

Biological and geochemical record of anthropogenic impacts in recent sediments from Lake Pupuke, Auckland City, New Zealand

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Abstract

Frozen sediment cores from Lake Pupuke in Auckland City, New Zealand, contain a high resolution decadal to annual scale record of changing lake paleoenvironments and geochemistry that reflects changing landuse and hydrology in the catchment over the past c. 190 years. A reliable chronology is available from AMS ¹⁴C and ²¹⁰Pb dating of the sediments, with the timing of the older part of the record supported by the first appearance of pollen of introduced *Pinus* and *Plantago lanceolata* associated with European settlement of Auckland in the early 1840s. Diatom stratigraphy, sediment elemental and carbon isotope geochemistry reflect changes in sediment sources and lake conditions commensurate with European development of the Lake Pupuke catchment, in particular enhanced algal productivity controlled by the influx of nutrients after c. 1920 AD. Attempts to prevent nuisance algal blooms in 1933, 1934 and 1939 using CuSO₄ addition produced Cu spikes in the sediment that allowed confirmation of the accuracy of the ²¹⁰Pb chronology. Hence, the elemental and isotopic composition of the Lake Pupuke sediments reflect the timing of significant anthropogenic activities, rather than climatic variations, that have occurred within the watershed over the past c. 190 years. The comparison of records of land use change in the catchment with the multi-proxy record of changes in the sediments usually allowed unambiguous identification of the signatures of change and their causes.

Introduction

The Auckland region of northern New Zealand (Figure 1) is important in a paleoenvironmental context since it forms an ecological boundary between the far northern North Island and

cooler regions to the south. The southern limit of closed forest during the last glacial maximum lies somewhere in the Auckland region (Lanashire et al. 2002). Prior to human settlement of New Zealand c. 800 year BP the Auckland region was covered by dense podocarp-hardwood

forest (McGlone and Wilmshurst 1999). In addition, it has an unusually dense cluster (about 50) of Quaternary volcanoes (Searle 1981), all within Auckland City, which is New Zealand's largest and most densely populated. The rich volcanic soils and abundant marine resources made the area a desirable location for early Polynesians who cleared the land by fire for horticulture and to promote bracken growth. European settlement of Auckland commenced c. 1840 with the local population reaching 500,000 in the first 120 years and 1.2 million in the subsequent 40 years.

Lake sediments are often excellent recorders of past climates and geological events via a number of proxy indicators (Battarbee 2000), and several studies of surface and Holocene lake sediments in central Auckland have been carried out (Newham and Lowe 1991; Horrocks et al. 2002, 2005; Lancashire et al. 2002) and recently, in other regions of New Zealand (e.g., Reid 2005; Wilmshurst and McGlone 2005; Woodward and Shulmeister 2005). However, urban sites are few and often disturbed, affecting stratigraphic continuity, resolution and age control. Furthermore, none of the lake sediment sequences studied to date from Auckland record the timing and nature of European impacts on the region, although cores taken from the Waitemata Harbour (Hayward et al. 2004) and Manukau Harbour (Matthews et al. 2005) record significant changes in estuarine sediment geochemistry and fossil content since the arrival of humans ca. 1300 AD, with further faunal changes associated with decreased salinity due to increased runoff associated with forest clearance in Polynesian (c. 1300–1840) and European (post 1840) times. Sedimentation has increased in the harbours since the 1950s due to accelerating urban subdivision (Hayward et al. 2004).

We present biological (diatoms and pollen), sedimentological, as well as isotopic and elemental geochemical proxies of environmental change from Lake Pupuke in the central Auckland region for the last c. 190 years, underpinned by an AMS ^{14}C and ^{210}Pb -based chronology. This deep lake provided the rare opportunity for sampling undisturbed Late Holocene sediments from within Auckland City and provides the only complete, high resolution environmental record of anthropogenic impacts from the region.

