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Assessing Long-Term pH Change in an Australian River Catchment Using Monitoring and Palaeolimnological Data

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Reviews of stream monitoring data suggest that there has been significant acidification (>1.0 pH unit at some sites) of Victorian streamwaters over the past 3 decades. To assess whether these declines are within the range of natural variability, we developed a diatom model for inferring past pH and applied it to a ca. 3500-yr diatom record from a flood plain lake, Callemondah 1 Billabong, on the Goulburn River, which has among the most substantial observed pH declines. The model has a jackknifed r^2 between diatom inferred and measured pH of 0.77 and a root mean square error of prediction of 0.35 pH units. In the pre-European period, pH was stable (range 6.5−6.7) for approximately 3000 yr. Since European settlement around 160 yr ago, diatom-inferred billabong pH has increased significantly by >0.5 units. We hypothesize that this increase in pH is related to processes associated with land clearance (e.g., increased base cation load and decreased organic acid load). There is no evidence of the recent monitored declines in the Callemondah record, which may indicate that that flood plain lakes and the main stream are experiencing divergent pH trends or that the temporal resolution in the billabong sediment record is insufficient to register recent declines.

Introduction

Substantial reductions in pH have occurred in many soft freshwater lakes and streams in the Northern Hemisphere, particularly Scandinavia and North America, as a result of acid rain (*1*). Such acidification of aquatic ecosystems can result in substantial modifications to their chemical and biological function. In particular, pH changes alter the mobility and toxicity of elements in the water column and sediments (*2*−*4*) at microscopic to ecosystem scale. The resultant biological changes occur at various levels in aquatic food webs, from elimination of key primary producer organisms to substantial modification of invertebrate (*5*), fish (*6*, *7*), amphibian (*8*), and aquatic plant populations (*9*). While the most severe biological responses occur at lower pH, increased pH can also markedly alter species composition (*9*).

Recent analysis of water quality data in Victoria, Australia, has revealed widespread declines in stream pH over the 25-yr-period of 1975−2000 (*10*). These pH decreases occurred in both regulated and unregulated streams (Figures 1 and 2) over an extensive area (>40 000 km^2) of stream catchments and a wide range of environments from forested upland catchments, which receive >1000 mm mean annual precipitation, to sparsely vegetated lowland sites where evaporation in many years exceeds precipitation (*10*). The potential seriousness of pH decline is emphasized in recent national-scale assessments of water quality problems in Australia, although no generic explanation is provided (*11*, *12*). In the Goulburn River catchment (Figure 1), the areally weighted pH decrease was 0.37 units over this period, with some sites experiencing declines in excess of 1.0 unit (*14*; Figure 2).

Previously, significant changes in streamwater pH in Australia have been associated with waterways draining acid sulfate soils (*7*), acid mine waste (*15*), and localized acid deposition (*16*). These impacts, while severe, are generally restricted to areas close to the pollution source (*7*, *15*, *16*). The severe reductions in lake water pH experienced in Europe and North America over extensive areas because of acid deposition (*1*) have not been demonstrated in Australia (*17*).

Quantitative diatom-based transfer functions have permitted high-precision reconstruction of pH in a large number of Northern Hemisphere lakes from stratigraphic sequences of subfossil diatom assemblages (*18*). In transfer functions, species' responses to pH are modeled following sampling surface sediment diatom assemblages in lakes representing a pH gradient (*18*). Diatom-based long-term records of catchment pH variation fill substantial knowledge gaps by providing estimates of pH derived in a consistent manner for the entire record and place observational data in the context of long-term trends.

