

Article

Possible Sediment Mixing and the Disparity between Field Measurements and Paleolimnological Inferences in Shallow Iowa Lakes in the Midwestern United States

Roger W. Bachmann * , Mark V. Hoyer and Daniel E. Canfield Jr.

School of Forest Resources and Conservation, University of Florida, Gainesville, FL 32611, USA; mvhoyer@ufl.edu (M.V.H.); decan@ufl.edu (D.E.C.J.)

* Correspondence: rbach@ufl.edu; Tel.: +1-352-273-3623

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Abstract: Field measurements of water quality in Iowa lakes contradict paleolimnological studies that used ^{210}Pb dating techniques in 33 lakes to infer accelerating eutrophication and sediment accumulation in recent decades. We tested this hypothesis by analyzing a series of water quality measurements taken in 24 of these lakes during the period 1972–2010. There was little change in the trophic state variables. Total phosphorus and algal chlorophylls did not increase, and Secchi depths did not decrease with no evidence that the lakes had become more eutrophic. Changes in daily sediment loads in the Raccoon River also did not match the paleolimnological inferred rates of soil erosion for the period 1905–2005, and an independent estimate of soil erosion rates showed a decline of 40% in the 1977 to 2012 period rather than an increase. We hypothesized that sediment mixing by benthivorous fish could be responsible for violating the basic assumption of ^{210}Pb sediment dating that the sediments are not disturbed once they are laid down. We developed a mathematical model that demonstrated that sediment mixing could lead to false inferences about sediment dates and sediment burial rates. This study raises the possibility that sediment mixing in Iowa lakes and similar shallow, eutrophic lakes with benthivorous fish may cause significant sediment mixing that can compromise dating using ^{210}Pb dating of sediment cores.

Keywords: ^{210}Pb dating; paleolimnology; eutrophication; carbon burial; bioturbation; sediment mixing; diatom-inferred phosphorus

1. Introduction

Paleolimnology offers the best tool that can be used to assess anthropogenic impacts to lakes when long-term field data are not available, and it can provide a basis for lake restoration and management. It is important for this reason that paleolimnological studies are done correctly. We compared in this study the published paleolimnological inferences of lake eutrophication and sediment accumulation rates from a study of several lakes in the state of Iowa, which is a major agricultural area in the Midwestern United States with field data, collected from the same lakes over a 38-year period. We found that the field data did not reflect the paleolimnological inferences from ^{210}Pb dating of sediment cores that showed increasing rates of eutrophication and rates of sedimentation during the same time period. We hypothesized that sediment mixing by benthivorous fish was responsible for violating the basic assumption of ^{210}Pb sediment dating that the sediments are not disturbed once they are laid down. We developed a mathematical model involving sediment mixing that could explain the observed vertical distributions of ^{210}Pb . This study emphasizes the importance of independent means of testing sediment dates derived from ^{210}Pb dating.

Many studies starting with Naumann [1] have associated eutrophic lakes with agricultural development in their watersheds. The state of Iowa is a good example with some of the most intensive and extensive row crop agriculture in the world surrounding its natural lakes. These lakes are also some of the most eutrophic in the United States [2]. It has been assumed that these agricultural activities have increased nutrient loading and caused significant eutrophication [3]. However, an alternative hypothesis is that the rich prairie soils that make Iowa so favorable for agricultural production also are responsible for the high productivity of the lakes. The question is what were the trophic states of Iowa lakes prior to European settlement in the 1800s, and how much have these lakes changed since then?

The Iowa lakes are important not only to Iowans, but to the limnological community for understanding the magnitude of the impact of cultural eutrophication on lakes. When we [4,5] estimated the extent of eutrophication in the natural lakes of the United States using the results of the United States Environmental Protection Agency's [6] paleolimnological study of lake sediment cores taken during the National Lakes Assessment of 2007, we concluded that the proportions of lakes categorized as oligotrophic, mesotrophic, eutrophic, and hypereutrophic for the presettlement time period were not significantly different from the proportions found in 2007. We were criticized in part by McDonald et al. [7] and Smith et al. [8] on the basis that our sample underrepresented the most eutrophic lakes in the most highly agricultural areas of the country. This problem arose because less than 0.2% of the estimated 29,308 natural lakes in the coterminous United States are found in the state of Iowa [6], thus they were not all selected in the USEPA's random sample of lakes.

A recent series of papers [3,9–11] seemed to provide the needed information to reject the conclusions of Bachmann et al. [4,5]. They described analyses of ^{210}Pb dated cores from 33 natural lakes in Iowa. Their analyses of 7 of those lakes indicated that Iowa lakes with the conversion of the native prairie to agriculture in the mid 1800s were now up to 4.5 times more productive of organic matter than they were prior to European settlement [3]. They based their conclusions of accelerated eutrophication on two findings. One was the increase in the rates of burial of organic carbon during the time period of 1850 to 2010 [3]. It was reasoned that agricultural activities increased nutrient loadings to the lakes, which in turn led to increased primary production and ultimately the delivery of increased amounts of autochthonous carbon to the sediments. The other finding, based on measurements in 8 of their lakes, was an increase in the rates of burial of biogenic silica [11]. Biogenic silica is produced by diatoms and has been related to primary production [12]. Increases in the rate of burial of biogenic silica in the sediments were therefore taken as an indication of increased primary production in the lakes. Furthermore, the authors also found a corresponding increase in the rates of deposition of inorganic materials that originated from outside of the Iowa lakes. These inorganic depositions were attributed to increased rates of soil erosion due to agricultural practices in the lake watersheds and therefore represented a failure of soil conservation practices that have been carried out from the 1930s to the present [10].

The increase in burial rates of organic and inorganic sediments and biosilica found in the studies of Heathcote et al. [9] are based on determining the ages of the sediments at different depths in the sediment cores. These ages were calculated by measuring the activity of naturally occurring ^{210}Pb at different levels in the sediment core following the method of Appleby and Oldfield [13]. An important assumption of this method is that the sediment layers are undisturbed over time and represent a chronological sequence. If the sediments are disturbed so that the sediments laid down in one year become mixed with sediments in previous years, an error is introduced that will yield calculated sedimentation rates that are too high in the upper portion of the sediment core. Such disturbances can be caused by wave action and sediment resuspension [14] and by biological factors such as the burrowing activities of benthic macroinvertebrates [15] and the foraging activities of benthivorous fish [16].

Oldfield and Appleby [17] and several others have since recommended that independent methods be used to verify dates obtained with the ^{210}Pb method because of the potential errors that come with sediment mixing. In the case of the Iowa lakes studied by Heathcote et al. [9], there was no independent

verification of the dates in the upper portions of the cores where the calculated sedimentation rates were increasing at an exponential rate (A. Heathcote pers. comm.). Their paleolimnological study indicated that the increase in sedimentation rates started in around the 1960s and continued to increase when the study ended in 2008 [10]. Because of the sediment mixing issue and the fact that the Heathcote et al. [9,10] findings did not comport with our experiences working on Iowa lakes [18,19], we initiated a study to make an independent verification of their paleolimnological findings.

As a check, we first used the results of field measurements of the trophic state variables total phosphorus, chlorophyll and Secchi disk depth taken during Iowa lake surveys. These surveys were initiated in 1972 and have continued to the present. If the loads of plant nutrients have been increasing since the 1970s as concluded by Heathcote et al. [9,10], the concentrations of total phosphorus and algal chlorophylls should be increasing. We then used an Iowa study [20] where sediment loads in the Raccoon River (near Des Moines, IA) have been measured on a daily basis since 1916 to determine if soil erosion rates have been increasing in an exponential manner in the past 100 years. This is a large watershed that encompasses the same kinds of landscapes and agricultural activities as the watersheds of the lakes under study. If true, Secchi disk depths should be decreasing due to increased concentrations of suspended inorganic particles as well as increased concentrations of algal chlorophylls. Finally, the United States Department of Agriculture has calculated soil erosion rates on agricultural lands in Iowa for every 5 years in the period from 1977 to 2012 [21]. These data were compared to Heathcote et al. [9,10] estimated rates of sediment burial in the natural lakes during the same time period.

The objectives of this study therefore were: (1) To determine if the trophic state variables total phosphorus, chlorophyll and Secchi depth in natural Iowa lakes have been changing since the 1970s in a way that would reflect increasing levels of eutrophication and suspended sediments as inferred by the paleolimnological studies; (2) To determine if the soil erosion rates in Iowa as inferred from lake sediment cores match the rates of soil erosion in Iowa as determined by independent studies; (3) If the field measurements do not correspond to the paleolimnological inferences, to determine if there is an alternative explanation for the ^{210}Pb vertical distributions in the sediment cores; and (4) To make an estimate of the trophic states of Iowa lakes prior to European settlement, and to determine how much they have changed since then.

2. Materials and Methods

2.1. Limnological Measurements

The state of Iowa has a relatively small number of natural lakes, and almost all are located on the Des Moines lobe of the Wisconsin glacial drift sheet (Figure 1, [22]). The referenced paleolimnological studies included most of those lakes, and long-term limnological measurements were available for 24 of the lakes with paleolimnological information.

