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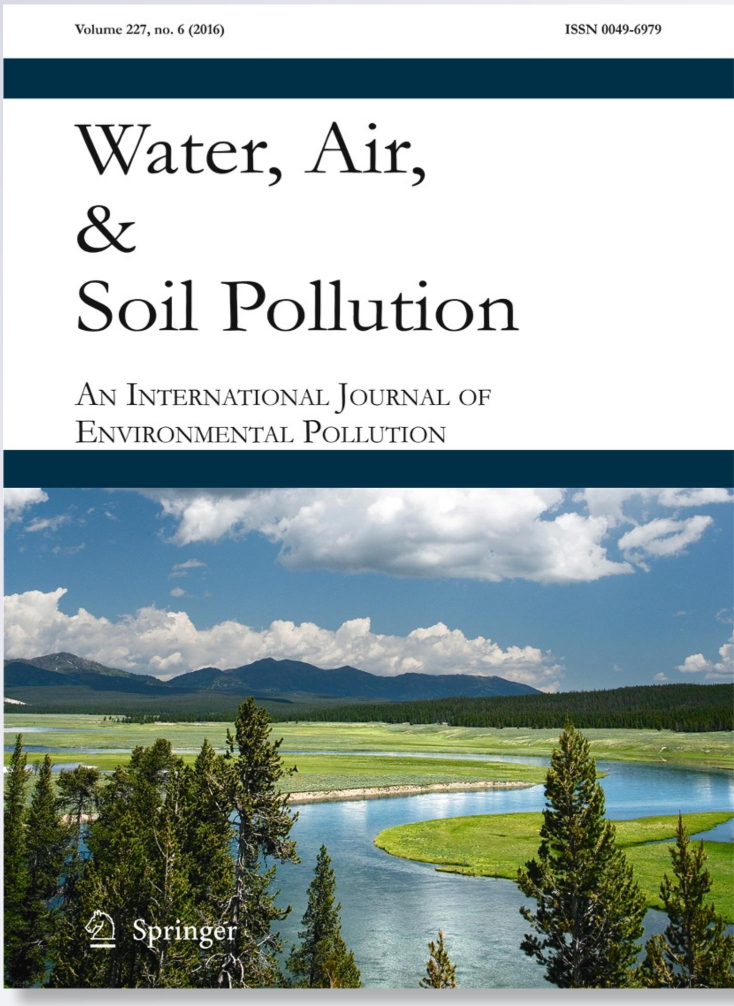
Water, Air, & Soil Pollution
An International Journal of Environmental Pollution

ISSN 0049-6979
Volume 227
Number 7

Water Air Soil Pollut (2016) 227:1-11
DOI 10.1007/s11270-016-2916-x



Springer

Water Air Soil Pollut (2016) 227:237
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Changes in Air Temperature and Precipitation Chemistry Linked to Water Temperature and Acidity Trends in Freshwater Lakes of Cape Cod National Seashore (Massachusetts, USA)

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Received: 19 February 2016 / Accepted: 31 May 2016

Abstract Freshwater lakes are an important natural and cultural resource in national parks across the USA. At Cape Cod National Seashore, in southeastern Massachusetts, the water quality of these water bodies (known as kettle ponds), along with local precipitation chemistry, has been measured since the 1980s. These datasets, along with air temperature obtained from a local weather station, were analyzed to assess temporal trends in the air temperature, precipitation acidity, pond temperature, and pond pH, and are interpreted within the context of regional air quality improvements and increasing temperatures from regional climate warming. The results suggest that all parameters have increased significantly during the last several decades. As temperature and pH regulate a wide variety of physical, chemical, and biological processes, these changes may be influencing the overall ecology of the kettle ponds. This analysis provides an opportunity to gauge the future trajectory of this important resource and may ultimately guide management strategies for their continued protection against a backdrop of climate change and atmospheric emission controls.