Lake Pupuke environment

Lake Pupuke (36°47.25' S, 175°46.25' E) occupies a c. 140,000 year old maar crater (Kermode 1992) on the North Shore of Auckland City (Figure 1). The area, including the lake catchment, is mainly residential. The eastern margin of the lake lies c. 200 m from the sea and c. 5 m above sea level. It is surrounded by a tuff cone, which has protected the freshwater lake from erosion and seawater influx (Searle 1981). The tuff ring of Pupuke crater consists of a mixture of juvenile and accidental ejecta deposited by base surges associated with the phreatomagmatic explosions (Horrocks et al. 2005). The lake is closed hydrologically and occupies 57% of its 1.9 km² catchment. The area and volume of the lake are 1.1 km² and 3.02 km³ respectively, with a maximum diameter of 1.4 km and depth of 57 m. Mean annual rainfall is 1119 mm (Tomlinson and Sansom 1994a), and is distributed evenly throughout the year. Mean daily air temperature is 15.6 °C and the average daily range is 6.0 °C (Tomlinson and Sansom 1994b).

The limnology of Lake Pupuke has been described by Cassie (1989) and Holmes (1994). Rainfall into the catchment accounts for the bulk of the water entering the lake and there are no significant inflows or outflows, although an adjacent coastal spring originates from the lake. The surface waters have a pH of c. 8.36 suggesting low levels of dissolved CO₂ and a predominance of bicarbonate. The surface waters are separated from the anoxic hypolimnion by a well-defined thermocline, with the depth to its lower boundary ranging from 21 to 25 m (Holmes 1994). The lake has been intensively used both as a sewage recipient and water supply over much of the past century.

Pollen records from Lake Pupuke indicate that apart from an expansion of *Agathis australis* suggesting increasingly dry conditions from c. 7000 years BP, the pre-human Holocene was a period of relative environmental stability (Horrocks et al. 2005). Dramatic vegetation change only occurred over the last c. 700 cal year BP as a result of large-scale Polynesian deforestation by fire.

The lake was first used as a water supply for Auckland in 1895 and by the mid 1920s nutrient enrichment was becoming a problem due to

increased farming and urban development in the catchment. A report in 1927 (ARWB 1979) indicated that only seven of the 62 houses in the catchment were on septic tanks and only 5 connected to a sewerage system. Nevertheless, Lake Pupuke continued to be used as a water supply until the early 1940s and was officially closed as a water supply in 1941 (ARWB 1979).

The lake is surrounded by private homes along most of its shores. The sedge *Arundo conspicua* is common on the south side of the lake and aquatic *Vallisneria gigantea* dominates the littoral zone (Coffey and Clayton 1987). The latter was introduced to the lake in 1885 and within 10 years had reached nuisance proportions (ARWB 1990). In 1980 the oxygen weed *Egeria* was first recorded in the lake and by 1988 had overtaken *V. gigantea* as the dominant lake weed (Coffey and Clayton 1987; NSCC 1992). The lake supports a diverse planktonic and phytobenthic flora (Cassie 1989; Holmes 1994). Between 1925 and 1940 there were several nuisance blooms of the alga *Ceratium* sp and more recently there have been blooms of the cyanobacteria *Microcystis* sp. and *Anabaena* sp., although phytoplankton biomass in the lake has fallen substantially since mid-1960s (Vant et al. 1990; Holmes 1994).

Methods

An 84 cm long core (Core P2) was obtained from Lake Pupuke (Figure 1) using a flat faced freeze corer (Neale and Walker 1996) that produces two intact slices of frozen sediment using CO₂ pellets (i.e., dry ice). The sediments retrieved were subjected to analysis for a range of proxies (described below) at intervals ranging from 1 to 10 cm. Grain size analysis was undertaken at 5 cm intervals. The samples were treated with H₂O₂ to remove organic matter, dispersed with sodium hexametaphosphate and sonified before measurement with a Malvern Mastersizer 2000 laser particle sizer.

Total organic carbon (TOC), total nitrogen (TN) and bulk organic matter $\delta^{13}\text{C}$ analysis of sediment organic matter first involved acidification with 1N HCL to remove any carbonate, after which samples were washed three times with de-ionised water, freeze-dried and crushed to a powder. The TOC and TN analyses were under-

taken at the Isotope Laboratory at the University of Waikato, Hamilton, New Zealand, using a Dumas elemental analyser (Europa Scientific ANCA-SL) interfaced to an isotope mass spectrometer (Europa Scientific 20–20 Stable Isotope Analyser) for $\delta^{13}\text{C}$ measurement.