This study focuses on the Goulburn River catchment, which covers 17% of Victoria and supports major agricultural (dryland and irrigated), food processing, forestry, and tourism industries. The Goulburn River is situated in northern Victoria (Figure 1) and flows in a northwest direction from the Great Dividing Range to enter the Murray River near Echuca. It has a mean annual discharge of 3 million ML and drains a catchment of around 17 000 km^2 in area (*19*). Rainfall over the catchment varies from more than 1400 mm/yr along the Divide to less than 500 mm/yr in the north, adjacent to the Murray River (*19*). Land-use within the catchment is dominated by grazing and broad acre cropping (60−70%), while irrigated land and intensive cropping covers approximately 10% of the catchment. Much of the remainder of the catchment (20−30%) is covered by mountain ash (*Eucalyptus regnans*) and mixed species forests as well as river redgum (*Eucalyptus camaldulensis*) flood plain woodland (*19*). The Goulburn River is highly regulated with diversions, primarily via Lake Eildon and Goulburn Weir, reducing the average annual flow into the Murray by more than 50% (*20*).

We compare the short-term (ca. 25 yr) trends in pH obtained from a water quality monitoring program with the long-term (ca. 3500 yr) pH trend obtained from a palaeolimnological reconstruction. Although the comparison is between essentially lentic (billabongs) and lotic environments, we can reasonably assume that the pH of each

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TABLE 1. Nature of Three Diatom Data Sets Merged in This Study[a]

locality	*n* sites (outliers)	pH range	*n* environmental variables measured	diatom-pH model performance r^2_{jack}	diatom-pH model performance RMSEP	source of data
Murray Basin billabongs	48 (8)	6.1−8.0	16	0.69	0.1772	*24*
southeast Australian water storages	35 (0)	6.8−8.9	8	0.42	0.3907	*25*
Lower Murray and Adelaide Hills water storages and lakes	44 (5)	6.9−9.4	13	0.64	0.3631	*26*

[a] pH range is before deletion of outliers (in parentheses), while model performance is following outlier deletion. Note that different outliers were removed in this study as a different rationale was adopted (see Methods).

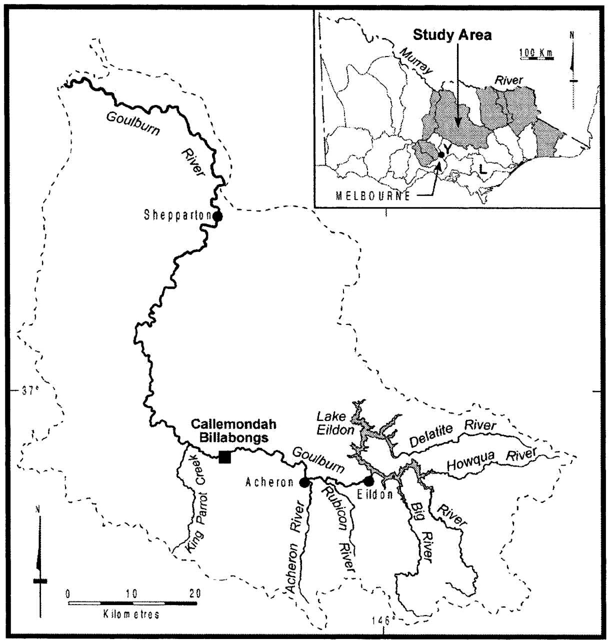

FIGURE 1. Locations of fossil study (■) and stream monitoring sites (●) referred to in the text. Shaded basins in the inset map are those where monitoring sites representing >50% of the catchment area have exhibited significant declines in pH (*10*). Y, Yarra River catchment; L, Latrobe Valley.

environment will follow the same trend over annual and greater time scales. Monitoring of billabongs and adjacent mainstream on the Murray River over 5 yr showed that, while billabongs experienced short-term extremes of pH, the median, 10th, and 90th percentile stream and billabong pH values were virtually identical (*21*). We suggest, therefore, that the pH histories derived from billabongs will reflect trends in the broader flood plain environment.

Methods

pH data for the Goulburn River catchment was obtained from the Victorian Water Quality Monitoring Network (VWQMN) (*10*, *14*). All pH measurement for the VWQMN sites was done in the field. Between 1977 and 1994, a variety of field pH meters were used, and since January 1995, low ionic strength Greenspan instruments have been employed. pH meters were calibrated prior to measurement in the field by the operator, and a check was made at the regional centers. Detailed analysis of the VWQMN data has questioned the reliability of the earlier data (*22*), but generalized linear modeling of the full data sets indicates that the observed pH declines are robust (*10*).

