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A sediment record of trophic state change in an Arkansas (USA) reservoir

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Abstract Reservoir sediments are used cautiously in paleolimnological studies because of dating uncertainties, possible sediment disturbances and even concerns that indicators of trophic status may behave differently in reservoirs as opposed to natural lakes. We measured loss on ignition (LOI), carbon to nitrogen ratio (C:N), diatom abundance, total nitrogen (TN), total phosphorus (TP), TN:TP ratio, and carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$) in an 83-cm sediment core to track recent trophic status changes in Beaver Reservoir, Northwest Arkansas, USA. Measurements showed that LOI, TN, TP and diatom abundance increased significantly from the bottom to the top of the core ($p < 0.001$). The C:N ratio and $\delta^{13}C$ indicated a predominantly algal source for organic matter in the sediments. Increases in TN and TP were positively correlated with human population growth ($p < 0.01$) and the TN:TP ratio recorded a shift from phosphorus to nitrogen limitation around 1990. This shift may have encouraged cyanobacterial growth that caused episodes of taste and odor problems in the reservoir. This study suggests that despite concerns about sediment dating and disturbance, reservoir sediments can provide valuable information on past water quality changes.

Keywords Paleolimnology · Reservoir · Sediments · Water quality · Geochemistry

Introduction

Paleolimnological studies in the south-central United States are rare relative to the northern USA because the former region lacks natural, glacial lakes and because there are concerns that reservoir deposits may not accurately record water quality history (Shotbolt et al. 2005, 2006; Filstrup et al. 2010). Of particular concern are the possibilities of sediment disturbance and the relatively young ages of reservoirs, which may hinder application of traditional dating techniques

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(Shotbolt et al. 2005, 2006; Filstrup et al. 2010). In young reservoirs, the unsupported/supported ^{210}Pb boundary may not be reached. Furthermore, the 1963 ^{137}Cs peak, produced by atmospheric nuclear bomb testing, and often used for dating validation, may not be present. Additionally, eutrophication indicators such as organic matter, nutrient concentrations, and isotopes of carbon (δ^{13}C) and nitrogen (δ^{15}N) may be more difficult to interpret in reservoirs than in natural lakes. This is because artificial water bodies age faster and have different mixing regimes and morphological characteristics (Shotbolt et al. 2005, 2006).

There are many reservoirs in the south-central USA, which have allegedly undergone water quality changes, but long-term monitoring data are generally lacking, making it difficult to attribute cause and identify solutions. In these situations, paleolimnological methods are employed for inferring past changes (Costa-Böddeker et al. 2012). For example, Filstrup et al. (2010) utilized a suite of geochemical variables in Lake Waco, Texas to reconstruct water quality. The study successfully documented the eutrophication history of the reservoir. Organic carbon, organic nitrogen, total phosphorus and δ^{15}N all increased, whereas C:N and N:P decreased. Although the study was successful, confounding factors such as large allochthonous organic matter (OM) loads, differing OM degradation rates and changes in external N sources complicated interpretation of the sediment isotope profile from the reservoir. The authors concluded that more research was needed to understand isotopes in reservoir sediments before interpretations of past water quality can be made (Filstrup et al. 2010).

Arkansas is officially known as the "Natural State" for its clear lakes, streams and abundance of wildlife. In particular, northwest Arkansas (NWA) is dotted with caves, sinkholes, losing streams, plateaus and valleys typical of a karst-dominated terrain. The northern region is home to the Buffalo River, the first National River to be designated in the United States. It remains one of the few rivers in the lower 48 states that have not been dammed. The northern region has experienced sustained economic and population growth since the 1970s, with increasing development pressure (United States Census Bureau 2000). Because soils are thin and poorly developed, typical of karsted landscapes, agricultural production has been limited to animal production. As of 2010, Arkansas was ranked second and third in chicken and turkey production, respectively, and 24th in hogs and pigs in the USA (USDA-NASS 2010). Approximately 55 % of Arkansas' animal production (primarily poultry) was confined to northwest Arkansas (Slaton et al. 2004). Feeding operations from these activities generated large quantities of manure, which were land-applied (Haggard et al. 2003) and later identified as major sources of nutrient loading to water bodies, as expressed by increased concentrations of nitrogen and phosphorus in streams (Davis and Bell 1998). In addition to agriculture, the human population quadrupled between 1963 (100,000) and 2007 (400,000) in NWA, placing stresses on land and water resources. Forest cover decreased from 518 to 492 km^2 between 1999 and 2006, while urban land use increased from 15.5 to 46.6 km^2 during the same period. Total phosphorus in the water column of Beaver Reservoir, the site of this study, increased from 40 μg L^{-1} in the 1970s to 60 μg L^{-1} in the 2000s, while total nitrogen averaged 800 μg L^{-1} over that time. Annual appearance of the taste-and-odor compound 2-Methyl Iso-borneol (MIB) in Beaver Reservoir during recent summers is hypothesized to be from deteriorating water quality and consequent toxic algae proliferation. Citizens, water managers and other stakeholders continue to express concern over water quality in this reservoir.