Keywords Freshwater · pH · Temperature · Cape Cod · Climate change · Air quality · Lakes · Northeast

S. M. Smith (✉) · S. E. Fox · K. D. Lee
National Park Service, Cape Cod National Seashore, 99 Marconi Site Road, Wellfleet, MA 02667, USA
e-mail: stephen_m_smith@nps.gov

1 Introduction

Improvements in air quality across the northeastern USA have been substantial over the past 30+ years, mainly due to the implementation of the Clean Air Act of 1970 and its subsequent amendments in 1990. For example, the acidity of precipitation (measured as pH) has generally declined (increase in pH), mostly due to reductions in sulfur dioxide (SO_2) and, to a lesser extent, nitrous oxides (NO_3 and NO_2) emissions (Bouchard 1997; Lynch et al. 2000a, b; Nilles and Conley 2001; Sickles and Shadwick 2015). In addition to the recent changes in air quality, the climate has warmed over the last few decades. Air temperatures around New England and in the larger northeast region of the USA have risen by at least 1 °C over the last century (Trombulak and Wolfson 2004; Frumhoff et al. 2007; Pilson 2008; Rogers and Young 2014).

Such atmospheric changes can be important to the functioning of aquatic ecosystems because they can drive changes in water temperature and pH (Driscoll et al. 2003; Warby et al. 2005; Burns et al. 2006; Adrian et al. 2009; Houle et al. 2010), which in turn can alter species composition, biological productivity, biodiversity, and invasive species distributions (Mandrak 1989; De Stasio et al. 1996; Meyer et al. 1999; Straile, et al. 2001; Jackson and Mandrak 2002; Heino et al. 2009). For example, nutrients such as phosphorus can be made more available under conditions where SO_4 is reduced (Caraco et al. 1993) and pH is elevated (Jansson et al. 1986; KopciCek et al. 1995). The taxonomic composition of phytoplankton communities and algal biomass

Published online: 18 June 2016

are highly sensitive to pH (Almer et al. 1974; Turner et al. 1991; Vinebrooke et al. 2002) and nutrient availability, and shifts in either can have cascading effects throughout the food web (Carpenter et al. 1985). Livingstone (2003) found that from the 1950s to the 1990s, high warming rates of a central European lake resulted in a 20 % increase in thermal stability (i.e., resistance to vertical mixing) and a consequent extension of 2–3 weeks in the stratification period, which influences nutrient availability. Hondzo and Stefan (1993) speculated that with climate change epilimnetic temperatures will be higher, evaporative water loss will be increased by as much as 300 mm, onset of stratification will occur earlier and overturn later in the season, and overall lake thermal stability will become greater in spring and summer. While there are many other factors that contribute to thermal stability, such as wind shear, dissolved organic carbon levels, etc. (Gorham and Boyce 1989; Pérez-Fuentetaja et al. 1999), temperature is one of the most critical parameters.

On the peninsula of Cape Cod (Massachusetts, USA), freshwater lakes are an important resource in that they provide habitat for numerous species of aquatic vegetation and wildlife, including a variety of rare species (LeBlond 1989; Portnoy 1990; Colburn and Garretson-Clapp 2006; Tupper et al. 2007), and offer opportunities for popular recreational activities. The majority of these permanent water bodies (known as “kettle ponds”) were originally formed by melting blocks of ice left behind by the glaciers on the outwash plain. Kettle ponds are essentially the intersection between the groundwater table and these ice-formed elevation depressions. Given that there are no rivers flowing in or out of the ponds, these systems are highly influenced by local climatic conditions.

On the outermost part of Cape Cod lies Cape Cod National Seashore (CCNS), covering ~18,000 ha of the glacial outwash plain and interspersed with numerous kettle ponds. CCNS has conducted a rigorous pond water quality sampling program since the mid-1980s. This program is part of the National Park Service (NPS) Inventory and Monitoring (I & M) program, with sampling occurring every year from March through November. In addition, an air quality monitoring program that tracks precipitation chemistry has also been implemented by CCNS since 1982. These parallel monitoring programs provide excellent datasets for evaluating long-term temporal change in important atmospheric and pond water quality variables.