Selected trace and major element concentrations (Pb, K, Na, P, Cu, Al, Zn) were measured on the acid extractable fraction prepared using the procedure of Bengtsson and Enell (1986). Samples collected at 5 cm intervals were acidified with concentrated HNO₃ and HCL to dissolve the sample, and measurements undertaken using a Varian Liberty AX Sequential ICP-AES at Auckland University of Technology.

Accelerator mass spectrometry (AMS) ¹⁴C age determinations were carried out on both purified pollen extract and bulk plant detritus subsamples from 81 cm depth in the freeze core by Rafter Radiocarbon Laboratory, Wellington, New Zealand. The sample received standard chemical pollen procedure: 10% HCL, 10% HNO₃, 5% KOH, then sieved at 150 and 6 μm with sodium polytungstate used on 150–6 μm fraction, with the best pollen concentrate obtained at a density of 1.15. For the same sample, the macroscopic plant matter in the fraction coarser than 150 μm was also dated. Radiocarbon ages are presented at one sigma, with radiocarbon age calibration undertaken using INTCAL98 (Stuiver et al. 1998).

²¹⁰Pb analyses were undertaken at ANSTO, Sydney Australia. The total ²¹⁰Pb activity was determined by measuring its granddaughter ²¹⁰Po, which was assumed to be in secular equilibrium with ²¹⁰Pb. The supported ²¹⁰Pb was estimated from measurement of ²²⁶Ra activity. About 1–4 g of dried, ground sediment was spiked with ²⁰⁹Po and ¹³³Ba as yield tracers, with each sediment sample then leached with hot concentrated acids to release Po and Ra from the sediment. Po was electroplated onto silver discs after reduction of Fe³⁺ with ascorbic acid and analysed by high-resolution alpha spectrometry. Ra was co-precipitated with BaSO₄ on a filter source. The chemical yield was determined by measuring the ¹³³Ba isotope with an HPGe-gamma detector.

The excess ²¹⁰Pb activity was calculated by removing the ²²⁶Ra activity from the total ²¹⁰Pb activity. The sedimentation rates were then calculated using the constant initial concentration