We analyzed geochemistry and diatoms in an 83-cm sediment core from Beaver Reservoir to determine if changes in water quality were preserved in the sediments and if these changes were correlated with anthropogenic activities in the watershed. We hypothesized that biological and chemical indicators of eutrophication in the sediments would increase in response to these water quality changes.

Site description

Beaver Reservoir (94°12′N, 36°18′W) is a large, multipurpose reservoir that was built in 1963 in the Upper White River Basin of northwest Arkansas (Fig. 1). The reservoir has a surface area of 114 km^2 and a maximum depth of 63 m. The catchment area is 3,087 km^2, of which 57 % is in forest, 32 % in agriculture, and 5 % in urban use (Galloway and Green 2006). The air temperature ranges from 0 to 38 °C, with a 30-year mean annual temperature of 20 °C (NOAA 2009). The main inflows to the reservoir are the White River and War Eagle Creek (Green 1996; Haggard and Green 2002; Galloway and Green 2006). River flows generally reflect precipitation. From 1964 to 2012, total annual precipitation averaged 1,169 mm, with 30 % falling during spring. During the

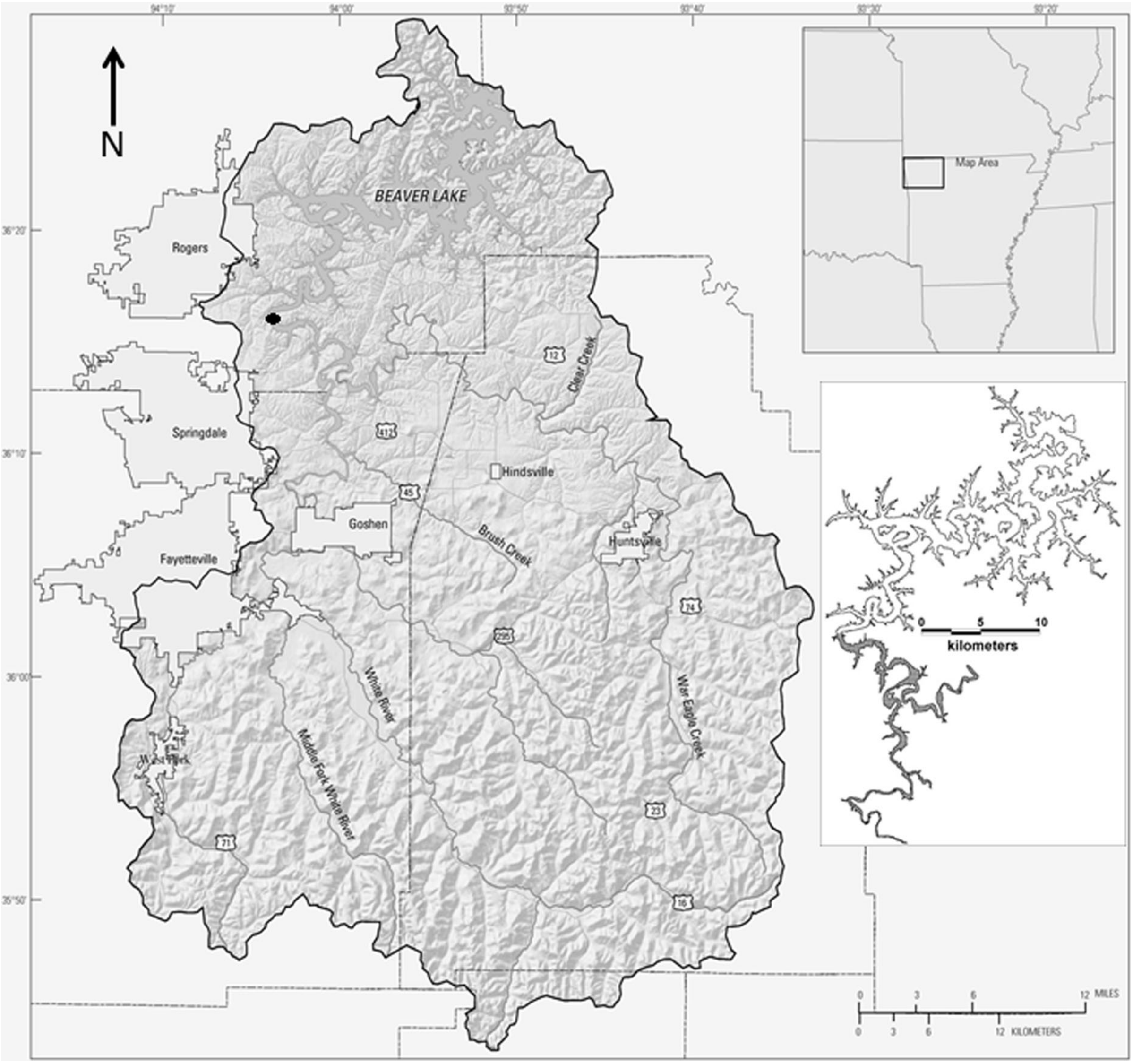

Fig. 1 Map of beaver reservoir, watershed boundaries and population centers within the *watershed*. Fayetteville and Rogers are not within the watershed boundary, but drain major streams that discharge into the reservoir. An 83-cm core was retrieved from the mid-reservoir zone indicated by the *black oval*

same period, average annual flow into the reservoir was 558 CFS with highest flows in the fall and spring. The reservoir is warm monomictic, with an average water residence time of 1.5 years (National Eutrophication Survey 1977). Average pool elevation is 341 m above sea level and average daily release (hydropower and spillway) is 3.4×10^6 m^3. Thermal stratification usually begins in May and complete mixing begins in October or November, with continued circulation throughout the winter season.