The focus of this study was to examine multidecadal trends in air and pond water temperature as well as rainfall and pond water acidity within CCNS. Although much is known about regional trends in air quality and air temperature, surprisingly little has been published on the impacts of atmospheric changes on lake waters in the northeastern USA and there appear to be no published studies from the Cape Cod region itself, which has a unique geology and over 1000 kettle hole ponds and lakes. Cape Cod is also greatly influenced by the Atlantic Ocean and has a coastal climate that is considerably different than the mainland, where most studies have been focused. Moreover, local-scale responses of freshwater lakes can be highly variable (Clair et al. 2002; Burns et al. 2006). Regardless, even small changes in the physical and/or chemical properties of lakes, particularly in pH and temperature, can have myriad effects on ecological processes (Raddum and Fjellheim 2002; Cahill et al. 2005; Conrad et al. 2010). For example, Ahrens and Siver (2000) reported that kettle ponds on outer Cape Cod were generally lower in alkalinity and pH, than those in the middle and upper part of the peninsula, and these conditions were associated with trophic state and phytoplankton species composition (Siver 2001; Siver et al. 2004).

2 Materials and Methods

Ten kettle ponds within CCNS were examined in this study, including Duck, Dyer, Great-T, Great-W, Gull, Herring, Long, Ryder, Snow, and Spectacle (Fig. 1). These selected kettle ponds exhibit a substantial range in terms of their position on the landscape and physical attributes (Table 1). Air temperature data were available from the Chatham airport (Chatham WSMO station, Northeast Climate Center database) approximately 32 km away from the cluster of CCNS kettle ponds (Fig. 1). Monthly means for daily maximum ($T_{\max}$) and minimum ($T_{\min}$) temperatures were calculated for the months from May through October for each year from 1973 to 2014 as previous analyses of November through April data revealed that there were no significant temporal trends during this time.

Precipitation chemistry has been determined from samples collected weekly since 1982 at CCNS's air quality monitoring station (MA01, 41.9759 W, −70.0241 E)

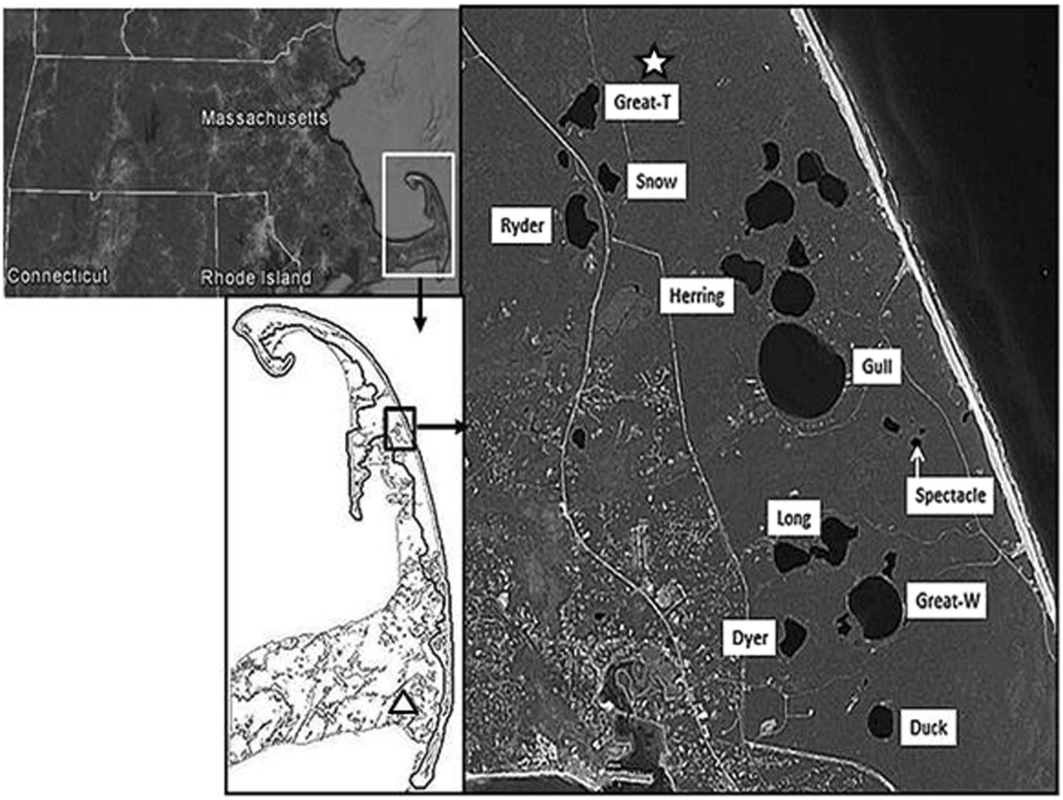


Fig. 1 Map of Massachusetts (*upper left*), Cape Cod (*bottom left*; *polygon* defines the boundary of CCNS), and the kettle ponds of Wellfleet and Truro within CCNS (*right*). *Star symbol* indicates location of the CCNS air quality monitoring station (MA01). *Triangle symbol* indicates location of Chatham airport weather station