The diatom-pH transfer function used to infer pH from Callemondah 1 Billabong was developed by amalgamating three existing diatom data sets from southeast Australia (Table 1) that consist predominantly of river-connected lakes and storages covering a wide geographic area (32°08′−38°10′ S;

TABLE 2. Water Quality Variables in the Merged Data Set

variable	range	median
pH	6.1−9.4	7.3
electrical conductivity at 25 °C (μS cm^{-1})	25.5−10 190	311
turbidity (NTU)	0.8−470	29
total phosphorus (μg L^{-1})	6.8−1680	112

138°36′−149°44′ E). Diatoms were sampled from the uppermost surface sediments that represent the past few years accumulation, generally at the deepest point in each site. In water storages, off-take areas were avoided. For the diatom study, pH and other water quality variables were determined in the field or laboratory using standard methods (*23*). The combined data set has a pH range of 6.1−9.4 and consists of samples from 127 sites with 475 diatom taxa.

In statistical analyses, diatom assemblages were related to the mean of water quality determinations over the 12 months before diatom sampling. Geometric mean was determined for pH, while arithmetic mean was derived for all other variables. An average of 6.5 determinations (range: 1−25) contributed to the mean pH value. The range of mean annual pH in the data set was 6.1−9.4; hence, the model is applicable to reconstructing pH over a relatively wide range, although an absence of sites with pH < 6.0 hampers our ability to reconstruct very acid waters.

Diatoms from surface and core sediments were extracted and mounted on microscope slides using standard methods (*27*). A minimum of 300 diatom valves was counted in each sample using standard references to aid identification (see ref *28* for details). Taxonomic quality control was maintained by consultation during initial counting and formalized workshops. Where taxon concepts differed (particularly at the subspecies level), taxa were merged at a higher taxonomic level.

Diatom data sets are suitable for reconstructing a particular variable (e.g., pH) when it explains significant variance in diatom composition and other variables are less important (*29*). Canonical correspondence analysis, which assesses the strength and significance of species−environment relationships (*30*), was used to determine the (relative) importance of pH in our diatom data set. Only pH, electrical conductivity (EC), total phosphorus, and turbidity were measured in all data sets (Table 2). Hence, we undertook a three-stage evaluation of the influence of pH on the diatom data. First, the statistical significance and relative explanatory power of pH and 7−15 other environmental variables (Table 1) in each existing data set were assessed using Monte Carlo permutation testing (9999 random permutations) of canonical correspondence analysis (CCA) axes constrained to each variable in turn. Second, a CCA with pH constrained as the only variable in the combined data set was performed. Third a partial CCA (*31*) of the combined data set, where the covarying influence of EC, turbidity, and total phosphorus was “partialled out” or removed before Monte Carlo testing of the significance of pH, was undertaken. Rare species were downweighted in the analyses.

The performance of a number of weighted averaging-based techniques for deriving pH models was compared, including weighting for taxa with narrow tolerance, classical and inverse deshrinking, and partial-least-squares modification of the technique (*29*). Weighted averaging models were calculated using CALIBRATE 0.8 (*32*), with model performance assessed by the degree of agreement between measured and diatom-inferred modern pH values, derived from jackknifing or "leave-one-out" resampling. Model performance is reported as the r^2_{jack} correlation coefficient between these values and the root mean square error of prediction (RMSEP) (*29*). The average bias of the model and amount and location of maximum average bias in the pH gradient divided into 10 equal sections is reported. We selected the model with low RMSEP and slightest trend in the residual difference between measured and inferred pH (hereafter termed "residuals"). Outliers, with residuals greater than the standard deviation of pH in the data set (*33*), were deleted ($n = 8$) until no further model improvement could be achieved. The degree of match between modern and fossil samples was assessed using squared chord distance in the computer program, MAT (*34*). We classify fossil samples that fall outside the 10th percentile of similarity distributions in our data set (value 0.8620) as having no analogue using the "conservative" criterion of ref *35*.

