up an experimental protocol to collect information on pH decreases that could be compared to hatching profiles of young-of-the-year (YOY) fish gathered later in the season. The effects of transient acidity on *Lepomis* sunfish recruitment in Maquan and Furnace Ponds were examined using a combination of the described remote-sensing pH monitoring system and in situ hatching profiles of pond sunfish [1]. Pond pH was continuously monitored over a 3-year period using this on-site computer-controlled data collection of pH and temperature values. YOY sunfish were collected and evaluated according to their hatching dates. This was accomplished by counting the number of daily rings in their otolith and backdating them from the known date of capture and sacrifice. Day classes of fish were constructed from YOY fish captured and sacrificed during the season. Maquan Pond, the poorly buffered pond, was found to experience irregular acid spikes, characterized as a lowering of pond pH to under 5.3 for an hour or more. These spikes were associated with rainfall $(p < 0.0005)$. No acid spikes were found at Furnace Pond. The YOY swim-up day class distribution was more irregular with pronounced gaps at Maquan Pond than it was for the better-buffered Furnace Pond. Tests for a relationship between acid spikes and diminished day classes using 2×2 contingency tables, found a significant relationship based on pooled data from the 3 years at Maquan Pond, with a X^2 value of 11.94 $(p = 0.0003)$. Transient acid spikes at Maquan Pond appeared to harm *Lepomis* YOY at the vulnerable stage of metamorphosis, when their gills become fully functional and exposed to the environment. This study was subsequently expanded to include other biota data previously acquired. Comparing the two ponds, Maquan showed differences in pH, and in survival profiles of young sunfish [1] and in planktonic distribution patterns [16,17]. It seems that transient [pH] effects are another important factor to consider when evaluating aquatic systems.

2. Materials and methods

We monitored surface water pH of two Southeastern Massachusetts ponds from 1990 to 1993 using a remote-sensing system that collected pH and temperature data on a continuous basis. The two freshwater bodies analyzed in this study are Maquan Pond, found in Hanson, MA, an acid-sensitive pond and Furnace Pond, located approximately 2-km away in Pembroke, MA, a less sensitive system. Maquan has a surface area of 19.4 ha and a maximum depth of 5.5 m. Maquan has an average alkalinity of 7.4 mg/l and an average pH of 6.0. Furnace has a surface area of 43.3 ha and a maximum depth of 2.7 m. Furnace has an average alkalinity of 14.9 mg/l and an average pH of 6.9. In other regions such as the Adirondacks of New York, these waters would be classified as healthy waters not affected by acidification. Maquan and Furnace Ponds were chosen for a comparative study on the effects of acidic precipitation specifically to show that marginally healthy aquatic systems are still vulnerable to anthropogenic inputs. In the process, differences in pH and the biota between these two study ponds were found [1,16–18].

Pond alkalinities were measured from samples collected on the same sampling days. The titration method consisted of acidifying 100 ml of pond water to pH 4 with 0.2 M HCl. The acidified sample was then titrated from pH 4 to pH 9 with 50 μl aliquots of 0.01 M NaOH. Using this procedure, alkalinity is defined as the amount of calcium carbonate, in milligrams, required to neutralize 100 ml of a solution from pH 4 to its original pH value. This can also be expressed as the acid-neutralizing capacity (ANC) of a pond measured in micro-equivalents per liter [19]. Alkalinity was calculated from the titration data using the following:

$$\mathrm{mg\,CaCO_3\ required} = \mathrm{Volume\ of\ NaOH\ added}^{*}\ 0.01\ \mathrm{M\ NaOH}^{*}\ 0.11.$$

The titrations were carried out to pH 9 to fully visualize any modulating ion and buffer present. The titration curves created by this method were used to compare the resistance to a change in pH of the ponds. The different shapes of the curve, such as areas, which flatten out and then rise steeply again, may indicate the presence of other acid-neutralizing substances in the pond water [19].

In situ pH and temperature values were obtained in Maquan and Furnace Ponds using our remote monitoring system. The system consisted of a combination pH electrode attached to an Orion pH meter with an RS232 connection to a Radio Shack model 102 computer. The pH meter and computer were powered by a 12-V marine battery using appropriate voltage control devices. Either an Orion Ross combination electrode or a Corning combination electrode was used for pH measurements. The combination pH electrode and temperature probe were suspended on a float in the pond, while connected to the pH meter and computer. The tip of the probe was 5 cm below the surface. This float ensured that the pH readings were always done below the surface of the pond, and would not vary in position. Temperature and pH readings were taken every 10 min and stored in a data file. The computer was programmed to request and acquire pH and temperature data every 10 min. Weekly visits were made to the ponds to transfer collected data to another computer, change the marine battery and calibrate the electrode [20].