We assembled summer measurements of total phosphorus, algal chlorophylls, and Secchi depths for the 24 lakes from a 1972–1973 comprehensive study of Lake West Okoboji, Big Spirit Lake, Lake East Okoboji, Upper Gar Lake, Lake Minnewashta, and Lower Gar Lake [18], and several published studies on Iowa lakes [22–25]. These data are available from the Iowa Lakes Information System [26], which also has additional data from statewide lake surveys in 1979 and 1994 as well as data collected by Iowa State University, the Iowa Department of Natural Resources, and the Iowa State Hygienic Laboratory from 2000 to 2015.

Summer averages for each of the three variables were calculated for each natural lake by first averaging by the months of June, July, and August and then by summer. There was a minimum of two measurements for each month. We then used linear regressions with each lake's summer averages of total phosphorus, chlorophyll, and Secchi depth as the dependent variables and years as the independent variable to determine if there were statistically significant trends over time. Not all lakes had data for the same years, so to look at the lakes as a group, we expressed each annual value

for each variable in each lake as a percent of the average value for that lake for the period of record. We used these percents for all lakes in a regression against time. Because we were making a large number of statistical tests on the same data, we used the false discovery rate procedure of Benjamini and Hochberg [27] to calculate an adjusted p -value. Statistical significance was indicated for a $p < 0.05$.

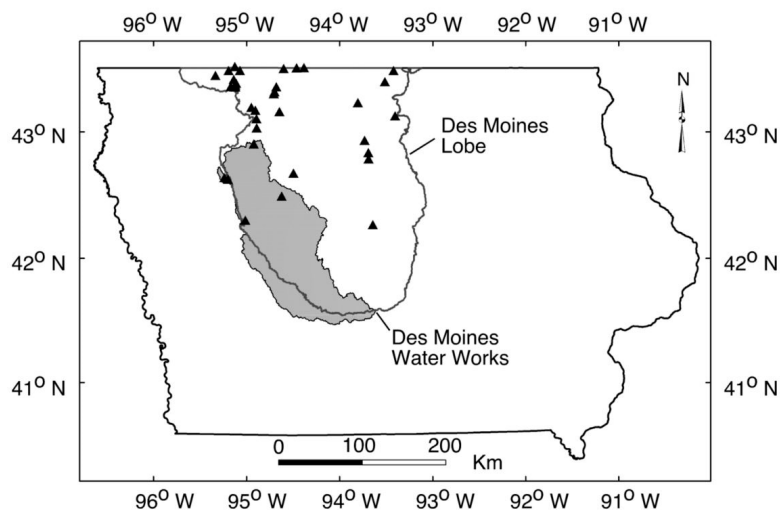


Figure 1. Location of the 33 natural lakes in Iowa discussed in this study (triangles). Most are located within the boundaries of the Des Moines lobe of the Wisconsin Glacier. The shaded area represents the watershed of the Raccoon River above the sampling station at Des Moines, Iowa. Map information is from the Iowa Department of Natural Resources.

2.2. Independent Estimates of Soil Erosion

The Des Moines Water Works has been measuring the turbidity of water from the Raccoon River on a daily basis since 1916. Jones and Schilling [20] converted the turbidity readings into total suspended solids concentrations, and in conjunction with water flow measurements calculated sediment transport in the river on a daily basis from 1916 to 2009. Schilling et al. [28] determined that agricultural activities dominated the land uses of the 9389 km² watershed with 77% of the basin in row crops of corn (*Zea mays* L.) and soybeans (*Glycine max* L. Merr.). Information from the Raccoon River, therefore, provided an indication of soil erosion in the upstream watershed, which is similar to the watersheds of the natural lakes in this study (Figure 1). We then compared decadal average values for total suspended solids concentrations, average discharge, and sediment loads from the Raccoon River with the calculated average accumulation rates of dry sediments in the 33 lakes studied by Heathcote et al. [11].

The United States Department of Agriculture [2] calculates soil erosion rates in each state for different agricultural land uses using the Revised Universal Soil Loss Equation, version 2. Results are summarized every 5 years and available for 1977 through 2012. We used their erosion estimates for cultivated crops, all croplands, and pasturelands to determine if soil erosion was increasing as inferred by Heathcote et al. [11].

2.3. Paleolimnological Data

We used the paleolimnological data from the sediment cores of the 33 Iowa lakes reported on by Heathcote and Downing [3] and Heathcote et al. [9–11]. C. Umbanhowar, Jr. (St. Olafs College, Minnesota) collected the sediment core from Big Spirit Lake, and those data were reported in Heathcote and Downing [3]. Sediments at different levels in the cores were dated using ²¹⁰Pb; and dry densities, % organic matter, % inorganic matter, % calcium carbonates, and other sediment characteristics were measured. Heathcote et al. [11] also examined the diatom communities located at the surface of the

sediments and at a depth in the sediments representing a presettlement time of about 1850. They used these data to find the diatom-inferred concentrations of total phosphorus in the lakes prior to settlement in order to compare these estimates with 2010 total phosphorus values. The same diatom data set was also used to determine floristic changes as quantified by the square chord distance (SCD) and other statistical procedures. Although the diatom communities did show changes in SCD, the magnitudes of change were not strongly correlated with Heathcote et al.'s [11] two indicators of eutrophication, the burial rates of organic carbon and biogenic silica. They reported that lake depth seemed to be more important in explaining the changes. Likewise the diatom-inferred concentrations of total phosphorus showed increases in most of the lakes, but their magnitudes were much less than expected from Heathcote and Downing [3] organic matter burial rates. They cited some problems that others had found in using transfer functions in shallow, productive lakes and concluded they should use other techniques (i.e., geochemistry and diatom ecology) to reconstruct the course of eutrophication in the Iowa lakes.

Two of the lakes (Clear and Storm) had cores where the lower sample dated to the early 1900s, while the dates for the remaining cores ranged from 1755 to 1895 [9]. We converted their diatom-inferred concentrations of phosphorus from logarithmic units (Table 5 of Heathcote et al. [9]) to $\mu\text{g}\cdot\text{L}^{-1}$ and ran *t*-tests to test the null hypothesis that there was no difference between the top and bottom diatom-inferred total phosphorus concentrations. Because we later found evidence of mixing of the surface sediments that might have influenced the diatom composition of the surface sediments, we also made comparisons between diatom-inferred concentrations of total phosphorus from the bottoms of the cores and 10-year measured summer average total phosphorus concentrations for the 24 lakes with field measurements.

2.4. Carbon and Dry Matter Sedimentation Rates by Decade

We found for 33 lakes the rates of organic sedimentation for 1905 and every 10 years thereafter up to 2005 from plots of calculated organic matter sedimentation rates versus calculated ages in the Heathcote et al. [9] sediment cores. Because lakes Upper Gar, Minnewashta, and Lower Gar did not have those plots, we used plots of dry sedimentation rates and percent organic matter in Heathcote et al. [9] to calculate organic matter sedimentation rates at different sediment ages. Carbon burial rates were found by multiplying the organic matter rates by 0.469 [29]. We also found the geometric means of the dry sediment accumulation rates for 33 individual lakes for each decade to make a composite plot of dry sediment burial versus time for the period 1905 to 2010, and ran a correlation analysis of the percent organic matter in each of 24 lakes in the period 2000 to 2010 and the average chlorophyll concentrations in the same lakes for the same time period.

2.5. Alternative Interpretation of ^{210}Pb Profiles

Heathcote et al. [9] inferred sediment ages at different depths in the cores and sedimentation burial rates from analyses of unsupported ^{210}Pb profiles in sediment cores from 33 Iowa lakes. The authors noted a “flattening” of the plots of the logarithms of unsupported ^{210}Pb activity versus depth in the sediments [11] and interpreted these flattening as increases in sedimentation rates in recent years, that diluted the annual input concentrations of ^{210}Pb . An alternative interpretation is provided from several other studies in both freshwater and marine environments [30–32]. These studies demonstrated that sediment mixing by disturbing the layering of the sediments leads to a false conclusion of accelerating sedimentation rates. Such mixing can move the ^{210}Pb activities downward in the sediments, which is then falsely interpreted as younger sediment ages at those depths.

2.6. Model Development

We developed a model to test the hypothesis that the observed ^{210}Pb activities in the Iowa lakes could be produced through sediment mixing in a lake that has had a constant sedimentation rate since

the mid 1800s. The details of the model are given in Appendix A, and the symbols are defined in Table 1.

Table 1. List of symbols and values of constants used for Lake West Okoboji model of sediment mixing. In this table ^{210}Pb refers to unsupported ^{210}Pb .