Materials and methods

Sediment coring, dating and geochemical analysis

An 83-cm sediment core was extracted from Beaver Reservoir using a UWITEC® percussion gravity corer on 18 September 2007. The core was taken in the middle zone of the reservoir in approximately 25 m of water. The collected core had approximately 20 cm of water above the sediment surface, which was gently removed using a tube and a 20-ml syringe. The core was then sectioned at 1-cm intervals from top to bottom, and samples were placed in Ziplock bags and kept on ice during transport to the lab.

The sediment chronology was determined by measuring ^{210}Pb, ^{137}Cs and ^{226}Ra in the Radioisotope Laboratory at the University of Manitoba, Canada. Sixteen sample depths were counted for ^{210}Pb and six samples were measured for ^{137}Cs. Five to 15 grams of sediment were sealed in petri dishes and "aged" for approximately 30 days to enable ^{226}Ra to equilibrate with daughters ^{214}Pb and ^{214}Bi. After aging, samples in the sealed dishes were counted on a gamma spectrometer (HyperpureGe detector) to determine ^{210}Pb, ^{137}Cs and ^{226}Ra activities. Unsupported ^{210}Pb activity in each sample was determined by subtracting ^{226}Ra activity (i.e. supported ^{210}Pb activity) from total ^{210}Pb activity at each level. Sediment ages were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1978; Oldfield and Appleby 1984) and the constant initial concentration (CIC) model (Robbins 1978). Age errors for the CRS model were propagated using first-order approximations and calculated according to Binford (1990). Because the reservoir was only 45 years old at the time of core collection, and reservoir sediments had accumulated for far <6 half-lives of ^{210}Pb, we could not measure the total integrated, unsupported ^{210}Pb (mBq cm^{-2}) that should have accumulated at the core site. We therefore used a novel approach to estimate the total unsupported ^{210}Pb value (A_0) expected at the site, had sediment been accumulating before the date of reservoir construction. That was accomplished as shown in the equations below, using the integrated unsupported ^{210}Pb measured in the core (A_{core}), i.e. since reservoir construction, to account for the "missing" unsupported ^{210}Pb that would have accumulated before the construction of the reservoir ($A_{pre\text{-}reservoir}$)

$$A_{pre-reservoir} = A_{core}\left(e^{(\text{reservoir age} * \text{decay constant})} - 1\right)^{-1}$$

$$A_{pre-reservoir} = 616.7\left(e^{(44.8 * 0.03114)} - 1\right)^{-1} = 203.3$$

$$A_0 = A_{core} + A_{pre-reservoir} = 616.7 + 203.3 = 820$$

We assessed organic matter (OM) content, carbon and nitrogen concentration and stable isotopic values in organic matter to determine past lake productivity. OM content was determined by loss on ignition (LOI) following Heiri et al. (2001). Approximately 2 g of dry sediment was combusted at 550 °C in a muffle furnace for 4 h. The difference between the dry weight and ash weight is expressed as % LOI. Organic matter $\delta^{13}C$ was determined to identify organic matter sources. Samples were acidified with 10 % HCl to remove carbonates and dried overnight in a low-temperature oven. Nitrogen and carbon concentrations and their stable isotopes were measured on an elemental analyzer and Thermo-Finnigan Delta Plus IR-MS, respectively, at the University of Arkansas Stable Isotope Laboratory (UASIL, Fayetteville, Arkansas). Measured organic $\delta^{13}C$ were adjusted to correct for anthropogenic changes in atmospheric carbon isotopic values in the past two centuries (Suess effect), using the equation from Verburg (2007). Total P in sediment was measured using the persulfate digestion method (EPA 365.4).

Diatom analysis

Sediments were treated with 30 % H_2O_2 and 10 % HCl at 80 °C. Once the organic matter was oxidized, test tubes were refrigerated overnight at 4 °C to stop the oxidation by H_2O_2 and allow diatoms to settle. The diatom slurry was spiked with microspheres (Batterbee and Kneen 1982) and mounted on round cover slips. The cover slips were dried overnight at room temperature and then mounted on slides using Naphrax®. Diatom taxonomy was determined using Krammer and Lange-Bertalot (1986–1991). At least 300 diatom valves were identified per sample. Statistical analyses were performed using SYSTAT® 12.0, with statistical significance set at $p < 0.05$ (Sokal and Rohlf 1995). Pearson correlation was used to test significant relationships between variables.