In a parallel study, the phytoplanktonic and zooplanktonic communities in Maquan and Furnace Ponds were examined from 1991 to 1993. The numbers and kinds of planktonic organisms were determined, along with seasonal fluctuations and Simpson’s diversity index, which were used to make comparisons between the two ponds. A total of 56 plankton samples were collected from Maquan Pond, the most sensitive system, and Furnace Pond, the least sensitive, on a weekly basis during the growing season using a standard 10 mesh plankton net with a porosity of 153 μm and analyzed using video microscopy [16].

3. Results and discussion

Fig. 1 is a titration profile of the two Southeastern Massachusetts ponds in this study from data collected in May of 1990. Titrations are one way to measure the sensitivity of ponds to acidic inputs. Maquan Pond has a lower alkalinity, and subsequently, is less resistant to anthropogenic additions of acids or bases. Furnace Pond has better buffering and is more resistant to acidic inputs. It is evident that Maquan Pond is more susceptible to acidic events.

Fig. 2 is a plot of the hourly pH of Maquan Pond during the summer and fall of 1991. Data were pooled for the measuring season and plotted vs. days. Most of the changes in pH were due to the respiratory and photosynthetic activity of pond organisms. During the daylight, photosynthetic uptake of carbon dioxide is greater than the respiratory processes and the pH increases. During the nighttime, respiratory processes bring the pH back down to 5.65, the pH of dissolved carbon dioxide equilibrated with water. Maquan Pond, which is buffered by dissolved carbon dioxide, shows a typical range from pH 8.5 during the day to a pH of 5.65 during the evening. Decreases in pH below 5.65 were

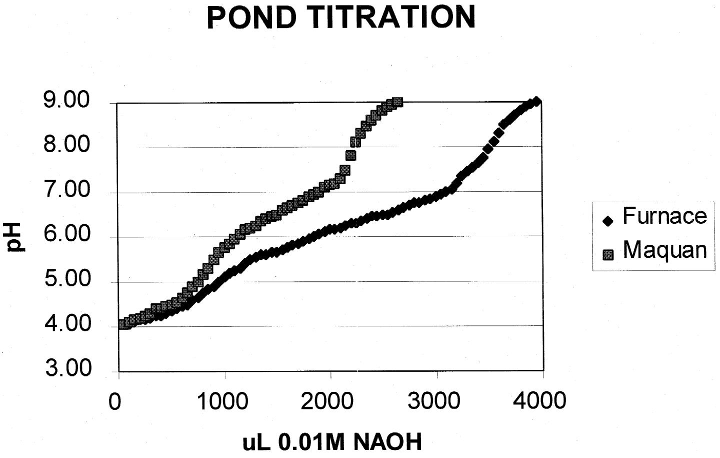

Fig. 1. Titration profile of the two Southeastern Massachusetts ponds in this study from data collected in May of 1990.

caused by precipitation events. Ponds such as Maquan, with an alkalinity of less than 8 mg $CaCO_3$ per liter, are most susceptible to acid precipitation events [18]. Precipitation events decreasing the pH below 5.3 for over an hour were considered to be transient acid spikes. Previous analyses have shown that transient acid spikes, which occurred during the breeding season were significantly associated with diminished survival of young sunfish [1].

In addition to the planktonic communities inhabiting Maquan and Furnace Ponds were examined. The numbers and kinds of phytoplanktonic and zooplanktonic organisms were determined along with seasonal fluctuations and