Constants	Description
α	The slope of the regression of the natural log of ^{210}Pb vs cumulative sediment mass in the mixed region of the sediment core ($0.1277 \text{ g}^{-1} \cdot \text{cm}^2$).
β	The slope of the regression of the natural log of ^{210}Pb vs cumulative sediment mass below the mixed region of the sediment core ($1.008 \text{ g}^{-1} \cdot \text{cm}^2$).
λ	The decay constant for ^{210}Pb (0.03114 yr^{-1}).
ρ	Density of sediments ($0.17 \text{ g} \cdot \text{cm}^{-3}$).
A_∞	The total inventory of ^{210}Pb in the sediment core ($28.40 \text{ pCi} \cdot \text{cm}^{-2}$).
D_b	The apparent diffusion coefficient in the mixed layer ($\text{cm}^{-2} \cdot \text{yr}^{-1}$).
i	Index value for the annual sediment layer below the surface.
m	The mass of dry sediment in an annual layer ($0.031 \text{ g} \cdot \text{cm}^{-2}$).
M_L	The depth of mixed sediments ($4.36 \text{ g} \cdot \text{cm}^{-2}$).
n	Index value for the number of years since the start of mixing
L	Layer number of the deepest mixed layer in year n (141).
F	The annual flux of ^{210}Pb to the sediment surface ($0.884 \text{ pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$).
R	The sediment accumulation rate ($0.031 \text{ g} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$).
Q	A constant equal to $m \sum_{i=1}^L e^{-\beta M_i}$ ($3.46 \text{ g} \cdot \text{cm}^{-2}$)
Variables	Description
$A_{L,n}$	The ^{210}Pb content of the mixed layer in year n ($\text{pCi} \cdot \text{cm}^{-2}$)
$C_{i,n}$	The concentration of ^{210}Pb in layer i in year n ($\text{pCi} \cdot \text{g}^{-1}$).
M_i	The cumulative mass of sediments for layer i in year n ($\text{g} \cdot \text{cm}^{-2}$).
K_n	Ratio $A_{L,n} / Q$ ($\text{pCi} \cdot \text{g}^{-1}$)

We selected from the several lakes that showed a flattening of the curves the unsupported ^{210}Pb sediment core data for Lake West Okoboji from Heathcote et al. [9] as an example. This lake was chosen because it has the longest record of water quality of any Iowa lake, and the field measurements overlap a period with paleolimnological inferences of sediment burial rates. We used data from the top 46 cm of the sediment core with 17 data points showing the activity of unsupported ^{210}Pb activity versus depth [9], as the deeper measurements were too close to the supported activities to give a reliable measurement. We plotted the natural logarithms of the unsupported ^{210}Pb activities against sediment depths as measured by the cumulative mass of sediments ($\text{g} \cdot \text{cm}^{-2}$) rather than linear depth. Cumulative mass removes concerns about lower sediment densities in the upper portions of the core [33]. Following the procedures of other investigators [32,34], we fitted a straight line (least squares) to the top 8 data points and another line to the bottom 9 data points, because the data supported the idea of a mixed layer overlying an unmixed layer of sediments (Table 1, Figure 2). The point where the two lines intersected was taken as the depth of sediment mixing (M_L in $\text{g} \cdot \text{cm}^{-2}$).

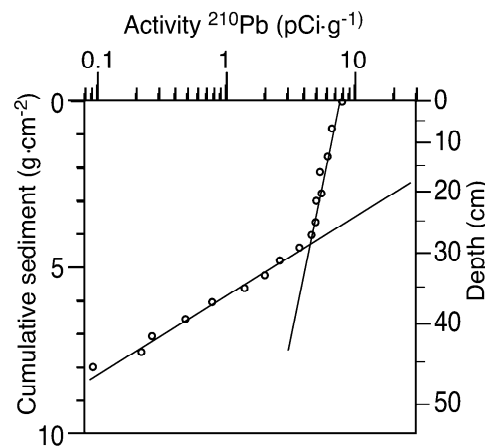


Figure 2. Semi-logarithmic plot of the unsupported ^{210}Pb activity (1 pCi = 0.037 Bq) versus cumulative sediment mass for Lake West Okoboji with least square fitted lines for the upper 8 and bottom 9 points. The intersection of the lines defines the depth of the mixed zone. Data points from Heathcote et al. [9].

Other investigators have interpreted the steep slope of the upper line as the result of a partial mixing of the upper zone that can be modeled as the result of an apparent diffusion process [32–34]. The slope of the upper line (α) is given by:

$$\alpha = \rho(\lambda/D_b)^{1/2} \quad (1)$$

where ρ is the sediment density (used because the depths were given as cumulative mass of sediments rather than as linear distance, cm) D_b is the apparent diffusion coefficient ($\text{cm}^2 \cdot \text{yr}^{-1}$), and λ is the decay constant for ^{210}Pb with a value of 0.03114 yr^{-1} [17]. From Equation (1), the value for the apparent diffusion coefficient is given by:

$$D_b = \rho^2 \lambda / \alpha^2 \quad (2)$$

According to others [17,32,34], the slope of the line below the mixed layer (β) is given by

$$\beta = \lambda / R \quad (3)$$

where R is the sediment accumulation rate ($\text{g} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$) for the region below the mixed zone. Equation (3) was rearranged to solve for the value of R .

$$R = \lambda / \beta \quad (4)$$

We used the data from the 17 points in the Lake West Okoboji profile in the spreadsheet of Binford [35] to calculate the total inventory of unsupported ^{210}Pb below the sediment surface (A_∞ as $\text{pCi} \cdot \text{cm}^{-2}$ where 1 pCi = 0.037 Bq). We calculated the annual flux of unsupported ^{210}Pb to the surface of the sediments using an equation from Oldfield and Appleby [17]:

$$F = \lambda A_\infty \quad (5)$$

where F is the annual flux of unsupported ^{210}Pb to the sediment surface ($\text{pCi} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$).

We used the values of R , F , D_b , α , β and other information from the Lake West Okoboji core (Table 1) to develop two models to calculate the activities of unsupported ^{210}Pb , the sediment ages, and sediment accumulation rates at different depths in the sediment core collected in the year 2009. The first model assumes a constant rate of sediment accumulation with no sediment mixing for the past 450 years. The second model also assumes a constant rate of sediment accumulation, but with sediment mixing starting 130 years before 2009 when the core was taken. The mixing depth (M_L),

the apparent diffusion constant (D_b), and upper slope (α) were kept constant during the 130-year period. For both models the final values for the activities of unsupported ^{210}Pb with depth were used to calculate sediment ages, and sediment accumulation rates at different depths. These were then compared with the values previously calculated by Heathcote et al. [9] for Lake West Okoboji on their assumption that the sediments were not mixed. The objective of the models was to test the hypothesis that the sediment accumulation rate in this lake has been constant for the past 130 years and that the apparent recent increases in sediment burial rates could be an artifact of sediment mixing.

We also analyzed the curves of unsupported ^{210}Pb versus cumulative sediment depths for lakes Center, East Okoboji, Lower Gar, Minnewashta, Silver (Dickinson), and Upper Gar to determine the sediment accumulation rate below the mixed layer (if present), the depth of the mixed layer and the number of years of sediment accumulation represented by the mass of sediments in the mixed layer. We chose to look at this sample of lakes, because they plus Lake West Okoboji were the lakes used by Heathcote et al. [3] to propose that the Iowa lakes were showing accelerated rates of carbon accumulation in recent decades.

3. Results

3.1. Limnological Measurements

For the 24 Iowa lakes with extended water quality data, there was little change in the trophic state variables in the period between 1972 and 2015 (Figure 3). Lake West Okoboji, with the most complete data set, showed no change in Secchi depths but decreases in chlorophyll and total phosphorus (Figure 4). Of the 72 tests of Secchi depths, total phosphorus, and chlorophyll with time, only 3 (Secchi depths only) of the 18 statistically significant tests indicated increased trophic states (Table 2, Figure S1). Of the 6 significant Secchi depth regressions only 3 lakes showed a decrease over time with 3 lakes showing increases in transparency. For both total phosphorus and chlorophyll, each variable had 6 lakes with significant changes, and in each of the 12 cases the slopes of the regressions were negative indicating a reduction in trophic state rather than eutrophication in the 1972–2015 period.

3.2. Paleolimnological Results

The calculated carbon burial rates in Lake West Okoboji as derived from ^{210}Pb -dated cores [9] showed exponentially increasing rates over time (Figure 4d). The same was true when examining a composite plot for 33 Iowa lakes (Figure 3d) and plots for the individual lakes (Figure S1). The calculated geometric mean carbon burial rate for the 33 lakes increased from $0.043 \text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ to $0.136 \text{ kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, an increase of 217% from 1905 to 2005. The calculated burial rates for dry sediments for the 33 lakes also showed the same exponentially increasing pattern (Figure 5d).

The plots of Secchi depths, total phosphorus, and chlorophyll versus time for the period after 1972 did not match the plots for carbon burial in the same time period (Figures 3, 4 and S1). While the calculated rates of carbon burial showed strong increases, algal chlorophylls and total phosphorus stayed the same or declined. Secchi depths mostly stayed the same.

3.3. Independent Estimates of Soil Erosion Rates in Iowa

The sediment loads in the Raccoon River also did not match the calculated increases in the rates of lake sedimentation of materials on a dry weight basis (Figure 5). As Jones and Schilling [20] pointed out, the concentrations of total suspended solids in the river peaked in the late 1920s and except for a peak in the 1970s continued to decline through the decade 2000–2010. The average volume of flow, however, increased in the same time period with the result that the sediment load, a product of suspended sediment concentration times flow, peaked in the 1970s and then showed a steady decrease through the decade 2000–2010. Hence a discrepancy because the calculated lake sedimentation is highest in the decade 2000–2010, while sediment transport down the Raccoon River is at its lowest.