Results

Core characteristics

The 83-cm-long sediment core consisted of brown gyttja with no observable differences in texture. Excess ^{210}Pb activity was greatest at the surface (76 Bq g^{-1}) and declined exponentially with accumulated dry mass ($r^2 = 0.62, p < 0.001$, Fig. 2a). The

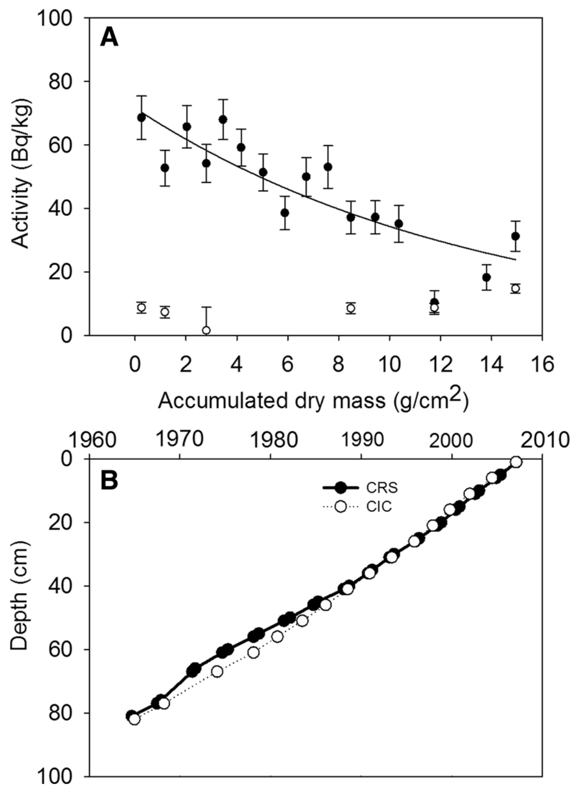

Fig. 2 **a** Activity of unsupported ^{210}Pb (filled circles) and ^{137}Cs (*open circles*) versus accumulated dry mass and (**b**) depth-age relationship using the CRS (*filled circles*) and CIC (*open circles*) models from beaver reservoir sediment, Arkansas. Error bars indicate one SD

mean sedimentation rate was calculated as 0.332 g cm^{-2} a^{-1} and was obtained by dividing total accumulated dry mass (14.93 g cm^{-2}) by the age of the reservoir (45 year). The CRS model estimated variable sedimentation in the core (0.2–0.8 g cm^{-2} a^{-1}). The ^{137}Cs activity remained relatively constant throughout the core, with a small increase in activity at the base (Fig. 2a).

Sediment chronology and bulk density

Sediment ages obtained using the CRS and CIC models are presented in Table 1. Mean dates provided by both models were similar (Table 1, Fig. 2b). The 95 % confidence intervals, however, were larger for the CIC model. For example, the date of the basal layer ranged from 1946–1984 using the CIC model, compared to 1962–1964 using the CRS model. The larger confidence intervals for CIC dates suggest that the variable sedimentation rates estimated by the CRS model more accurately reflect sedimentation in the core. The sediment core had an average bulk density of 0.18 ± 0.04 g cm^{-3}, but showed a decreasing trend from 1975 to 1998, followed by an increasing trend from 1999 to 2007 (Fig. 3).

Table 1 Comparison of dates and 95 % confidence intervals from the beaver reservoir core, using the CRS and CIC ^{210}Pb models

Max Depth (cm)	CRS			CIC		
	Low	Mean	High	Low	Mean	High
1	2005.2	2007.1	2009.1	2006.8	2007.1	2007.4
6	2002.9	2004.9	2006.9	2003	2004.5	2006
11	2000.6	2002.6	2004.6	1999.4	2002	2004.6
16	1998.4	2000.4	2002.5	1996.2	1999.8	2003.4
21	1996.3	1998.4	2000.5	1993.5	1997.9	2002.4
26	1993.8	1995.9	1998.1	1990.5	1995.9	2001.2
31	1990.9	1993.1	1995.4	1986.9	1993.4	1999.9
36	1988.5	1990.8	1993.1	1983.4	1991	1998.5
41	1985.7	1988.1	1990.4	1979.9	1988.5	1997.2
46	1982.3	1984.7	1987.2	1976.3	1986.1	1995.9
51	1979	1981.5	1984	1972.6	1983.5	1994.5
56	1975.6	1978.1	1980.7	1968.6	1980.8	1992.9
61	1972.1	1974.7	1977.3	1964.8	1978.1	1991.5

Geochemical and biological indicators

LOI increased from 5.4 % at the bottom of the core to 7.0 % at the top (Fig. 4a). Although the range was small (1.6 %), the increase was significant ($r^2 = 0.42$, $p < 0.001$). The C:N molar ratio averaged 7.42 ± 0.43, but did not show a clear trend with age (Fig. 4b). Similar to LOI, diatom abundance increased significantly from the bottom to the top of the core (Fig. 4c, $r^2 = 0.12$, $p = 0.003$). The diatom *Aulacoseira ambigua* (Grunow) Simonsen was the most abundant taxon throughout the core and reached a maximum relative abundance of 40 % around 2004 (Fig. 4d).