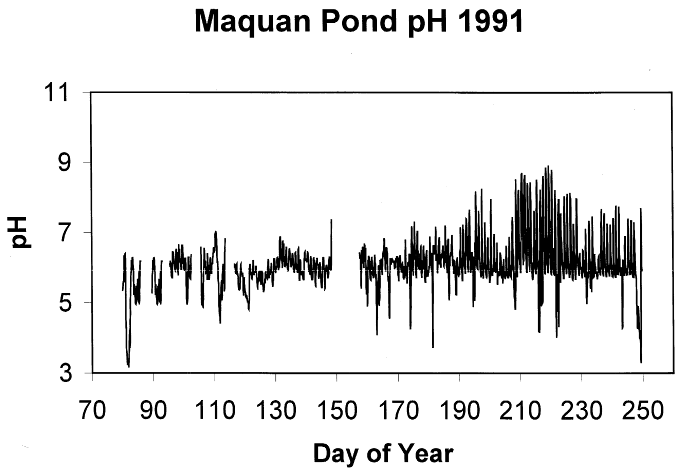

Fig. 2. Plot of the hourly pH of Maquan Pond during the summer and fall of 1991.

Simpson's diversity index and interpond comparisons were made. Fifty-six plankton samples were analyzed from each pond.

Collectively, 33 phytoplanktonic and 44 zooplanktonic genera were characterized and counted. The phytoplankton genera identified from both ponds represented the same five phyla. Individually, 33 genera were identified from Maquan and 27 were identified from Furnace. In Maquan and Furnace, the same three phytoplanktonic phyla, the Chlorophyta, Chrysophyta and Cyanophyta were the most prevalent. In Maquan, the Chlorophyta was dominated by *Spirogyra*, the Chrysophyta was dominated by *Tabellaria* and the Cyanophyta was dominated by *Anabaena*. Furnace was dominated by the same genera of Chlorophyta and Cyanophyta, but the dominant Chrysophyte was *Fragilaria* [16,17].

The zooplankton genera identified from Maquan Pond represented eight different phyla, while that for Furnace represented those eight and two additional phyla. Individually, 39 genera were identified from Maquan and 33 were identified from Furnace. In Maquan and Furnace, the same three zooplanktonic phyla, the Crustacea, Protozoa and Rotifera were the most important contributors. The same three genera of zooplankton dominated the communities of both ponds. *Daphnia* was the most dominant Crustacean, *Vorticella* was the most dominant Protozoan and *Keratella cochlearis* was the dominant Rotiferan. Absent from Maquan were members of two zooplanktonic phyla, the Nemertea and the Tardigrada, which tend to be sensitive to acidity [16,17].

The phytoplanktonic and zooplanktonic communities in Maquan and Furnace Ponds exhibited seasonal fluctuations in abundance. The spring bloom of phytoplankton was followed by an increase in the number of zooplankton, after which the number of phytoplankton decreased, and the number of zooplankton subsequently fell. Usually, there was a second bloom of phytoplankton in the autumn, which was of lesser magnitude than the spring bloom. A decrease in the number of planktonic organisms followed as the level of photosynthetic activity decreased.

Simpson's index was used to compare phytoplanktonic and zooplanktonic diversity in the two ponds. The 3-year average Simpson's index for phytoplankton was $0.64 + / - 0.03$ SE for Maquan and $0.76 + / - 0.03$ SE for Furnace. Phytoplankton exhibited more of a difference in diversity than did the zooplankton. The 3-year average Simpson's index for zooplankton for Maquan and Furnace was virtually identical, $0.38 + / - 0.03$ SE for Maquan and $0.37 + / - 0.03$ SE for Furnace. Maquan, unlike Furnace, is subject to acid spikes from acidic precipitation. Such intermittent disturbances may be related to the difference in phytoplankton biodiversity seen in this interpond comparison [16,17,21].

References

[1] B.W. Stallsmith, J.E. Ebersole, W.G. Hagar, The effect of acid episodes on *Lepomis* sunfish recruitment and growth in two ponds of different buffering capacity in Massachusetts, Freshwater Biology 36 (1996) 730–740.

[2] L.A. Baker, A.T. Herlihy, P.R. Kaufmann, J.M. Eilers, Acidic lakes and streams in the United States: the role of acidic deposition, Science 252 (1991) 1151–1154.

[3] P.T. Bradt, J.L. Dudley, M.B. Berg, D.S. Barrasso, Biology and chemistry of three Pennsylvania lakes: responses to acid precipitation, Water, Air, and Soil Pollution 30 (1986) 503–513.