Estimated annual sheet and rill erosion rates on rural lands in Iowa during 1977 to 2012 (Table 3) also did not match the increased rates of erosion inferred from the paleolimnological study of Heathcote et al. [10]. The soil erosion estimates were highest in 1977, but had declined 40% by 2012. This was true for cultivated cropland, all cropland, and pastureland.

Table 2. Results of regressions of Secchi depths, chlorophylls, and total phosphorus versus time for 24 Iowa lakes as indicated by direction of relation (+ or −), R^2 -value, and probability. NS indicates not statistically significant with $p < 0.05$.

Lake	Secchi Depth	Chlorophyll	Total Phosphorus
Big Spirit	NS	NS	NS
Black Hawk	$+R^2 = 0.25 \ p = 0.04$	$-R^2 = 0.27 \ p = 0.03$	NS
Center	NS	NS	NS
Clear	NS	$-R^2 = 0.58 \ p < 0.001$	$-R^2 = 0.65 \ p = 0.001$
Cornelia	NS	NS	$-R^2 = 0.46 \ p = 0.003$
Crystal	NS	NS	NS
East Okoboji	NS	$-R^2 = 0.30 \ p = 0.009$	NS
Five Island	$-R^2 = 0.39 \ p = 0.008$	NS	$-R^2 = 0.29 \ p = 0.03$
Ingham	$-R^2 = 0.45 \ p = 0.003$	NS	NS
Iowa	NS	NS	NS
Little Spirit	NS	NS	NS
Little Wall	$-R^2 = 0.59 \ p = 0.003$	NS	NS
Lost Island	NS	$-R^2 = 0.27 \ p = 0.03$	NS
Lower Gar	NS	NS	NS
Minnewashta	NS	NS	$-R^2 = 0.45 \ p < 0.001$
North Twin	NS	NS	NS
Silver (Dickinson)	NS	NS	NS
Silver (Palo Alto)	NS	NS	NS
Silver (Worth)	NS	NS	NS
Storm	NS	$-R^2 = 0.34 \ p = 0.014$	NS
Trumbull	NS	NS	NS
Tuttle	NS	NS	NS
Upper Gar	$+R^2 = 0.31 \ p = 0.008$	$-R^2 = 0.40 \ p = 0.003$	$-R^2 = 0.38 \ p = 0.003$
West Okoboji	$+R^2 = 0.22 \ p = 0.009$	NS	$-R^2 = 0.36 \ p = 0.021$

3.4. Diatom-Inferred Concentrations of Total Phosphorus

Heathcote et al. [11] dismissed the results of their diatom-inferred total phosphorus concentrations because of literature reports of poor results in shallow lakes and because of bias for low and high TP concentrations in their calibration curve. The inferred concentrations did not comport with their other estimates of change in the lakes. We found the precision and accuracy of the transfer functions used by Heathcote et al. [9] were similar to those used in other regional paleolimnological studies (Table 4). While the bootstrapped root mean squared error of predication of 0.30 log units was greater than that used in a study of Minnesota lakes of 0.25 log units [36], it was smaller than that (0.34 log units) for the transfer functions used in a study of the lakes of the northeastern United States [37] and the natural lakes (0.36 log units) of the United States in the National Lakes Assessment of 2007 [38]. We used the Heathcote et al. [11] results in part because Saulnier-Talbot [39] noted that while there are problems with diatom transfer functions, great strides have been made using this approach and that their use at present can hardly be discarded. In this case of the Iowa lakes, diatom-inferred concentrations of total phosphorus from the sediment cores provided the only quantitative estimate of the magnitude of lake productivity change.

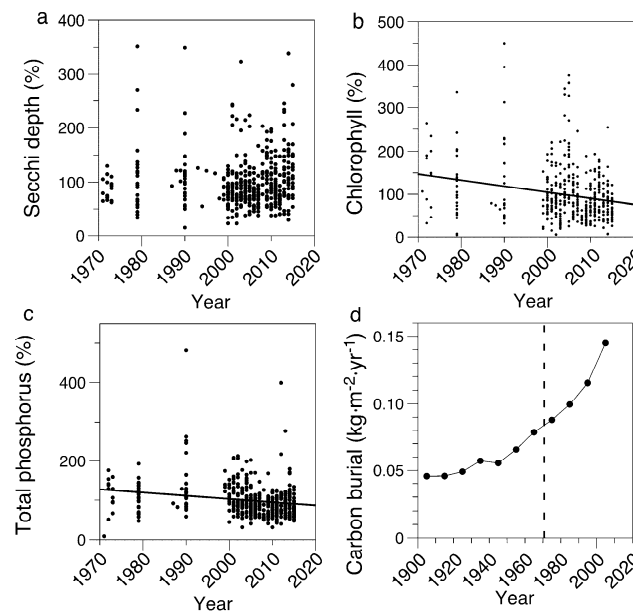


Figure 3. Composite plot of Secchi disk depths for the 24 Iowa lakes with field measurements expressed as per cents of the lake average versus year of sampling (a). The same kind of plots showing statistically significant slopes of chlorophyll ((b) $R^2 = 0.05$, $p < 0.0001$) and total phosphorus ((c) $R^2 = 0.05$, $p < 0.0001$) Decadal geometric averages for rates of carbon burial based on ²¹⁰Pb dating of sediment cores from 33 Iowa lakes using data from Heathcote et al. [11] (d). The vertical dashed line indicates the year 1971 to identify the period with field measurements.

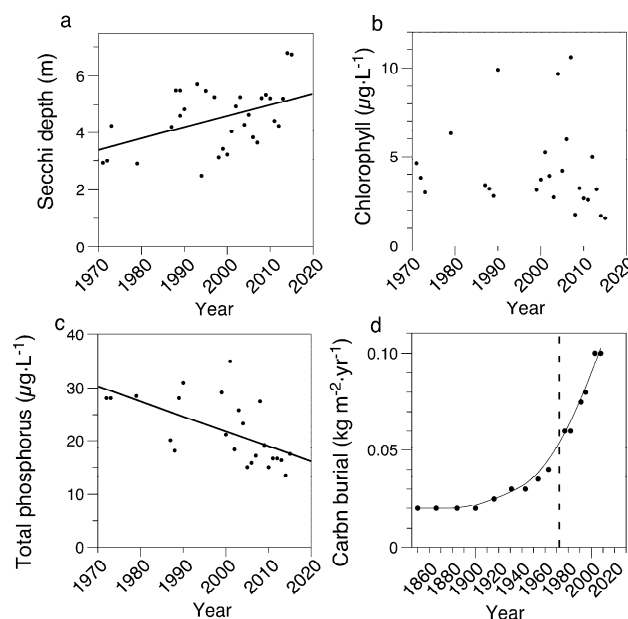


Figure 4. Plots of summer average measurements of Secchi disk depth ((a) $R^2 = 0.22$, $p = 0.009$) chlorophyll (b), and total phosphorus ((c) $R^2 = 0.33$, $p = 0.002$) for the period from 1971 to 2015 in Lake West Okoboji. Lines are shown for statistically significant regressions. Rates of carbon burial based on ²¹⁰Pb dating of sediment cores from Lake West Okoboji using data from Heathcote et al. [11] for the period 1850–2008 (d). The vertical dashed line indicates the year 1971 to identify the period with the field measurements.

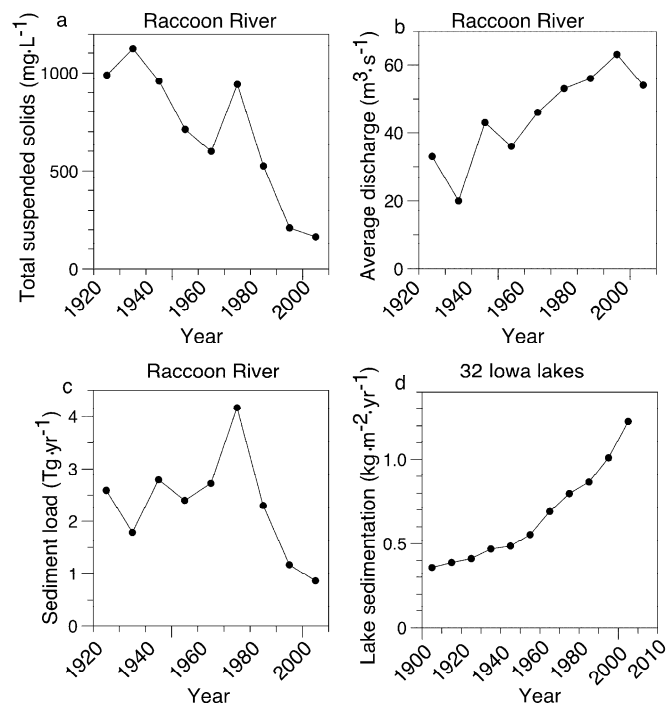


Figure 5. Decadal averages for total suspended solids (a), discharge (b) and sediment loads (c) (1 Tg = 10^{12} grams) from 1916 to 2009 in the Raccoon River, Iowa. Data are from Jones and Schilling [20]. Decadal geometric means for lake dry sediment accumulation rates (d) based on ^{210}Pb dating of sediment cores from 33 Iowa lakes using data from Heathcote et al. [11].