A sediment core taken from Callemondah 1 Billabong, a Goulburn River flood plain lake, was used to reconstruct pH over the past ca. 3500 yr. Several billabong records have been obtained from the southeast region of the Murray Basin, which includes the Goulburn and Upper Murray Rivers (*36*). All records show declines in the relative abundance of acidophilous diatoms (principally *Eunotia* spp.), which suggest that pH increase has been a feature of their history, particularly in the last ca. 200 yr (*36*, *37*). Importantly, pH reconstructions have not been possible due to the narrow pH range of available data sets (Table 1) and a lack of analogues for the pre-European diatom flora. The most marked pH changes appear to occur in records from the Callemondah Billabongs. Accordingly, in this paper, we present a reconstruction of pH from this locality because it represents the greatest apparent long-term variability in pH but stress that the pattern and sequence of change is repeated in the records of several geographically separate flood plain lakes. Importantly, Callemondah 1 Billabong lies on a reach of the Goulburn River with some of the most marked monitored stream pH declines (*14*; Figure 2).

Radiocarbon (^{14}C) dates and the first appearance of introduced *Pinus* pollen determined the age of the diatom sequence and the timing of European settlement, respectively (*37*). Calendar age equivalents (reported as before the common era or B.C.E.) for ^{14}C dates were calculated using CALIB 4.0 (*38*) to derive the median of the 2σ probability distribution of ages using the decadal atmospheric tree ring data set in ref *39*. ^{210}Pb dating was not implemented because of the difficulties in applying this method to riverine sedimentary sequences with a substantial subsoil component (*40*). Volume-specific magnetic susceptibility, an indicator of catchment sediment erosion (*41*), was determined with a Bartington Instruments MS1 magnetic susceptibility meter, with a MS1C core scanning loop at 2-cm intervals, and expressed as dimensionless units.

Results and Discussion

Canonical correspondence analysis of each existing data set indicates that pH exerts significant influence ($p < 0.005$; *24*−*26*) and explains the greatest or second greatest amount of diatom variance in refs *26* and *25*, respectively. In the combined data set, pH accounts for a significant (F ratio = 5.14; $p = 0.001$) amount of the variance in the species data. The amount of variance explained by pH is reduced from 4.0% to 2.3% when the variance attributable to EC, TP, and turbidity is removed (partial CCA). However, it remains highly significant (F ratio = 3.06; $p = 0.001$), indicating that the combined set is suitable for generating a pH transfer function.