in Truro (Central Analytical Laboratory, National Atmospheric Deposition Program, University of Illinois, Champaign, IL). This analysis focused on precipitation pH, and two important contributors to pH—nitrate (NO_3) and sulfate (SO_4) concentrations (mg/L). Mean annual values of each were used since preliminary analyses confirmed that seasonal trends for each parameter were virtually identical. pH was measured using a Broadley-James combination electrode with a Mettler-Seven™ MultiMeter. Sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations were determined by ion chromatography (Dionex ICS-2000, Chromeleon™ Software) (Lehmann 2015).

All pond pH and temperature data originated from samples collected in March through November since the mid-1980s. Pond pH and surface water temperature were measured at a water depth of 0.5 m using precalibrated Hydrolab™ water quality sondes until 2002 and YSI™ sondes (the latter with YSI6560 temperature/conductivity and pH/ORP sensors), thereafter at the same location in each year. These locations are marked with permanent buoys in the deepest part of each pond.

Table 1 Various physical attributes of the CCNS kettle ponds analyzed in this study

Pond	Distance from ocean (m)	Area (ha)	Volume (millions m^3)	Max depth (m)
Duck	1667	5.1	1.5	18
Dyer	2154	4.8	1.0	10
Great-T	1897	7	1.0	11
Great-W	1282	17.8	3.9	16
Gull	949	44	24.4	19
Herring	1154	8.1	0.5	4
Long	1410	15	no data	15
Ryder	2384	8.3	2.3	10
Snow	2102	2.3	0.3	8
Spectacle	641	0.5	0.0	7

N/A data not available

Table 2 Results from linear regression analysis on mean daily maximum (T_{max}) and minimum (T_{min}) air temperature changes between 1983 and 2014 by month (change = absolute increase or decrease over the specified time period according to regression equation in °C)

	T_{max}				T_{min}			
Month	R^2	p	Trend	Change (°C)	R^2	p	Trend	Change (°C)
May	0.12	0.03	+	0.16	<0.01	0.79	+	0.96
June	0.04	0.21	+	0.65	0.30	<0.01	+	1.60
July	0.08	0.09	+	0.87	0.41	<0.01	+	2.16
August	0.08	0.09	+	0.51	0.30	<0.01	+	1.22
September	0.15	0.01	+	1.15	0.42	<0.01	+	2.25
October	0.09	0.06	+	1.19	0.17	0.01	+	1.76

Highlighted rows indicate months with statistically significant trends

2.1 Statistical Analyses

The daily temperature data (T_{min} and T_{max}) were reduced to mean values for each month and year. The reason for doing so lies in the fact that regressions using large quantities of data are extremely difficult to interpret since these will invariably produce significant results, regardless of whether or not the trends are real. Data availability for both pond water temperature and pH was variable by pond and year. As a rule, mean monthly values were calculated from two replicate samples collected during July and August, when pond temperatures are maximal and biological productivity is highest (Portnoy et al. 2001). Where there were more than two values per month for some ponds, the earliest and latest sampling dates during that month were selected for averaging, although in some years, only one sample value was available. In addition, there were occasionally missing data for a particular year, but all analyses were restricted to a time series that encompassed no more than two consecutive years of missing values since large gaps in time series can influence trend analysis.

For pond pH, all data collected in months with the highest biological productivity (May–September) were excluded from the analysis since water column photosynthesis can greatly elevate pH through the depletion of CO_2 on diel and seasonal scales (Talling 1976; Andersson et al. 1978; Maberly 1996; Lampert and Sommer 2007). Changes in pH due to algal photosynthesis have even been used as an indicator of primary productivity (Axelsson 1988). Thus, by excluding growing season pH data, we avoided this confounding effect and overestimation of pH. The pH data in this study are from sampling events that occurred during March–April or October–November.