Table 3. Estimated annual sheet and rill erosion ($\text{kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) on non-federal rural land in Iowa. Data from United State Department of Agriculture [21] and recalculated from English units.

Year	Cultivated Cropland	All Cropland	Pastureland
1977	2.29	2.22	0.63
1982	1.84	1.79	0.36
1987	1.57	1.52	0.38
1992	1.35	1.30	0.36
1997	1.17	1.14	0.34
2002	1.30	1.26	0.34
2007	1.32	1.28	0.29
2012	1.37	1.32	0.29

Table 4. Performance metrics (R^2_{boot} and $\text{RMSEP}_{\text{boot}}$) for transfer functions used to predict total phosphorus from diatom species composition from several regional studies.

Lake Region	R^2_{boot}	$\text{RMSEP}_{\text{boot}}$	Reference
Minnesota lakes	0.68	0.25	[36]
Iowa lakes	0.61	0.30	[9]
Northeastern US lakes	0.59	0.34	[37]
United States lakes	0.67	0.36	[38]

The average and standard error for the diatom-inferred concentration of total phosphorus at the bottoms of the 33 cores were $98.9 \pm 5.4 \mu\text{g}\cdot\text{L}^{-1}$, while at the tops of the cores were $123.3 \pm 4.3 \mu\text{g}\cdot\text{L}^{-1}$. From this phosphorus information, the Iowa lakes would be classified as eutrophic to hypereutrophic at a predisturbance period and at the present time (Figure 6a). The difference between inferred values at the bottom and top of the sediment cores was statistically significant ($p < 0.001$), but this group of Iowa

lakes only showed a 25% increase of total phosphorus concentration since the 1800s. An alternative comparison for the 24 lakes with field measurements showed that the average diatom-inferred total phosphorus concentration at the bottoms of the cores was $95.3 \pm 13.9 \mu\text{g}\cdot\text{L}^{-1}$ and that the measured concentration in the lake water was $126.8 \pm 6.5 \mu\text{g}\cdot\text{L}^{-1}$ (Figure 3b). This difference was also significant ($p = 0.049$), but indicated the increase in total phosphorus following European settlement was approximately 33%.

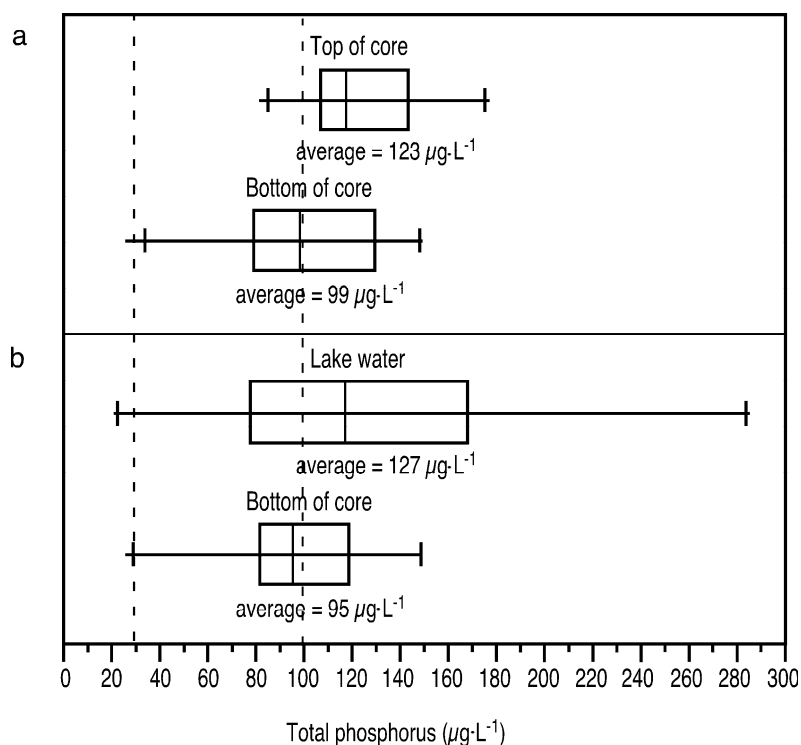


Figure 6. (a) Box plots (minimum, 5%, 25%, median, 75%, 95%, maximum) of diatom-inferred total phosphorus concentrations at the tops and bottoms of sediment cores from 33 Iowa lakes as reported by Heathcote et al. [9]; (b) Box plots for 22 lakes with diatom-inferred concentrations of total phosphorus at the bottoms of cores and average measured concentrations of total phosphorus in the lake waters for 2000–2010. Left dashed line shows the boundary between mesotrophic and eutrophic lakes ($30 \mu\text{g}\cdot\text{L}^{-1}$) and the right dashed line shows the boundary between eutrophic and hypereutrophic lakes. ($100 \mu\text{g}\cdot\text{L}^{-1}$).

3.5. Sediment Organic Matter and Chlorophyll Concentrations

The organic matter content of the sediments in the 24 lakes with chlorophyll data ranged from 6% to 60% and the chlorophyll concentrations ranged from 5 to $113 \mu\text{g}\cdot\text{L}^{-1}$ in the period 2000 to 2010. There was no correlation between the chlorophyll concentrations and the organic matter content ($r = 0.01$, $p = 0.95$, $n = 23$). The lakes with the highest chlorophyll concentrations also were not necessarily the ones with the highest concentrations of organic matter in their sediments.

3.6. Mixing Models

The mixed layer in the Lake West Okoboji sediments extended to a depth of 29 cm or $4.36 \text{ g}\cdot\text{cm}^{-2}$ of accumulated sediment (Table 1, Figure 2). The sedimentation rate (R) below the mixed layer was $0.031 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$, so the mass of sediments in an annual layer with a constant sedimentation rate would be $0.031 \text{ g}\cdot\text{cm}^{-2}$ (Table 1). At this sedimentation rate, it would take about 141 years to accumulate the sediments in the mixed layer.

The results of the model with no mixing (Figure 7a–c) were consistent with the model input (Table 1). There was a linear relationship between the log of unsupported ^{210}Pb concentrations vs. cumulative sediments, the calculated sedimentation rates were a constant $0.031 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ at all depths, and the calculated ages changed linearly with cumulative sediment mass. These results provided a validation for our model and procedures for calculating sedimentation rates and ages at different depths.

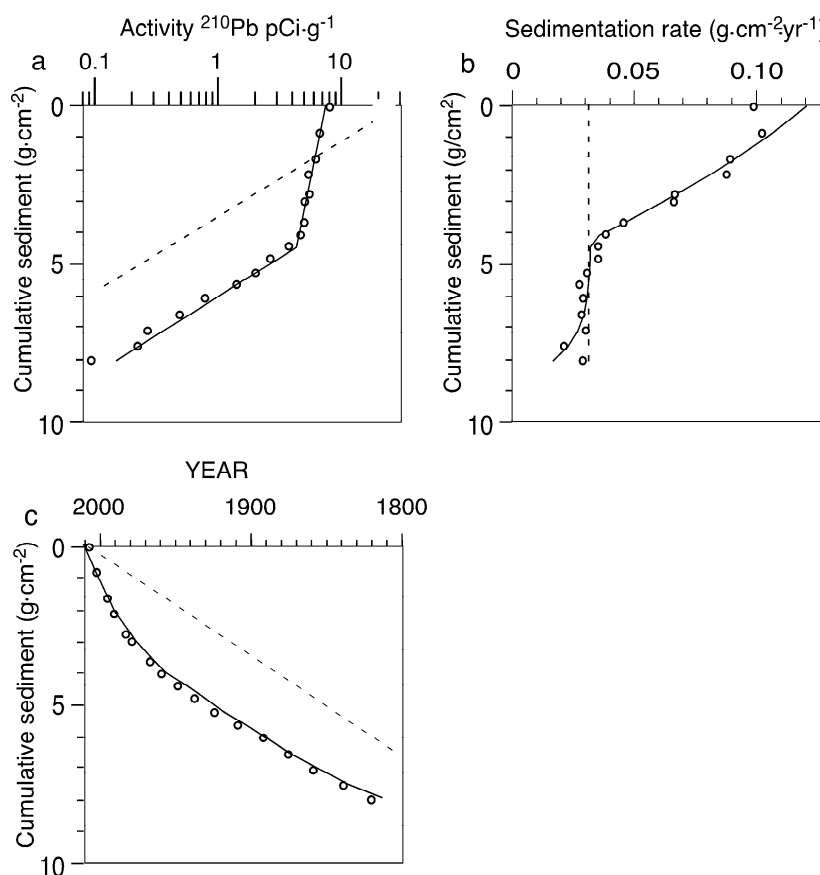


Figure 7. For each figure open circles represent original data for Lake West Okoboji [9]. Solid lines represent modeled values assuming sediment mixing. Dashed lines represent modeled values assuming no sediment mixing. (a) Unsupported activity of ^{210}Pb versus cumulative mass of sediments from the surface. (b) Calculated sedimentation rates versus cumulative mass of sediments from the surface. (c) Calculated years versus cumulative mass of sediments from the surface.