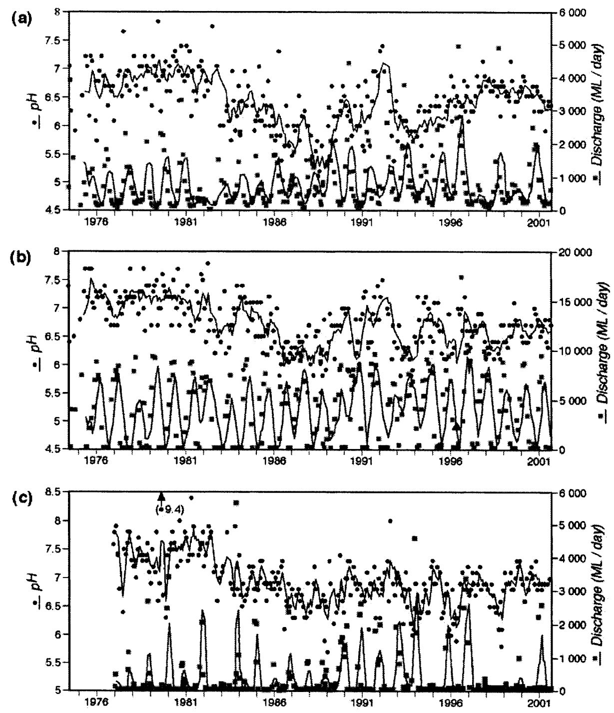

FIGURE 2. pH (●) and mean daily discharge (■) in (a) the Acheron River, an unregulated tributary of the Goulburn River, at Acheron (VWQMN site 405209); (b) the Goulburn River at Eildon (VWQMN site 405203); and (c) the Goulburn River at Shepparton (VWQMN site 405204). Data from the unregulated Acheron River are illustrated as it has the highest discharge of any tributary upstream of the Callemondah Billabongs, although other tributaries exhibit greater pH decline (*10*, *14*). Lines shown are three-point moving averages. Data obtained from www.vicwaterdata.net. Note that the pH data point in panel b marked with ▲ was removed before development of a regression relationship between flow and pH (see text).

Comparison of weighted averaging techniques for inferring pH in our data set showed that simple weighted averaging with classical deshrinking had a slightly higher RMSEP (0.3505 pH units) than 1 and 2 component WA-PLS models (0.3426 and 0.3477 pH units, respectively), while other alternatives assessed performed less well (RMSEP > 0.38 pH). However, the classical deshrinking model yielded the weakest, although still significant, relationship between measured pH and the residuals ($r^2 = 0.07$; $p = 0.004$, residual $= -0.1271$ pH $+$ 0.9223; see Figure 3; as compared with $r^2 = 0.28$, $p < 0.005$ for a 1 component WA-PLS model and $r^2 = 0.18$, $p < 0.005$ for the 2 component model). Additionally, the WA classical deshrinking model provided the most accurate estimates at low pH values and was adopted for use in the study. It had a measured versus diatom-inferred (DI) correlation coefficient of $r^2_{\mathrm{jack}} = 0.77$ and a root mean square error of prediction of 0.35 pH units.

Although the new diatom-pH model developed reduces the extent of the "no analogue" problem observed in the Callemondah 1 record (*37*), a number of pre-European samples have no analogue in our data set (Figure 4). This, in part, is a reflection of the substantial representation of *Eunotia incisa* in the core sequence, which does not exceed 5% in our data set. The lack of modern analogues is potentially most important for core sections 40−52 and 72−88 cm;

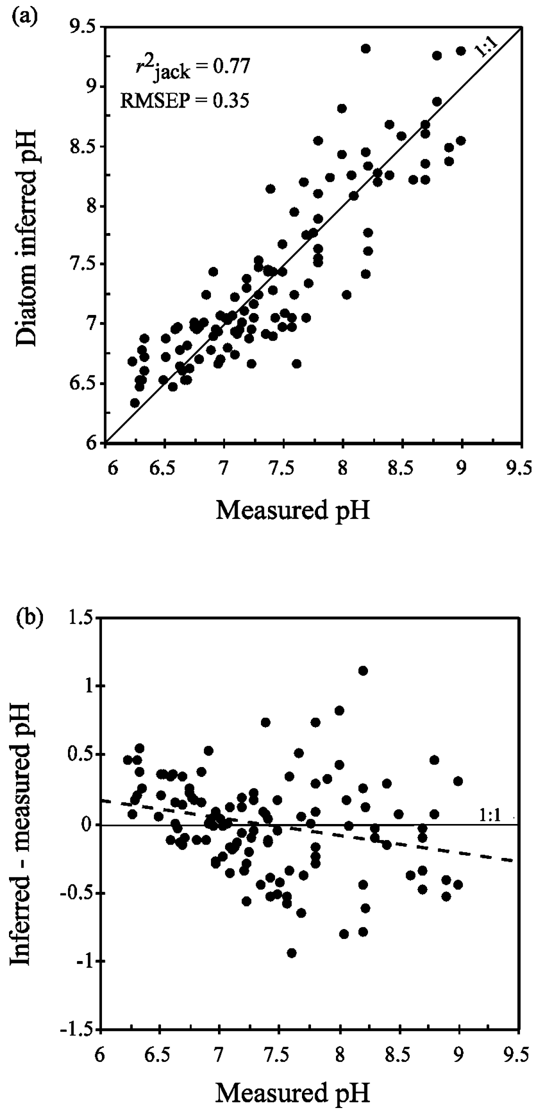

FIGURE 3. Relationship between measured pH and (a) diatom inferred pH and (b) model residuals (inferred pH − observed pH) in the data set. Also shown is the line of equivalence and in panel b the linear trend line (dashed), highlighting the tendency for DI-pH to be overestimated at low observed pH and underestimated at high observed pH.

however, DI-pH at these depths is, for the most part, within the range of DI-pH above and below these sections. We are therefore confident in the general interpretation from this site, although actual pH values for some samples may be poorly estimated.