All data were determined to have normal distributions and could therefore be analyzed by linear regression (JMP ver. 10.0.2). To determine total changes in the parameters over time, the regression equations were used to calculate values at the beginning and end of the sampling period. To evaluate the relationships between air and pond water temperatures, mean pond water temperatures for the months of July and August (all ponds pooled except Spectacle) were regressed against mean annual values for daily maximum and

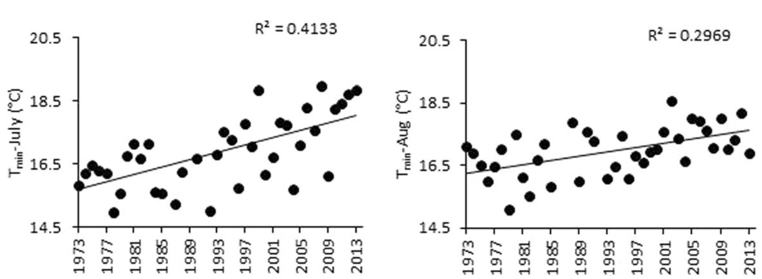


Fig. 2 Minimum daily temperature trends in July and August from 1973 to 2014

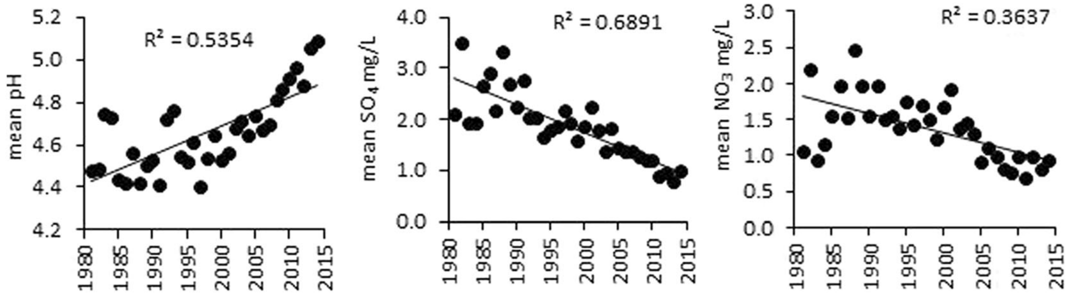


Fig. 3 Temporal trends in mean annual precipitation pH and $SO_4$and NO_3 concentrations from 1981 to 2014

minimum air temperatures. For precipitation and pond pH, mean annual values for the former were regressed against mean spring values for the later. This was done to understand the chemical connectivity between the atmospheric contribution and pond waters. In analyzing trends, both linear and curvilinear regressions were applied and the best-fit relationships discussed.

3 Results and Discussion

3.1 Air Temperature

An examination of air temperature trends over the last several decades revealed clear increases over time (Table 2). In every month except April and November, there were positive significant trends in either daily maximum (T_{max}) or minimum (T_{min}) temperatures or both. The trends in daily minimum temperatures were somewhat stronger and occurred consistently in June through October with large total increases in temperature over the last three decades. The absolute change for significant regressions ranged between 0.16 °C (May) and 1.15 °C (September) for T_{max}, while T_{min} ranged from 1.60 °C (June) and 2.25 °C (September) (Table 2). Figure 2 illustrates the upward trend in T_{min} during July and August.

3.2 Precipitation Chemistry

There were very clear temporal trends in all three constituents of precipitation, with mean annual pH increasing ($p < 0.001$) and mean annual SO_4 and NO_3

Table 3 Results of linear regression analysis on pond surface water temperature changes over time for the month of July (R^2 = correlation coefficient, p = probability value, n = number of years of data, change = total change in temperature over the time series, % change = total percent change over the time series, time series = data used in analyses)

July	R^2	*p value*	Number	Change (°C)	% Change	Time series
All ponds	0.23	0.04	18	1.9	8%	1996–2013
Duck	0.29	0.00	26	2.6	11%	1988–2013
Dyer	0.34	0.02	16	2.3	9%	1998–2013
Great-T	0.10	0.12	25	1.3	5%	1988–2013
Great-W	0.34	0.01	18	2.3	10%	1996–2013
Gull	0.26	0.01	25	2.0	8%	1988–2013
Herring (Aug)	0.30	0.02	17	1.6	7%	1996–2013
Long	0.32	0.01	18	2.4	10%	1996–2013
Ryder	0.22	0.03	21	1.8	7%	1992, 1994–2013
Snow	0.22	0.05	18	1.9	8%	1996–2013
Spectacle	0.09	0.19	22	1.3	5%	1998–2000, 2002–2013