The modeled results for a constant rate of sedimentation since the 1870s with sediment mixing showed a good agreement with the values for unsupported ^{210}Pb concentrations, calculated sedimentation rates, and calculated sediment ages as presented by the inferences of Heathcote et al. [9] (Figure 7). The model with sediment mixing produced a near vertical profile of unsupported ^{210}Pb concentrations in the upper portion of the core that was very similar to that found in the original core (Figure 7a). There was a strong correlation between the modeled values for $\log^{210}\text{Pb}$ and measured values for $\log^{210}\text{Pb}$ at the same depths ($R^2 = 0.99$). Likewise the modeled values for sedimentation rates and calculated sedimentation rates ($R^2 = 0.96$) and modeled years versus calculated years ($R^2 = 0.99$) showed strong agreement. The models showed that sediment mixing has the effect of moving ^{210}Pb deeper into the sediments than it would move with no mixing (Figure 7a). The effect of this is to underestimate the age of the sediments at different depths (Figure 7c). The mixing also resulted in the calculation of artificially high values for sedimentation rates at the top of the core (Figure 7b).

For our sample of 7 lakes we found that 6 of them showed a flattening of the ^{210}Pb curves that could indicate sediment mixing (Figure 8). The mixing depths ranged from 13 cm to 29 cm and the sediment accumulation rates from $0.02 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ to $0.24 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ (Table 5). The profile of Lake Minnewashta did not show a flattening like the other lakes; however, because of its high rates of sedimentation there were few data points in the top portion of the curve.

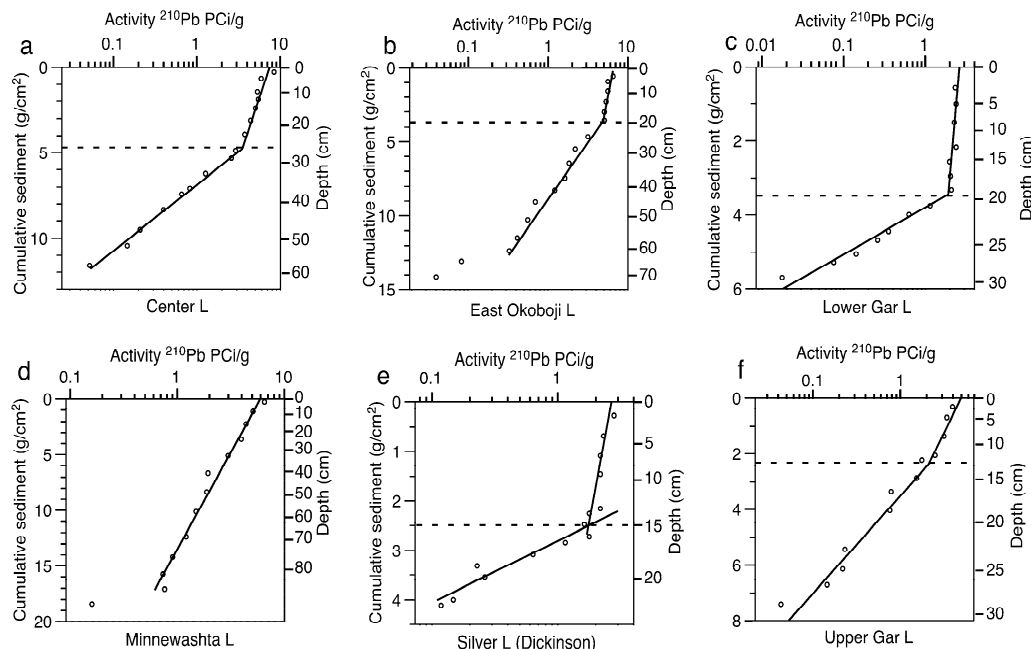


Figure 8. Semi-logarithmic plots of the unsupported ^{210}Pb activity versus cumulative sediment mass for Center Lake (a), East Okoboji Lake (b), Lower Gar Lake (c), Minnewashta Lake (d), Silver Lake (Dickinson) (e), and Upper Gar Lake (f). The dashed lines indicate the depths of the proposed mixed layers of sediments.

Table 5. Sediment accumulation rate, depth of the mixed layer as a cumulative sum and in cm, and the number of years of sediment accumulation represented in the mixed layer. Lake Minnewashta did not show a mixed layer.

Lake	Sediment Accumulation Rate ($\text{g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$)	Mixed Layer Depth ($\text{g}\cdot\text{cm}^{-2}$)	Mixed Layer Depth (cm)	Years of Sediment in Mixed Layer
Center	0.05	4.87	26	91
East Okoboji	0.10	2.97	18	28
Lower Gar	0.02	3.52	20	222
Minnewashta	0.24	NA	NA	NA
Silver (Dickinson)	0.02	2.50	15	142
Upper Gar	0.05	2.26	13	48
West Okoboji	0.03	4.36	29	141

4. Discussion

4.1. Field Measurements Versus Paleolimnological Inferences

Our analyses of field measurements on Iowa lakes starting in 1972 do not support the conclusions from the paleolimnological studies that there has been eutrophication with an exponential increase in the burial of inorganic and organic materials [10]. If there were increased loads of eroded soil particles to the Iowa lakes, there should have been decreases in Secchi depths. That was not the case for individual lakes or the population averages. If there were significant increases in the loadings

of phosphorus, there should have been increases in total phosphorus concentrations and increases in chlorophyll concentrations. Neither total phosphorus nor chlorophyll concentrations increased since 1972, thus the reported field measurements provide no evidence for massive eutrophication in the Iowa lakes during the period 1972 to 2015. Other studies based on field measurements also do not support the paleolimnological inferences of increased eutrophication of Iowa waters in recent decades. Wang et al. [40] studied records of total phosphorus concentrations in 40 Iowa rivers between 1999 and 2013 and found that total phosphorus concentrations were decreasing at a rate of 2.6% per year. Lottig et al. [41] examined water clarity records from 8 states in the Upper Midwest including Iowa in the period between 1938 and 2012 and found for the entire population of lakes Secchi depths were increasing at 1% per year. On an individual lakes basis 7% of the lakes showed increased water clarity and 4% showed decreased water clarity. Oliver et al. [42] examined lake nutrient and chlorophyll trends for lakes in the period 1990 to 2013 in 17 states of the Midwest and northeast United States including Iowa, and for the population of lakes as a whole the only significant trend was a reduction in total nitrogen at a rate of 1.1% per year while total phosphorus and chlorophyll did not change.

Heathcote et al. [10] used the results of their paleolimnological study of sediment burial rates in Iowa lakes to conclude that the rates of soil erosion in Iowa were on an upward trend with their highest value in 2005. They concluded this represented a failure of soil conservation programs in Iowa. In contrast, we found no agreement between paleolimnological estimates of sediment burial for Iowa lakes in the period 1916–2009 and field measurements of sediment loading in the Racoon River (based on daily measurements) for the same time period (Figure 5). Total suspended solids concentrations in the river were much greater in the early 20th century and declined to their lowest values by 2005. Water discharges increased during this period and sediment loads increased to a peak in the early 1970s followed by declines in sediment loads with the lowest value found in 2005. These measurements in the Racoon River do not support the paleolimnological inferences from lake sediments. Likewise the estimated soil erosion rates from croplands and pasturelands in Iowa as calculated by the United States Department of Agriculture [21] showed a decline of 40% from 1977 to 2012 (Table 3). These data also do not support the idea of a failure of soil conservation programs in Iowa.

4.2. Problems with Sediment Dating

The lack of agreement between paleolimnological inferences about conditions in the Iowa lakes and field measurements in the period 1972–2009 is probably due, in our opinion, to errors in sediment dating that have the effect of artificially increasing the calculated burial rates at the top levels of sediment cores. These errors originate because mixing of the sediments breaks down the original sediment layers. Appleby and Oldfield [13] in their early paper on the use of ^{210}Pb to date lake sediments stated that an important assumption was that there was no significant mixing within the sediment column. Oldfield and Appleby [17], therefore, recommended the use of independent methods of age determination for as many points in the profile as possible. Other paleolimnologists have repeated this warning over the years [31,43]. We demonstrated in our ^{210}Pb model using a constant sedimentation rate for a system that mixing of the upper few centimeters of the sediment surface results in a false indication of exponentially increasing sediment burial in recent years.

Sediment mixing results from sediment disturbance and resuspension due to wind-driven waves in shallow lakes [14], the activities of benthic macrobenthos [15], and the activities of bottom feeding fish [16]. Conditions at the sediment core locations in the Iowa lakes were favorable for bioturbation. We note that, with the exception of Lake West Okoboji (maximum depth 42 m), the rest of the natural lakes in Iowa are shallow, and all of these lakes studied have a layer of flocculent sediments. The core in West Okoboji was not taken at the deepest point where there is an anoxic summer hypolimnion, but at the mouth of a bay at a depth of 9.8 m. In the early summer the core location lies in the metalimnion, but the epilimnion thickens in about July and descends below the sampling depth so that the sediments are always oxic [24]. The fish fauna of Iowa lakes includes several native benthivorous fish [44] and

the European carp (*Cyprinus carpio*) that was introduced in about 1870 and widely distributed in the Iowa lakes [45]. This fish is known to disturb bottom sediments and increase the turbidity of Iowa lakes [29,46]. Their mouth morphology is designed to burrow into and suction up soft bottom sediments. Within the mouth the branchial sieve filters out the benthic organisms, and the remaining sediments are spit out into the surrounding water [47]. A recent study on a shallow, eutrophic lake in Minnesota, about 200 km north of the state of Iowa followed the vertical distribution of aluminum salts applied to the surface of the sediments and found that European carp mixed the surface sediments to depths from 13.5 to 16 cm in a 5-month period [16]. It is therefore likely that benthic invertebrates and fish such as European carp are mixing the surface sediments in the Iowa lakes and leading to a misinterpretation of the sedimentation rates in the Iowa lakes.