Following the initiation of the diatom record, there is a decline in diatom-inferred pH from a maximum of 6.85 at 120 cm to 6.52 at 104 cm, largely driven by a decline in *Aulacoseira ambigua* (pH optimum 7.26). This decline occurred over 500 yr or less as constrained by calibrated ^{14}C ages of 1820 B.C.E. for sediments which pre-date the *A. ambigua* decline in the adjacent Callemondah 2 Billabong (*42*) and an age of 1340 B.C.E. at 105−109 cm in the Callemondah 1 core (Figure 2). Following this initial shift, there is remarkable stability in reconstructed pH (range of 6.48−6.65) for over 3000 yr until the first appearance of *Pinus* pollen in the sediments (argued to occur ca. 1900; *42*).

The first appearance of introduced *Pinus* pollen at 20−21 cm is associated with DI-pH of 6.77, a figure unprecedented in 3000 yr. Although there is a slight downward DI-pH trend between 18 and 10 cm, associated with a reduction in *Cocconeis placentula* (optimum 7.24), DI-pH in the European period always remains above that inferred for the previous 3000 yr. At 9 cm, here is a sharp increase in DI-pH associated with elevated values of *Cocconeis placentula*. From 8 cm to the surface, DI-pH is essentially stable (range of 7.05−7.16). This latter phase of heightened pH is largely co-incident with expanded grasslands in the catchment as indicated by higher values of *Poaceae* pollen (*37*). Reconstructed pH (7.10) for the uppermost core sample (extracted December 1994) accurately estimates monitored pH in Callemondah 1 Billabong (mean = 7.18, n = 12) for the period May 1993−May 1994 (*42*), providing confidence in the model and its applicability to this site.

Eunotia incisa (optimum: 6.97), the dominant taxon in pre-European sediments, has a considerably lower pH optimum in Tasmanian (optimum: 4.56; *43*) and European lakes (5.1 and 5.5 in the SWAP and AL:PE surface sediment data sets, respectively; *44*). This, in combination with the model's overprediction at low pH and underprediction at high pH (Figure 3b), suggests that the pre-European pH of the Callemondah Billabongs may be overestimated and that the magnitude of pH increase following European arrival was greater than inferred.

It is clear that increased pH occurred in Callemondah 1 soon after European arrival in the catchment. This timing, in combination with an increased sediment accumulation and sediment magnetic susceptibility (Figure 4), suggests a possible link with land clearing. By far the major change to the landscape with the arrival of European settlers was removal of native vegetation, followed by major periods of erosion (*45*). Although much of the south and east of the Goulburn catchment above Callemondah 1 Billabong remains forested, the north and west of the catchment (including areas up and downstream of what is now the Eildon Dam) was subject to widespread tree clearance during the late 1800s. At a local level, the catchment of Callemondah Billabong, which incorporates around 58 ha of hills bounding the southern margin of the flood plain, has been almost entirely cleared of trees (*24*). Clearance of native vegetation was associated with a phase of intensive soil erosion followed by severe gullying during the period from the 1880s through the 1920s in the Goulburn catchment (*46, 47*) The second half of the 20th century, however, appears to have been characterized by relative stability in the landscape (*46*, *47*).