Total nitrogen and total carbon were positively correlated ($r = 0.80$, $n = 83$, $p < 0.001$), suggesting both were bound in the organic matter. Total nitrogen displayed a general increasing trend from 1963 to 2007 (Fig. 5a, $r^2 = 0.29$, $p < 0.001$). The minimum TN was 2.4 mg g^{-1}, a value that occurred several

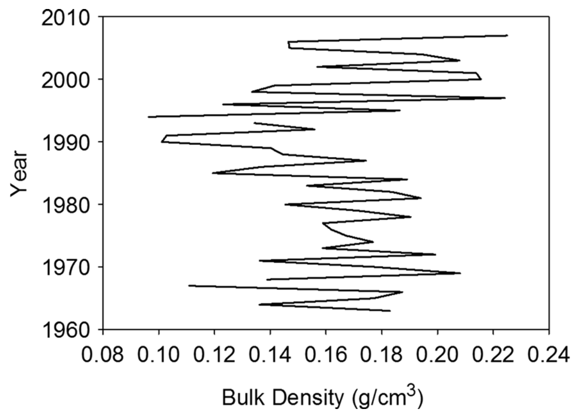

Fig. 3 Sediment bulk density of the beaver reservoir sediment profile

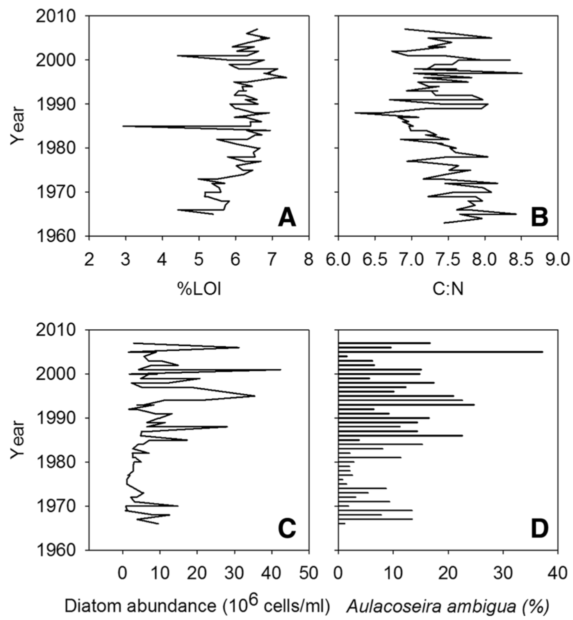

Fig. 4 **a** % LOI, **b** carbon to nitrogen (C:N) ratio, **c** diatom abundance and **d** *Aulacoseira ambigua* abundance versus date in the beaver reservoir sediment profile

times along the core. The maximum TN of 3.4 mg g^{-1} was measured at the top of the core in 2007. Total phosphorus concentration also increased significantly between 1963 and 2007 (Fig. 5b, $r^2 = 0.40$, $n = 24$, $p < 0.001$). TP was approximately 0.10 mg g^{-1} from the 1960s to 1990, then generally >0.20 mg g^{-1} to 2007. Maximum TP measured was 0.55 mg g^{-1} in 1998 (Fig. 5b). TN:TP decreased significantly from 1963 to 2007 (Fig. 5c, $r^2 = 0.28$, $p < 0.01$). Between 1963 and 1990 the TN:TP was generally >20, with values <15 after 1990 (Fig. 5c). Both TN and TP were significantly correlated to human population increase (Fig. 6, both $p < 0.001$).

Stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$)

The uncorrected and corrected $\delta^{13}C$ values were highly variable from 1963 to 1982 (Fig. 7a), with three periods of lighter $\delta^{13}C$, around 1968, 1976 and 1982. From 1982 to 2007, the $\delta^{13}C$ values are much less variable (Fig. 7a), with corrected values generally remaining between −25 and −24 ‰ (Fig. 7a). The $\delta^{15}N$ averaged 7.45 ± 0.44 ‰ (Fig. 7b). There was a general decline from 8 to 7 ‰ from *ca*. 1964 to 1990, but no apparent trend from 1990 to 2007 (Fig. 7b). The $\delta^{15}N$ did not display an overall trend from the bottom to the top of the core and was not correlated with any other measured variable.

Discussion

Results from our study suggest that sediment cores can serve as useful archives for trophic status change in reservoirs, particularly in areas where natural lakes do not exist. The use of cores to assess change and ascribe these changes to watershed activity is largely based on the ability to demonstrate that the sediment was not disturbed and to reliably date the sediments. Once this has been accomplished, observed changes in the core, such as increased nutrients, can be correlated to watershed activities. Several models for sediment dating with ^{210}Pb and ^{137}Cs have been developed. These are discussed extensively in Robbins (1978) and Appleby and Oldfield (1978). Here, we used our ^{210}Pb dates cautiously to place observed geochemical changes in the sediment core in a general temporal context. We did so because our results illustrate some of the challenges in using radioisotopes to date reservoir sediments.