In the case of the core from Lake West Okoboji, the mixed zone encompassed $4.36 \text{ g}\cdot\text{cm}^{-2}$ of dry sediment or about 29 cm (Table 1, Figure 2). With a dry sedimentation rate of $0.031 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$, that indicates that the mixed layer includes about 141 years of sediment. This does not mean that mixing started 141 years ago, just that the mixed zone encompasses a mass of sediments that would have accumulated in 141 years with a constant rate of sedimentation. Others have shown that it is not possible to apply ^{210}Pb dating techniques to sediments in a mixed zone; however, sediments below that zone can be used to measure long-term sedimentation rates [17]. If the sediments below the current mixed zone were deposited during a period of mixing, it may not be possible to use ^{210}Pb dating to determine the sediment ages in that zone. There are several implications of this finding for the previous paleolimnological studies of the Iowa lakes. Without the ability to date the sediments in the mixed zone, it is not possible to calculate the burial rates of dry sediments in these lakes, so the inferred burial rates cannot be used to estimate soil erosion rates in Iowa over the past century. Likewise it is not possible to estimate the burial rates of organic carbon over the past century, so it is not possible to determine if those rates have been increasing due to either eutrophication or soil erosion. Without the ability to estimate sediment burial rates, it is therefore not possible to estimate the burial rates of biosilica, so this value cannot be used to infer increasing biological productivity in the Iowa lakes. Lastly, it is not possible to use a regression of the burial rates of organic carbon versus magnetic remembrance measurements to find the fraction of organic carbon that is produced within the lakes as opposed to allochthonous sources [9], because we do not have an accurate measurement of the burial rates of organic carbon.

4.3. Estimate of Extent of Eutrophication

Our original question concerned the trophic state of Iowa lakes prior to European settlement and how much these lakes have changed since then. We demonstrated that we could not use ^{210}Pb dating of the sediments, inferred burial rates of organic carbon or biosilica to answer questions about lake productivity because of sediment mixing. The analysis of the species and abundance of the diatoms from the sediment cores by Heathcote et al. [11] remains as the best evidence to answer our question. Their results indicated that at least some of the lakes were highly productive prior to European settlement. They found that in 4 of the lakes (Morse, Pickerel, Silver in Palo Alto Co., and West Swan) there were low or no floristic changes between historic and modern diatom communities. All 4 lakes currently are hypereutrophic with total phosphorus concentrations ranging from $158 \mu\text{g}\cdot\text{L}^{-1}$ to $298 \mu\text{g}\cdot\text{L}^{-1}$. We can conclude that these 4 lakes were naturally hypereutrophic prior to European settlement, because the diatom species composition did not change over time.

The results of the diatom-inferred concentrations of total phosphorus from the pre-settlement portion of the cores indicated that 1 lake was mesotrophic, 13 lakes were eutrophic, and 15 were hypereutrophic prior to European settlement (Figure 6). The modern concentrations based on diatoms from the surface of the cores indicated that 4 of these lakes are currently eutrophic and 29 are hypereutrophic, and that the total phosphorus concentrations have increased by 25% (Figure 6). Because it is possible that sediment mixing could have biased the diatom species composition from the tops of the cores by including older diatoms from deeper in the cores, we compared

diatom-inferred concentrations from the bottoms of the cores with recent measured total phosphorus concentrations in the lake waters. This showed an increase in total phosphorus of 33% (Figure 6). The diatom-inferred increases in total phosphorus in the Iowa lakes are also comparable to those found by Ramstack et al. [36] for lakes in agricultural areas of Minnesota. These authors examined sediment cores for 5 lakes in the Western Corn Belt Plains ecoregion and 9 in North Central Hardwood Forests ecoregion and found that diatom-inferred TP concentrations increased from an average of 35 $\mu\text{g/L}$ in 1800 to 43 $\mu\text{g/L}$ in 1995 for an increase of 23%. The Iowa and Minnesota data would therefore indicate that eutrophication in the natural Iowa lakes is only on the order to 25% to 35% as opposed to the increase in carbon burial rates of 217% from 1905 to 2005 calculated from the data of Heathcote et al. [9]. This is a significant finding, because these lakes are located in a region with intensive row crop agriculture

On the other hand, if sediment mixing has been consistent for several hundred years, the diatoms from the lower portion of the cores may represent a mixture of diatoms that accumulated for a long period of time before settlement and may not yield an accurate picture of trophic state in the mid 1800s. The other evidence indicates they were eutrophic to hypereutrophic but not how much they have changed.

5. Conclusions

This study raises the possibility that sediment mixing in Iowa lakes and similar shallow, eutrophic lakes with benthivorous fish may cause significant sediment mixing that can compromise dating using ^{210}Pb dating of sediment cores. Field measurements of water quality in several Iowa lakes from 1972 to 2010 failed to validate paleolimnological inferences based on ^{210}Pb dating of sediment cores from some of the same lakes that had indicated exponentially increasing rates of eutrophication and sedimentation in recent decades. Independent estimates of soil erosion from agricultural watersheds in Iowa also did not agree with paleolimnological inferences of increasing rates of soil erosion in recent decades.

We found that a likely cause for the discrepancy was sediment mixing by benthivorous fish like the European carp that moved ^{210}Pb downwards in the sediments leading to errors in calculated ages at different depths in the sediments. This conclusion was based on a sediment-mixing model that demonstrated the effects of sediment mixing on the vertical distribution of ^{210}Pb in lake sediments and its effect on calculated ages of sediment layers. A recent study of the depths of sediment mixing by European carp in a Minnesota lake indicted that the depth of the mixed layer could be much greater than previously shown for freshwater lakes.

Based on diatom-inferred total phosphorus concentrations of Heathcote et al. [9,11] the Iowa lakes sampled were highly productive prior to European settlement with about half of the sample lakes in the hypereutrophic category. These lakes have not shown order of magnitude increases in nutrients due to intensive row crop agriculture, for the data showed that by 2010 total phosphorus concentrations in the Iowa lakes had only increased by 25% to 35% since European settlement.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3263/8/2/40/s1>, Figure S1: Plots of summer measurements of Secchi depths, chlorophyll, and total phosphorus from 1972 to 2015 in each of 23 Iowa lakes. Model Spreadsheet: Excel spreadsheet modeling the effects of sediment mixing on the vertical distribution of ^{210}Pb in Lake West Okoboji.

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Author Contributions: Roger W. Bachmann, Mark V. Hoyer, and Daniel E. Canfield, Jr. jointly conceived of the study. Mark V. Hoyer and Daniel E. Canfield, Jr. conducted some of the initial field sampling and laboratory analyses. Roger W. Bachmann conducted the statistical analyses and wrote the first draft with Mark V. Hoyer and

Daniel E. Canfield, Jr. contributing to subsequent rewritings and revisions. All three authors have reviewed and approved the final manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

The two models used to simulate the vertical distribution of unsupported ^{210}Pb with and without sediment mixing are in an Excel spreadsheet (.xls) with 461 rows and 136 columns. The entire spreadsheet is in a supplemental file for this paper. For convenience in this explanation images of portions of the spreadsheet are presented as Figures A1 and A2.

◇	A	B	C	D	E	F
	$Q = m \sum_{i=1,n}^L e^{-\alpha M_i}$			Total ^{210}Pb in mixed layer pCi-cm $^{-2}$	Total ^{210}Pb in mixed layer pCi-cm $^{-2}$	Total ^{210}Pb in mixed layer pCi-cm $^{-2}$
1						
2	3.34588422			28.4661756	28.4661796	28.3305487
3				Year	Year	Year
4				0	1	2
5					k_n	k_n
6		M_i		No mixing	8.51	8.47
7	$e^{-\alpha M_i}$	cum sum g-cm $^{-2}$	Layer number	Conc ^{210}Pb in layer pCi-g $^{-1}$	Conc ^{210}Pb in layer pCi-g $^{-1}$	Conc ^{210}Pb in layer pCi-g $^{-1}$
8	0.99606240	0.031	1	28.516	8.474	8.434
9	0.99214030	0.062	2	27.641	8.441	8.401
10	0.98823365	0.093	3	26.794	8.408	8.368
11	0.98434238	0.124	4	25.972	8.375	8.335
12	0.98046643	0.155	5	25.175	8.342	8.302
146	0.57786965	4.295	139	0.387	4.916	4.893
147	0.57559423	4.326	140	0.376	4.897	4.874
148	0.57332777	4.357	141	0.364	4.878	4.855
149		4.388	142	0.353	0.353	4.728
150		4.419	143	0.342	0.342	0.342
151		4.450	144	0.332	0.332	0.332
152		4.480	145	0.321	0.321	0.321
455		13.843	448	0.000	0.000	0.000
456		13.874	449	0.000	0.000	0.000
457		13.905	450	0.000	0.000	0.000
458						
459						
460	Check sum rows 4 to 457			929.77	929.77	929.77
461	(Should remain constant over years)					

Figure A1. Portions of the Excel spreadsheet for the first 6 columns.