Highlighted rows indicate statistically significant trends. "All ponds" does not include Spectacle

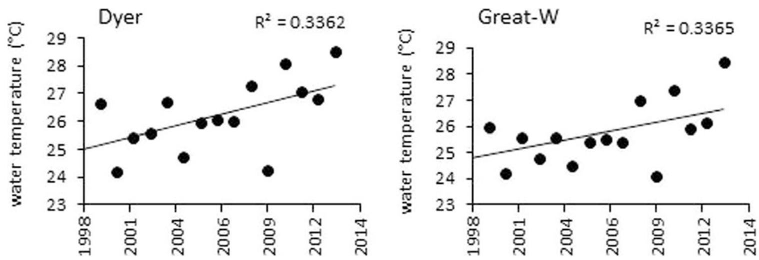


Fig. 4 Examples of surface water temperature trends in July for Duck and Great-W ponds

concentrations decreasing significantly ($R^2 = 0.69$ and 0.37, $p < 0.001$) (Fig. 3). These changes correspond with a rise in precipitation pH of 0.45 and a reduction in SO_4 and NO_3 by 1.84 and 0.88 mg/L, respectively. The latter represents a >50 % decline in the concentrations of these rainwater constituents.

3.3 Pond Temperature

Pond water temperatures showed up to a 2.4 °C increase (Long) during the month of July over the last several decades (Table 3). There were no statistically significant trends in pond temperature for any months except July and August (only for Herring). Collectively, all ponds (except Spectacle, which was excluded due to insufficient data for the span of the time series analyzed) exhibited a significant positive trend in July, with water temperatures increasing by ~2 °C (Table 3). Duck, Dyer, Great-W, Gull, and Long increased by ≥2 °C in July, while Herring increased significantly by 1.6 °C in August (Table 3; Fig. 4). Of the ten ponds analyzed, only Great-T and Spectacle exhibited no significant trends in July or August. Further temperature analysis showed tight coupling between atmospheric conditions and pond surface waters. Pond water temperatures (all ponds pooled except Spectacle, where data availability for the time series was less than the other ponds) were highly correlated (R^2 values > 0.6) with mean annual daily maximum and minimum air temperatures in July from 1996 to 2013 (Fig. 5). This was also true for the month of August, although R^2 values were somewhat lower (0.4–0.6; data not shown).

3.4 Pond pH

Pond waters showed clear trends of decreasing acidity over recent decades. Pond pH has been increasing in every pond, significantly so in five of ten ponds (Table 4). Collectively (all ten ponds pooled), pH significantly increased with a change of nearly one pH unit over the 14-year time period. Change in pH units ranged between 0.4 (Long) and 2.0 (Ryder) (Table 4). Figure 6 illustrates the pH trend in two of the ponds (Duck and Dyer ponds). Analysis of pH showed coupling between atmospheric conditions and pond surface waters. Pond surface water pH was significantly correlated with mean annual precipitation pH between 2000 and 2013, although the R^2 value was only ~0.5 (Fig. 7).

4 Discussion

In general, air and pond temperatures and precipitation/pond pH values have risen considerably over the past several decades. Furthermore, the relationship between pond and corresponding atmospheric variables strongly suggests that rising air temperatures (particularly daily minimum temperatures) are driving water temperature increases, and that decreases in the acidity of rainwater are contributing to elevated pH in ponds. Because pond

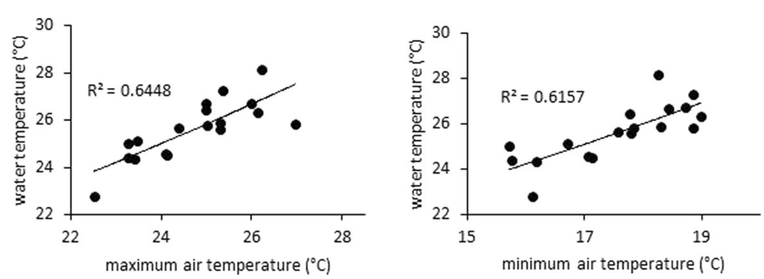


Fig. 5 Mean pond surface water temperature (all ponds) plotted against mean annual daily maximum and minimum air temperature for the month of July 1996–2013