The reduction in natural organic matter inputs to the river system resulting from removal of sclerophyllous vegetation is difficult to quantify. It is possible that concentrations of dissolved organic matter reaching Callemondah Billabongs (Figure 1) would have been reduced by as much as 30−40%. We estimate that such a change could have contributed ca. 0.2 units to the pH increase. A further contribution to increased pH is likely to have been erosional delivery of base cations into the Goulburn River and associated wetlands, which increased their ability to neutralize organic acids. Such a phenomenon has been documented in Northern Hemisphere lakes following early agricultural clearance (*48*), the retreat of glaciers (*49*), and fire (50). Given the widespread nature of early landscape clearance, it is likely that pH increase affected both the Goulburn River and a large number of flood plain wetlands including Callemondah 1.

The most recent period of the record is characterized by the highest DI-pH and coincides with the expansion of grassland in the catchment. Extrapolation of a post-European sedimentation rate of 0.2 cm yr^{-1} suggests that this phase began approximately 40 yr prior to coring in 1994. However, the magnitude of this recent pH increase in the Callemondah 1 record is not matched in the adjacent Callemondah 2 record, which otherwise follows the Callemondah 1 record closely (Reid, unpublished data). The divergence of these records may result from the institution of a more regulated flow

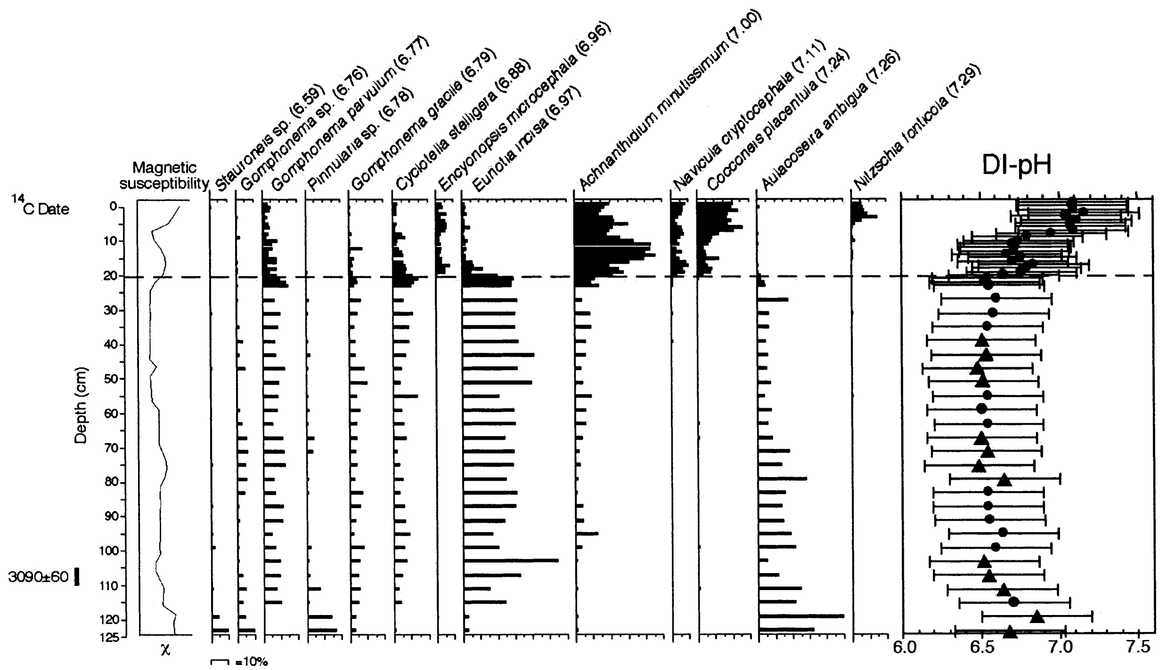

FIGURE 4. Sediment magnetic susceptibility, diatom composition, and diatom-inferred pH (DI-pH) of Callemondah 1 Billabong core C1T4. Magnetic susceptibility is expressed as a dimensionless unit (χ). Diatom taxa with relative abundances >7.5% are displayed and are ordered by weighted-averaging derived pH optima (shown in parentheses). DI-pH is displayed along with positive and negative RMSEP and values illustrated with ▲ have a minimum distance outside the 10th percentile and lack analogues in the data set (see Methods for details). The dashed line is the depth of first appearance of exotic *Pinus* pollen in the record.

regime in the Goulburn River, following an almost order of magnitude increase in the capacity of Eildon Reservoir to 3390×10^3 ML in 1955. We contend that reduced billabong flooding would have reduced the delivery of flood plain organic matter and accentuated differences in the subcatchments of the Callemondah Billabongs (*42*).