In our study, we compared dates and sedimentation rates estimated by the CIC and CRS models. Ideally the core should extend below the unsupported/supported ^{210}Pb horizon. The core in our study did not extend below the unsupported/supported ^{210}Pb horizon because of the reservoir's young age, so we estimated the "missing" component of the total unsupported ^{210}Pb inventory from the ^{210}Pb inventory

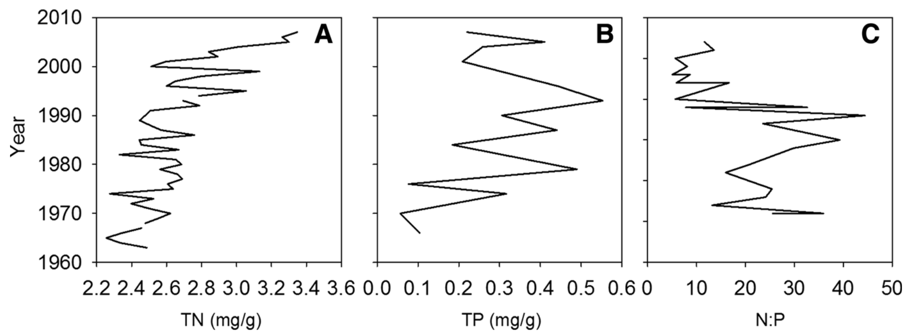

Fig. 5 **a** Total nitrogen, **b** total phosphorus, **c** nitrogen to phosphorus (N:P) ratio versus date in the beaver reservoir sediment profile

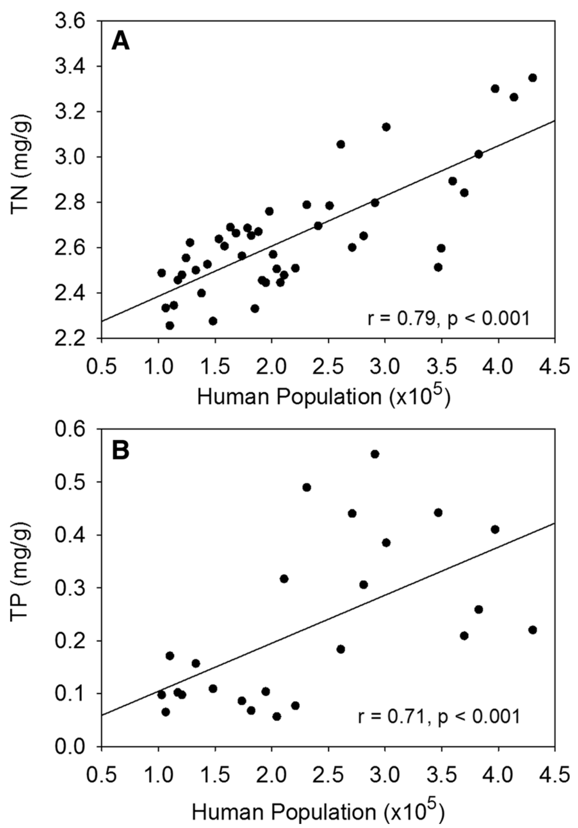

Fig. 6 Human population in the beaver reservoir watershed versus concentrations of (**a**) total nitrogen (TN) and (**b**) total phosphorus (TP) in the beaver reservoir sediment profile

in the core and the reservoir's age. Again, under ideal circumstances, the ^{137}Cs profile should display a down-core increase in activity to a sharp peak, below which there is a rapid decrease to zero. This peak corresponds to the 1963 maximum in atmospheric atomic bomb testing and can sometimes be used to verify dates generated from the ^{210}Pb model. Whereas there was a slight increase in ^{137}Cs at the core base in the Beaver Reservoir core, there was no defined peak and pre-1963 sediments were not obtained. Absence of the peak hinders the ability to independently verify the ^{210}Pb dates and highlights the challenge of sediment dating in young reservoirs. Despite this challenge, the exponential decline in excess ^{210}Pb with accumulated dry mass indicates orderly deposition of sediments since reservoir construction. Although we found general agreement between CRS and CIC dates, the larger confidence intervals for CIC dates indicate variable sedimentation rates over time and the CRS model confirmed these variable sedimentation rates. Because the CRS and CIC models yielded similar dates and indicated changing sedimentation rates over time, we have confidence that the changes we see in sediment variables over time are placed in a reasonable temporal framework.

To demonstrate that the sediments provide an accurate representation of past conditions, we correlated historical information on land use change in the watershed and changes in environmental conditions in the reservoir. Historical information on the drainage basin was sparse. The best proxies for environmental change were the growth in population, which quadrupled between 1963 (100,000) and 2007 (400,000), and the increase in annual broiler (poultry) production, from $259{,}850 \times 10^3$ to $1{,}175{,}900 \times 10^3$ over the same period (http//nass.usda.gov). Our results and those of others (Davis and Bell 1998) suggest that these anthropogenic activities impacted nutrient conditions and biological productivity in the reservoir. For example, the increase in sediment TN and TP was significantly correlated to population growth. Biological activity also increases up-core, as indicated by the significant increases in LOI, diatom abundance and higher percentages of *A. ambigua*, an indicator of eutrophic conditions (Interlandi et al. 1999; Zalat and