Table 4 Statistical data on surface water pH changes over time by pond (R^2 = correlation coefficient, p = probability value, change = absolute increase or decrease over the time period, % change = percent change in value over the time period, time series = data used in analyses, Obs/year = number of data points available for each year of sampling)

Pond	R^2	p value	Number	Change	% Change	Time series	Obs/year
All ponds	0.59	0.01	10	0.9	17%	2000, 2003–2004, 2006–2007, 2009–2013	10 (1/pond)
Duck	0.62	<0.01	14	1.5	32%	1998, 2000, 2002–2013	2
Dyer	0.75	<0.01	12	1.3	28%	2000, 2003–2007, 2009–2013	2
Great-T	0.21	0.16	11	0.3	6%	2003–2013	2
Great-W	0.35	0.03	14	0.9	20%	1996–1998, 2000–2013	1
Gull	0.18	0.15	13	0.4	6%	2000–2013	2
Herring	0.23	0.06	16	0.7	11%	1996–1998, 200–2001, 2003–2013	1
Long	0.20	0.11	14	0.4	9%	1998, 2000, 2002–2013	2
Ryder	0.45	<0.01	16	2.0	44%	1997–1998, 2000–2013	1
Snow	0.02	0.71	11	0.1	1%	2002, 2004–2013	2
Spectacle	0.03	0.55	15	0.2	4%	1997–1998, 2000–2001, 2003–2013	1

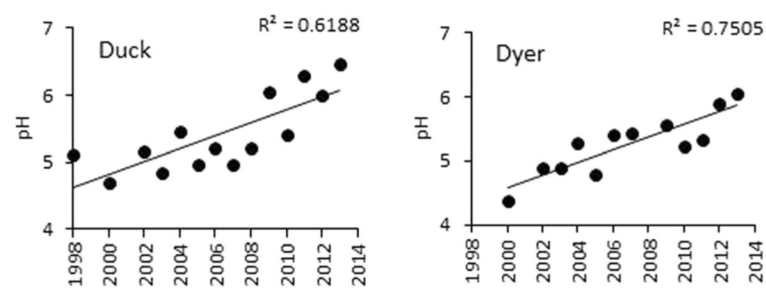
Highlighted rows indicate statistically significant trends

pH is also regulated by factors other than precipitation such as substrate properties, groundwater chemistry (including nutrients), and surface runoff (Anderson and Bowser 1986; Henriksen and Brakke 1988; Kenoyer and Anderson 1989; Lampert and Sommer 2007), the correlation with precipitation pH is weaker than that of air vs. water temperature.

Rising pH of rainwater has been documented in other locations across the northeast (e.g., Siver et al. 2004; Sickles and Shadwick 2015), and in CCNS this is reflected in measurements of both increasing precipitation and pond pH values. It is also possible that the pH increases observed in this analysis are in some part the result of in-lake alkalinity generation through sulfate reduction and burial, although this is dependent upon water column sulfate concentrations (Schindler 1986; Giblin et al. 1990), which have greatly decreased over the last two decades. In addition, sulfate reduction tends to be low in oligotrophic systems (Holmer and Storkholm 2001), which generally describes CCNS kettle ponds. Moreover, in some cases, increasing lake temperatures can directly affect pH, regardless of atmospheric inputs (Psenner and Schmidt 1992; Koinig et al. 1998). Notwithstanding, while the pH trends lacked statistical significance in four ponds, all trends were positive. Lack of significant change within Great-T pond may be due the several limings (addition of calcium carbonate) that occurred in the 1980s and 1990s. Thus, the older pH values were likely elevated above what they naturally would be. Snow and Spectacle ponds are the smallest in size and may be more influenced by groundwater, which tends to be higher in pH, thus elevating historic values and obscuring temporal trends related to atmospheric coupling.