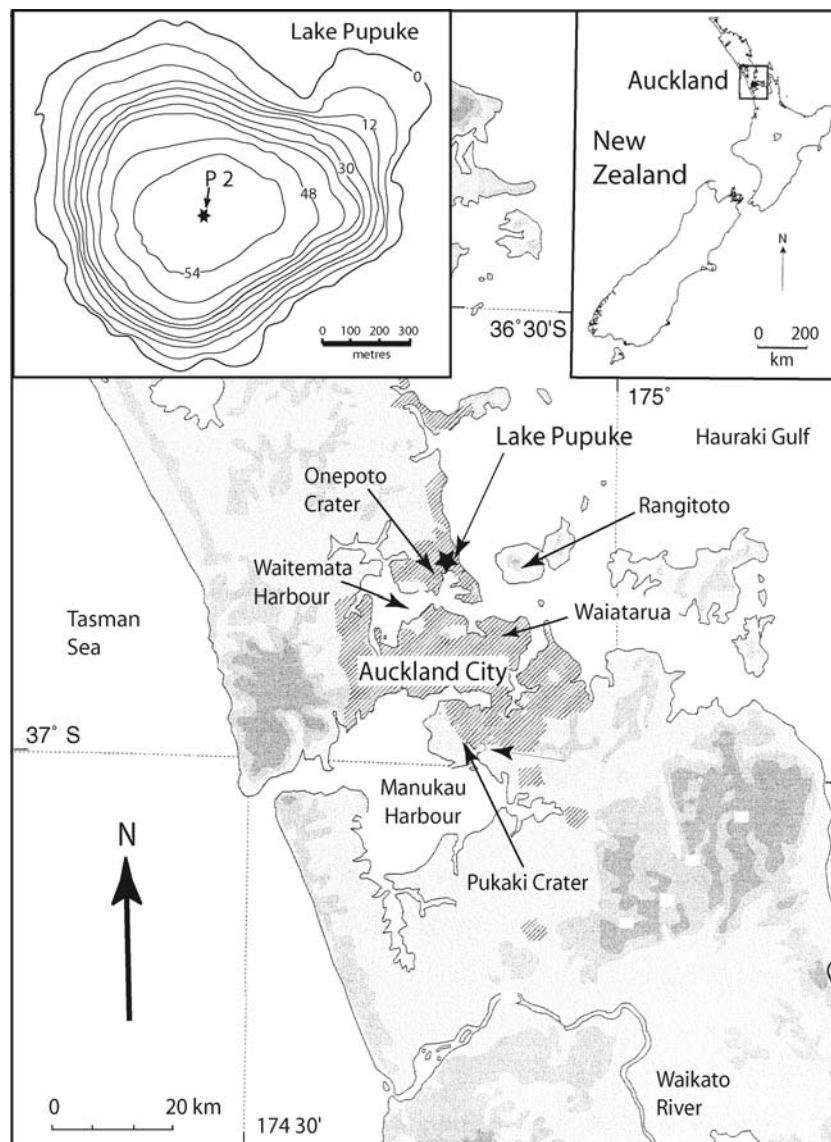


Figure 1. Location map showing Lake Pupuke bathymetry (inset). Shading indicates elevated regions, with darker shading indicating increasing elevation.

(CIC) method (Goldberg 1963; Robbins et al. 1975; Harle et al. 2002) using the formula:

$$t_1 = 1/\lambda \cdot \ln(A_0/A_1) \quad (1)$$

where A_0 = unsupported ^{210}Pb activity at sediment-water interface in dpm/g of dry sediment; A_1 = unsupported ^{210}Pb activity at depth in dpm/g of dry sediment; λ = decay constant of ^{210}Pb (0.03114 years), and t_1 = the difference between the age of the sediment at the sediment-water interface and sediment at depth in years.

The sedimentation rate was determined from the slope of the least-squares fit for ^{210}Pb excess values plotted vs. depth, with the application of the CIC model requiring that ^{210}Pb activity drops monotonically with increasing depth. The slope (plotted logarithmically) vs. depth in the sediment profile is a measure of the sedimentation rate. The CIC model was used as the sediment is laminated and undisturbed except for the uppermost 5 cm of the core so that an approximately constant rate of sedimentation was expected.

Pollen analysis was undertaken both for purposes of validation of the ^{210}Pb chronology, and for conventional paleoecological reconstruction. The former is possible since the European settlement of the Auckland region commenced c. 1840 and other studies (i.e., Hayward et al. 2004; Matthews et al. 2005) have successfully used the first appearance of *Pinus* pollen as a chronostratigraphic marker in sediment cores. The samples were prepared for pollen analysis by the standard acetylation and hydrofluoric acid method (Moore et al. 1991), and bleached. The pollen sum was at least 250 grains, excluding *Leptospermum* type, herbaceous swamp plants and ferns except *Pteridium*, which can form a dominant vegetation cover (McGlone 1983).

Diatom analysis was carried out on sub-samples of approximately 1 cm^3 taken at 10 cm intervals from 0 to 80 cm, with an additional sample taken from the base of the frozen core at 84 cm. Diatom samples were prepared for analysis by oxidation with dilute hydrogen peroxide (10%) heated in a water bath at $70\text{ }^\circ\text{C}$ for 2 h, or until obvious organic residue had been removed. Samples were then rinsed by repeated washing with distilled water. Sub-samples of processed sediment were mounted using Naphrax[®].

At least 300 diatom valves per sample were identified and enumerated using a Leica DMLB microscope at $1000\times$ magnification (oil immersion) with differential interference contrast. Taxonomy was based on Foged (1979), Krammer and Lange-Bertalot (1986, 1988, 1991a, b). Taxa that could not be identified were assigned to morphotypes. All morphotypes and most identified taxa were photographed and the images archived using a Zeiss Axiocam digital camera and Axiovision 3.0 (2001) image processing and analysis software. Diatom species abundances were expressed as percentages, calculated using total number of valves recorded for each sample. Diatom assemblages were used to infer a range of trophic-related variables: total phosphorus (TP), dissolved reactive phosphorus (DRP), chlorophyll *a* (Chl *a*) and pH using weighted averaging calibration models developed specifically for New Zealand lakes (Reid 2005). Reid (2005) developed models for inferring annual means as well as means for mixed (isothermal) and stratified periods. The specific variables (annual, isothermal or stratified means) reconstructed in this study were based on which-

ever model performed best (Reid 2005). Hence, annual mean TP and pH and isothermal mean DRP and Chl *a* were reconstructed.