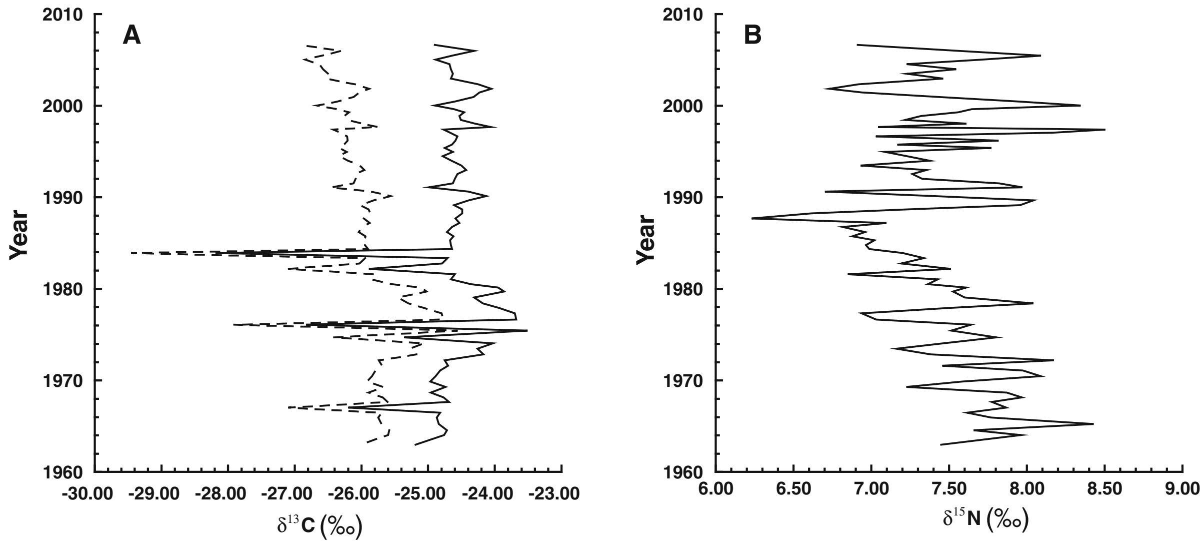

Fig. 7 **a** Uncorrected $\delta^{13}C$ (*solid line*) and $\delta^{13}C$ corrected for the Suess effect (*dotted line*) and (**b**) $\delta^{15}N$ versus date in the beaver reservoir sediment profile

Vildary 2007). Between 1993 and 1995, a study was conducted to examine the amount of poultry waste production, and potential impacts on water quality (Haggard et al. 2003). The study revealed that the Beaver Reservoir basin produced about 200,000 metric tons a^{-1} of poultry litter, with most being land-applied as fertilizer to meet forage N requirements (Haggard et al. 2003). Land-applied poultry litter had been cited for increasing N and P in northwest Arkansas (NWA) streams (Petersen 1992; Haggard et al. 2003). Observed increases in sediment TN and TP may have been a consequence of animal manure application and subsequent stream runoff to the reservoir.

The impact of increased TP was evident in the TN:TP ratio, which fell from an average of 27 between 1963 and 1990 to 11 between 1990 and 2007 (Fig. 5). Smith (1982) reported that TN:TP mass ratio < 15 indicates N limitation, whereas N:P >16 indicates P limitation. Nitrogen limitation often leads to cyanobacteria proliferation. It appears that the reservoir switched from P limitation between 1963 and 1990 to N limitation from 1990 to 2007. Over the last 10 years, the reservoir has experienced episodic outbreaks of taste and odor compounds that have been linked to cyanobacterial proliferation in other reservoirs (Watson 2003; Youngstead 2005). In addition to poultry litter application, other aspects of human population growth probably contributed to increased nutrient concentrations. In NWA, unpaved roads were much more common in the 1960s and 1970s compared to today. The decrease in sediment bulk density in the mid-1980s might reflect reduced allochthonous sediment from unpaved roads. Regional water authorities are reducing sediment input from the watershed by paving streets. Our study suggests that the recent change in sediment type was driven by an increase in the input of nutrients, not inorganic material.

Algal OM and terrestrial OM (C_3 plants) have overlapping $\delta^{13}C$, which range from -25 to -30 ‰. Thus, $\delta^{13}C$ is often used in combination with the C:N ratio to differentiate organic matter source. Typically, algal-derived organic matter has a C:N atomic ratio from 2 to 10, whereas terrestrially derived organic matter has C:N from 20 to 80 (Meyers and Lallier-Vergès 1999). In our study, the C:N atomic ratio was consistently <10 throughout the core and the $\delta^{13}C$ was in the range expected for algal-derived OM, with $\delta^{13}C$ values between -23.5 and -30 ‰. The study suggests that algal organic matter was the predominant source of organic matter to the sediments, providing further evidence for deteriorating water quality and enhanced biologic production in the reservoir.

The $\delta^{13}C$ can also be used to infer past productivity because of the carbon isotope fractionation that occurs during photosynthesis. Periods of very high productivity generally lead to greater incorporation of ^{13}C into the OM as algae draw down the supply of ^{12}C. Greater $\delta^{13}C$ values are thus found in the sediment core organic matter (Hodell and Schelske 1998; Mizutani and Wada 1982). The trend toward higher organic matter $\delta^{13}C$ during periods of greater productivity was not observed at Beaver Reservoir. Several factors could account for the lack of an increasing trend in organic matter $\delta^{13}C$ accompanying enhanced productivity (Gu et al. 2004, 2006; Rosenmeier et al. 2004; Woodward et al. 2012). Atmospheric CO_2 equilibrates with aqueous CO_2, thereby bringing down the carbon isotopic value in water and algal OM, obscuring inferences about productivity (Verburg 2007). Sewage effluent may also influence the $\delta^{13}C$ of sediments. Rosenmeier et al. (2004) attributed depleted ^{13}C in recent sediments of Lake Petén Itza, Guatemala, to sewage effluent, because sewage OM is low in ^{13}C relative to OM produced by phytoplankton. Given that our Beaver Reservoir core was retrieved downstream from a wastewater treatment plant, it is possible that the carbon isotope values in the sediment OM reflect, in part, sewage effluent input.