Rows 8 through 457 represent conditions in 450 annual layers of sediment that are numbered sequentially from the surface (i) in Column C. The symbols are defined in Table 1 and the values for the constants are derived from the Lake West Okoboji sediment core obtained by Heathcote et al. [9]. Because the sediment accumulation rate (R) is assumed to be constant over time, for each layer in each year the mass of sediments (m) is a constant (g-cm $^{-2}$) and is equal to R times 1 year. The cumulative mass of sediments for any layer (i) for any year is given by:

$$M_i = i \cdot m \quad (\text{A1})$$

values for M_i are given in Column B and represent the mass of dry sediment in that layer plus the sum of the masses of the sediments in the layers above it. Because the sediment accumulation rate is assumed to be constant, the values for M_i for any row i will be the same for all years in columns D through DF.

The cells in columns D through EF in rows 8 through 457 contain unsupported ^{210}Pb concentrations ($\text{pCi}\cdot\text{g}^{-1}$). A matrix notation with subscripts is used for each cell, so $C_{i,n}$ is the concentration of unsupported ^{210}Pb in row i in year n where the years are numbered starting in the first year of sediment mixing. For example $C_{3,6}$, would represent the unsupported ^{210}Pb concentration ($\text{pCi}\cdot\text{g}^{-1}$) in the third layer from the sediment surface and in the sixth year since the initiation of sediment mixing.

◇	EB	EC	ED	EE	EF
	Total ^{210}Pb in mixed layer $\text{pCi}\cdot\text{cm}^{-2}$	Total ^{210}Pb in mixed layer $\text{pCi}\cdot\text{cm}^{-2}$	Total ^{210}Pb in mixed layer $\text{pCi}\cdot\text{cm}^{-2}$	Total ^{210}Pb in mixed layer $\text{pCi}\cdot\text{cm}^{-2}$	Total ^{210}Pb in mixed layer $\text{pCi}\cdot\text{cm}^{-2}$
1	24.7164639	24.7151442	24.7138717	24.7126448	24.7114618
2	Year	Year	Year	Year	Year
3	128	129	130	131	132
4	k_n	k_n	k_n	k_n	k_n
5	7.39	7.39	7.39	7.39	7.39
6	Conc ^{210}Pb in layer $\text{pCi}\cdot\text{g}^{-1}$	Conc ^{210}Pb in layer $\text{pCi}\cdot\text{g}^{-1}$	Conc ^{210}Pb in layer $\text{pCi}\cdot\text{g}^{-1}$	Conc ^{210}Pb in layer $\text{pCi}\cdot\text{g}^{-1}$	Conc ^{210}Pb in layer $\text{pCi}\cdot\text{g}^{-1}$
7	7.358	7.358	7.357	7.357	7.357
8	7.329	7.329	7.328	7.328	7.328
9	7.300	7.300	7.299	7.299	7.299
10	7.271	7.271	7.271	7.270	7.270
11	7.243	7.242	7.242	7.242	7.241
12					

146	4.269	4.269	4.268	4.268	4.268
147	4.252	4.252	4.252	4.251	4.251
148	4.235	4.235	4.235	4.235	4.234
149	4.106	4.105	4.105	4.105	4.105
150	3.980	3.980	3.979	3.979	3.979
151	3.858	3.858	3.858	3.857	3.857
152	3.740	3.740	3.740	3.739	3.739

455	0.000	0.000	0.000	0.000	0.000
456	0.000	0.000	0.000	0.000	0.000
457	0.000	0.000	0.000	0.000	0.000
458					
459					
460	929.77	929.77	929.77	929.77	929.77
461					

Figure A2. Portions of the Excel spreadsheet for the last 5 columns.

Column D ($n = 0$) is the initial condition for the model prior to the initiation of sediment mixing where the unsupported ^{210}Pb flux and sedimentation rates have been constant for a long period of time. The concentration of ^{210}Pb in the top layer initially is given as

$$C_{1,0} = F/R = F/m \quad (\text{A2})$$

where F is the annual flux of unsupported ^{210}Pb to the sediment surface ($\text{pCi}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$).

Because we assume constant rates of both sediment accumulation and unsupported ^{210}Pb flux for a long period of time, the concentration of unsupported ^{210}Pb in the next layer down will be reduced by radioactive decay so

$$C_{i+1,0} = C_{i,0}e^{-\lambda} \quad (\text{A3})$$

where λ is the decay constant for unsupported ^{210}Pb (yr^{-1}).

This becomes

$$C_{i+1,0} = 0.96933C_{i,0} \quad (\text{A4})$$

From Equation (A4) the activity in any layer in Column D ($n = 0$) is found by multiplying the activity in the above layer by 0.96933. Starting with the initial activity in the top layer, we did this to find the unsupported ^{210}Pb activities for the underlying 449 layers. This process yields the expected distribution of unsupported ^{210}Pb activities with depth for a system with constant sedimentation rates and no mixing.

The mixing model starts in Column E ($n = 1$) on the assumptions that the sediment mixing starts in the mid 1870s. We use the vertical distribution of unsupported ^{210}Pb in the first column as the starting point for the second model. Sediment mixing is initiated and extends to the previously determined mixing depth M_L . The number of layers involved (L) would be equal to the integer value for M_L/R , which in this example is 141. Since sediment mixing is involved, the layers no longer represent the annual layers but each contains the mass of sediment that accumulates each year (m). Going from one year to the next the ^{210}Pb content of the sediments is reduced by radioactive decay and increased by the flux of new ^{210}Pb that is added at the surface along with a new layer of sediment. The lowest of the mixed layers is no longer being mixed in the next or future years. The total amount of unsupported ^{210}Pb in the new mixed layer in year n will be given by

$$A_{L,n} = F + 0.96933m \sum_{i=1}^{L-1} C_{i,n-1} \quad (\text{A5})$$

where $A_{L,n}$ is the ^{210}Pb content of the mixed layer in year n ($\text{pCi}\cdot\text{cm}^{-2}$)

We will assume that in the mixed zone the same diffusion driven gradient in unsupported ^{210}Pb concentrations will be in effect. The distribution of unsupported ^{210}Pb in the range of i from 1 to 141 is given by:

$$C_{i,n} = k_n e^{-\alpha M_i} \quad (\text{A6})$$

The mixing process will move the ^{210}Pb downwards in the sediments each year, so the value of the constant k_n will change from year to year until equilibrium is attained. To find its value for each year, we developed a relationship between k_n and $A_{L,n}$.

We multiplied both sides of Equation (A6) by the mass of a layer (m) to get the total unsupported ^{210}Pb activity and summed over the depth of the mixed layer.

$$m \sum_{i=1,n}^L C_{i,n} = k_n m \sum_{i=1,n}^L e^{-\alpha M_i} \quad (\text{A7})$$

By definition

$$A_{L,n} = m \sum_{i=1}^L C_{i,n} \quad (\text{A8})$$

where $A_{L,n}$ is the total activity of unsupported ^{210}Pb in the mixed layer in year n .

Substituting in Equation (A7)

$$A_{L,n} = k_n m \sum_{i=1,n}^L e^{-\alpha M_i} \quad (\text{A9})$$

On the right side of Equation (A9) we can find the value of the summation term by using the cumulative mass (M_i) in Column B and calculating a column of values for the expression $e^{-\beta M_i}$ for L rows and storing them in Column A. We then find the sum and multiply times m. This will be a constant for all years and is called Q and is stored in row 1, col A.

$$Q = m \sum_{i=1,n}^L e^{-\alpha M_i} \quad (\text{A10})$$

By substituting in Equation (A9) and rearranging, we find the value of k_n for each year which is stored in Row 5 for Cols E through EF.

$$k_n = A_{L,n}/Q \quad (\text{A11})$$

For any year we can calculate the distribution of unsupported ^{210}Pb in the individual layers in the mixed zone as

$$C_{i,n} = (A_{L,n}/Q)e^{-\alpha M_i} \quad (\text{A12})$$

This will give the distribution of unsupported ^{210}Pb concentrations in the top L layers of the mixed zone for year n.

In the layers below the mixed zone the unsupported ^{210}Pb concentrations are calculated using Equations (A3) and (A4).

$$C_{i,n} = C_{i-1,n-1}e^{-\lambda t} = 0.96933C_{i-1,n-1} \quad (\text{A13})$$

Once the distribution for the first year is calculated the process is repeated year after year until 130 years have elapsed. Using the spreadsheet of Binford [35] we used the distribution of unsupported ^{210}Pb in the final year to calculate the sediment ages and sedimentation rates for the same 17 depths as used for Lake West Okobojo in Heathcote et al. [9].

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