[4] M.L. Jones, C.K. Minns, D.R. Marmorek, F.C. Elder, Assessing the potential extent of damage to inland lakes in Eastern Canada due to acidic deposition, Canadian Journal of Fisheries and Aquatic Sciences 47 (1990) 67–80.
[5] D.W. Schindler, Ecological effects of experimental whole-lake acidification, in: S. Shriner, R. Richmond, E. Lindberg (Eds.), Atmospheric Sulfur Deposition, Environmental Impact and Health Effects, Ann Arbor Sci. Publ., Ann Arbor, MI, 1980, pp. 453–546.
[6] D.W. Schindler, M.A. Turner, Biological, chemical and physical responses of lakes to experimental acidification, Water, Air, and Soil Pollution 18 (1982) 259–271.
[7] D.W. Schindler, K.H. Mills, D.F. Malley, D.L. Findlay, J.A. Shearer, I.J. Davies, M.A. Turner, G.A. Linsey, D.R. Cruikshank, Long term ecosystem stress: the effects of years of experimental acidification of a small lake, Science 228 (1985) 1395–1401.
[8] D.W. Schindler, Detecting ecosystem responses to anthropogenic stress, Canadian Journal of Fisheries and Aquatic Sciences 44 (1987) 6–25.
[9] D.W. Schindler, Effects of acid rain on freshwater ecosystems, Science 239 (1988) 149–157.
[10] P.L. Brezonik, C.E. Mach, G. Downing, N. Richardson, M. Brigham, Effects of acidification and trace metal chemistry in Little Rock Lake, Wisconsin, Environmental Toxicology and Chemistry 9 (1990) 871–885.
[11] J.G. Eaton, W.A. Swenson, J.H. Mc Cormick, T.D. Simonson, K.M. Jensen, A field and laboratory investigation of acid effects on Largemouth Bass, Rock Bass, Black Crappie, and Yellow Perch, Transactions of the American Fisheries Society 121 (1992) 644–658.
[12] P.J. Wigington Jr., J.P. Baker, D.R. DeWalle, W.A. Kretser, P.S. Murdoch, H.A. Simonin, J. Van Sickle, M.K. Mc Dowell, D.V. Peck, W.R. Barchet, Episodic acidification of small streams in the Northeastern United States: episodic response project, Ecological Applications 6 (1996) 374–388.
[13] P.J. Wigington Jr., D.R. DeWalle, P.S. Murdoch, W.A. Kretser, H.A. Simonin, J. Van Sickle, J.P. Baker, Episodic acidification of small streams in the Northeastern United States: ionic controls of episodes, Ecological Applications 6 (1996) 389–407.
[14] J. Van Sickle, J.P. Baker, H.A. Simonin, B.P. Baldigo, W.A. Kretser, W.E. Sharpe, Episodic acidification of small streams in the Northeastern United States: fish mortality in field bioassays, Ecological Applications 6 (1996) 408–442.
[15] J.P. Baker, J. Van Sickle, C.J. Gagen, D.R. DeWalle, W.E. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W Bath, W.A. Kretser, H.A. Simonin, P.J. Wigington Jr., Episodic acidification of small streams in the Northeastern United States: effects on fish response populations, Ecological Applications 6 (1996) 422–437.
[16] B.A. Crosby, Seasonal variations in plankton populations in freshwater ponds of differing alkalinity, MS Thesis, University of Massachusetts-Boston, Boston, MA, 1995.
[17] W. Hagar, B. Crosby, B. Stallsmith, Fossil fuels and acid-sensitive ponds symposium on the impact of fossil fuel utilization, in: Division of Environmental Chemistry, National American Chemical Society Meetings Boston, MA, 23–27 August Vol. 38 1998, pp. 150–152.
[18] J.N. Jarrett, M.B. Cutler, J.P. Ebersole, W.G. Hagar, Seasonal variation in pH and alkalinity of ponds and recruitment of sunfish populations, Freshwater Biology 30 (1993) 409–417.
[19] L.O. Hedin, G.E. Likens, K.M. Postek, C.T. Driscoll, A field experiment to test whether organic acids buffer acid deposition, Nature 345 (1990) 798–800.
[20] W. Hagar, B. Stallsmith, Acid rain- and acid-sensitive ponds in Massachusetts acidic deposition revisited symposium, in: 27th Northeast Regional Meeting of American Chemical Society A59 1997, p. 63.
[21] H.G. Washington, Diversity, biotic and similarity indices: a review with special relevance to aquatic ecosystems, Water Research 18 (1984) 653–694.