Photosynthesis by lacustrine algae results in a stable carbon isotope fractionation of about 20 ‰ (Hecky and Hesslein 1995). Fractionation, however, is reduced and $\delta^{13}C$ of OM is consequently greater when productivity is high and CO_{2aq} is in short supply. Respiration on the other hand contributes CO_2 with low ^{13}C content to the water. Because most lakes with a significant supply of allochthonous OM are net heterotrophic (respiration exceeds photosynthesis), and supersaturated with CO_2 (Cole et al. 1994), there is perhaps an abundant supply of $^{12}CO_2$ for photosynthesis. This supply may mask the effects of high productivity that would be observed in lakes where $^{12}CO_2$ is in short supply.

Increased $\delta^{15}N$ has also been used as an indicator of algal productivity in numerous studies (Altabet and Francois 1994; Teranes and Bernasconi 2000; Filstrup et al. 2009). As epilimnetic dissolved inorganic nitrogen (DIN) pools become progressively enriched with ^{15}N from preferential assimilation and hypolimnetic transport of ^{14}N, phytoplankton discriminate less against ^{15}N (Hodell and Schelske 1998). The $\delta^{15}N$ in our study did not demonstrate a trend of enrichment as observed in natural lakes experiencing increased primary productivity. Rather, the $\delta^{15}N$ in our core decreased, but only from 8 to 7 ‰ between 1963 and 1990. The lack of a large change in $\delta^{15}N$, in response to greater productivity in the reservoir, may have been a consequence of several factors. Only 26 % of the variation in $\delta^{15}N$ ($r^2 = 0.26$, $n = 37$) was accounted for by TN concentration, suggesting other factors influenced both N concentration and its isotopic ratio. Because N was non-limiting before 1990, phytoplankton discriminated against ^{15}N and readily incorporated ^{14}N into their biomass, thus displaying relatively low $\delta^{15}N$ up to 1990. When the reservoir became N-limited after 1990, the $\delta^{15}N$ of sediments fluctuated, perhaps in response to availability and source of nitrogen. For example, in the late 1990s and 2000, $\delta^{15}N$ was as high as 8.5 ‰, which suggests lower N concentrations and thus greater incorporation of ^{15}N by phytoplankton (Fig. 3). Conversely, low $\delta^{15}N$ *ca.* 2002 and 2003 suggests greater overall N concentrations and more discrimination against ^{15}N. The $\delta^{15}N$ of 8.5 ‰ may also be a reflection of sewage effluent because sewage $\delta^{15}N$ ranges from 10 to 20 ‰.

The shift in the N:P ratio towards N limitation may have led to greater cyanobacterial proliferation in the reservoir which, in turn, could have affected N dynamics in two ways. First, because cyanobacteria fix N directly from the atmosphere, the amount of ^{14}N in the water column available for incorporation into algal biomass could also increase. Although the phenomenon has not been shown in freshwater systems, approximately 52 % of fixed nitrogen can become available for algal uptake in oceans (Mullholand et al. 2006). Second, cyanobacteria $\delta^{15}N$ values are generally close to zero, reflective of their substrate, air. Therefore, high abundances of cyanobacteria will pull $\delta^{15}N$ values down toward zero. This may explain the lower $\delta^{15}N$ *ca.* 2002 and 2003. Lower $\delta^{15}N$, possibly initiated by cyanobacterial fixation, is further supported by the observation that 2002 had the highest level of the cyanobacterially-produced taste and odor compound 2-Methyl-Isoborneol on record. Other mechanisms, perhaps N mineralization (Bernasconi et al. 1997), may have led to lower $\delta^{15}N$ in sediments, whereas selective loss of N through denitrification or immobilization (Talbot and Laerdal 2000; Teranes and Bernasconi 2000; Savage et al. 2004) led to higher $\delta^{15}N$. Grantz et al. (2012) demonstrated that denitrification accounts for significant losses of N in reservoirs. These losses further suggest a significant impact on the $\delta^{15}N$ signature of sediments.

Conclusions

We demonstrated that sediments of Beaver Reservoir recorded increasing concentrations of N and P through time and chronicled a shift from P limitation to N limitation around 1990. These increases coincided with increases in human population in the watershed, land application of poultry manure and documented increases in N and P concentrations in streams. The study also documented a significant increase in organic matter concentration derived from algal sources, based on the C:N ratio and $\delta^{13}C$ values. Stable isotope analysis of C and N suggested several processes influenced the $\delta^{13}C$ and $\delta^{15}N$ signature of the sediments. Further studies are needed to better understand the behavior of $\delta^{13}C$ and $\delta^{15}N$ in reservoir sediments to more effectively enable their use in historical water quality investigations. Despite these challenges, sediment studies could provide valuable information on historical water quality in reservoirs.

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