In contrast to the recent diatom inferred pH stability, water quality monitoring data for Goulburn River upstream and particularly downstream of Callemondah 1 Billabong suggests that pH has *decreased* by 0.5−1.0 units over the most recent 25 yr, although there is considerable variability in the data. These pH trends are illustrated in Figure 2 for three representative sites—the Acheron River at Acheron and the Goulburn River at Eildon and Shepparton—over a ca. 25-yr period. Mechanisms by which streams may acidify (including climate variability, agricultural activities, forest regeneration, acid rain, and acid mine drainage) (*7*, *14*−*17*) are considered in light of the absence of an acidifying trend in Callemondah 1. In the Goulburn catchment, a climate link seems unlikely as stream pH show little seasonal (Figure 2) or long-term pattern that may be related to temperature (e.g., mean maximum air temperature at Eildon vs stream pH at Eildon, $r^2 = 0.01$, $p = 0.07$). It is only on the Goulburn River at Eildon that a (very weak) significant relationship between discharge and pH ($r^2 = 0.03$, $p = 0.005$, $n > 297$) is exhibited, following deletion of an outlying low pH value (Figure 2), while at the other sites the relationship is not significant ($p > 0.01$). A similar situation appears to exist at other monitored Victorian sites (*10*).

Widespread decreases in pH in the Goulburn River due to acid mine drainage, agricultural practice, and forest regeneration are unlikely. Acidic runoff from former gold mining areas in the upper Goulburn catchment only influenced streamwater pH close to the source of the runoff (*51*). While agricultural practices can lead to soil and waterway acidification, acidic soils in Goulburn catchment are downstream of the Eildon and Acheron sites reported here (*52*). Forest regeneration can substantially acidify soils. For example, a study near Bendigo, Victoria, revealed that following forest clearing over 50 yr ago the soil under regenerated forest had acidified, on average, by 45 kmol H^+ ha^{-1} as compared with nearby soil under pasture (*53*). This effect could have been caused by the net accumulation of organic anions in the forest regrowth (*52*). There is, however, little evidence that there has been significant forest regeneration in the catchment areas above the three water quality sites. We are not able to totally discount the possibility that acid rain from Melbourne (or the industrialized Latrobe Valley) may have influenced the acidity of waters in the Goulburn catchment, and the diatom model presented here will allow an assessment of this possibility by examining the pH history of lakes removed from land-use change.

While it is possible that the apparently contradictory trends revealed in the monitored (declining pH) and fossil (stable pH) data result from the fossil record's relatively coarse temporal resolution, they may also indicate similar response to catchment perturbation and recovery. Most erosion associated with land clearance in the upper Goulburn catchment and much of upland southeastern Australia occurred prior to 1920 (*44*). Since this time, there has been a degree of stabilization of soil surfaces. This would lead to a reduction in the rate of delivery of base cations to streams and hence lowered pH in the stream. The different response from Callemondah 1 Billabong may result from the increased isolation of the site from the river resulting from the flood mitigating effects of Eildon Reservoir, particularly since 1955.

The billabong pH response to land clearance observed in this study appears widespread. Qualitative diatom data indicate sustained elevated pH following European arrival in southeast Australian flood plain lakes on the Upper Murray ($n = 5$; *35* and Reid, unpublished data), Lower Murray ($n = 1$; *26*), and Yarra Rivers ($n = 3$; Leahy, unpublished data) (see Figure 1 for river locations). Commensurate with observations from Callemondah 1, pH increase occurred at or shortly after the first evidence for European arrival.

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