Increasing pond pH and surface water temperature (of ≥ 2 °C in 5 ponds) may have considerable implications for primary productivity. Elevated pH can elevate concentrations of dissolved organic carbon (DOC) in the water column (although this is not universally true), which reduces water clarity (Monteith et al. 2007; Keller et al. 2008; SanClements et al. 2012). Shifts in pH can also alter the proportions of various algal functional

Fig. 6 Examples of temporal trends in surface water pH in Duck and Dyer ponds



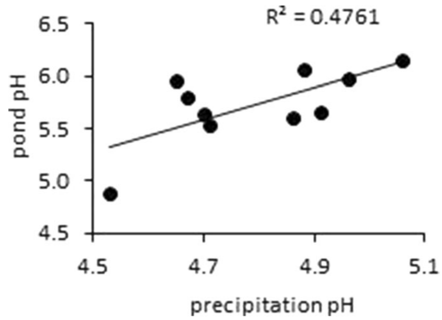


Fig. 7 Mean pond pH (all ponds pooled) plotted against mean annual precipitation pH for the period of 2000–2013

groups in that acidic waters tend to favor benthic algae (Turner et al. 1991), whereas higher pH conditions typically result in systems dominated by suspended phytoplankton (Vinebrooke et al. 2002). Low pH has been shown to reduce algal biomass in some lakes (and vice versa) (Kwiatkowski and Roff 1976; Almer et al. 1974), and it has long been known that both algal species composition (Moss 1973) and aquatic macrophyte vegetation are influenced by pH (Jackson and Charles 1988). In fact, Siver (2001) and Siver et al. (2004) found that chrysophytes and diatoms in Cape Cod kettle ponds were highly influenced by pH gradients across the peninsula. Changes in the primary producers of kettle ponds will likely influence the structure and functioning of higher organisms within lake food webs that depend on these communities (Carpenter et al. 1985; Declerck et al. 2005).

With respect to water temperature, CCNS's kettle ponds appear to be responding to regional climate change in a predictable way. While people enjoying the recreational activities that these ponds provide may appreciate warmer waters throughout the summer, numerous physical, biogeochemical, and ecological processes within these lakes may be altered (Butcher et al. 2015). These alterations may include increased algal biomass, higher productivity and lower dissolved oxygen, and changes in water clarity to name a few. Because lakes are characterized by a large number of biotic and abiotic variables that act both synergistically and antagonistically, forecasting whole-lake ecological responses to warming is difficult (Winder and Schindler 2004). Although there are a number of ways to calculate indices of thermal stability in lakes (Schmidt 1928; Idso 1973; Sundaram and Rehm 1973), warmer surface water temperatures tend to enhance conditions for thermal stratification (Fang and Stefan 2009; Adrian et al. 2009). Lower summertime wind speeds, which have shown a decrease over the past few decades (Pilson 2008), can also allow stratification to develop somewhat irrespective of water temperature (Henderson-Sellers 1977; Schindler et al. 1990, 1996). In turn, such processes may result in higher rates of nutrient diffusion from sediments, although this process depends on a number of other variables and can be quite complicated. More intense thermal stratification can also put additional stress on, or benefit, lake fauna and further alter trophic relationships and ecosystem function (King et al. 1999).

Temperature can influence pH and other aspects of water quality—either directly or indirectly—since it regulates chemical reactions as well as organismal physiology. Houle et al. (2010) found that changes in climate, particularly higher annual temperatures, were often correlated with lake acidity. Although thermal stratification limits seasonal nutrient inputs to the photic zone that fuel biomass production, warming itself may alter algal species composition. For example, increased abundances of cyanobacteria, including species posing risks to human health, may result (McQueen and Lean 1987; Paerl and Huisman 2009; Wagner and Adrian 2009; Huber et al. 2012; Kosten et al. 2012).

5 Conclusions

In summary, this study reveals the extent to which atmospheric/pond warming and reduced precipitation/pond acidity is occurring within CCNS. The changes appear to be tied to the regional rise in air temperatures and air quality improvements and have likely manifested themselves in altered physical, chemical, and biological properties within the lakes, which warrant further study. Assessment of these trends also provides a basis for predicting their future trajectories and, ultimately, managing these ecosystems within the context of a rapidly changing climate.

Acknowledgments This work was supported by the National Park Service, Cape Cod National Seashore. Many thanks to all of the past and present CCNS employees and interns who have collected air and pond water quality data for the last several decades within the park.

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