Results

Stratigraphy and sedimentology

Core P2 comprises of highly organic muds laminated at 2–5 mm scale (Figure 2), although the sediments at the top 5–8 cm of the core are disturbed, and the lower 10 cm are largely weekly laminated organic muds. At 30–25 cm depth there are two black bands <1 mm thick, surrounding which are thick (2–4 cm), cream to white diatom-rich ooze (Figure 2).

Mean grain sizes display a trend to fining upwards from 22 to $14.3\ \mu\text{m}$, with grain size minima at 65 and 30 cm depth (Figure 4). The percentage of grains greater than $63\ \mu\text{m}$ (sand size fraction) displays exactly the same trend with reducing sand content up core. Sand size material is absent at 30 cm depth after which a gradual increase in percentage of the sand size clastic material occurs towards the top of the core sequence. A dominance of fine silt to clay size sediment (less than $10\ \mu\text{m}$) is also apparent at 30 cm depth, with a trend towards increasing dominance of sediment coarser than $10\ \mu\text{m}$ towards the top of the core (Figure 4). Note that we were unable to extract enough sediment from the top 10 cm of the freeze core for particle size measurement.

Dating

One horizon near the base of the freeze core was dated using AMS ^{14}C (Table 1, Figure 3). Pollen extracted from sample from 81 cm depth was dated at $1419 \pm 45^{14}\text{C}$ year BP (NZA 17532) and bulk plant matter from same sample at $824 \pm 35^{14}\text{C}$ year BP (NZA 20336). The calibrated ages for the samples using INTCAL98 (Stuiver et al. 1998) are 1289–1343 year BP, and 1197–1261 year BP respectively Table 1).

The results of the ^{210}Pb analysis are shown in Figure 3. The activity of unsupported ^{210}Pb measured for each sample is plotted as log-linear graph and demonstrates a steady decrease in ^{210}Pb activity with depth down to 60 cm, suggesting that

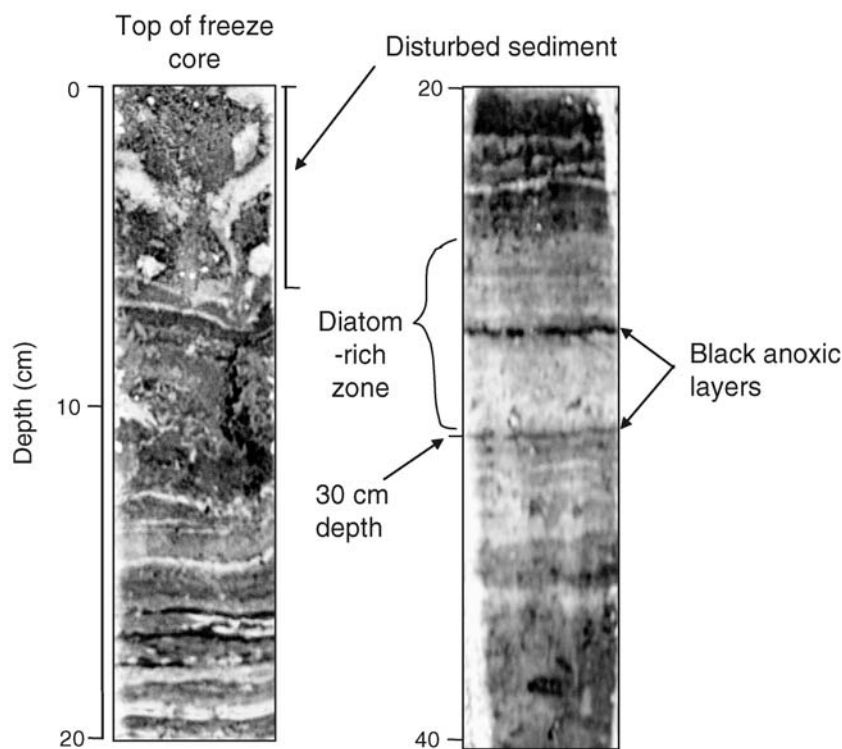


Figure 2. Photographs of the Lake Pupuke freeze core showing deformed and well-laminated sections of the core.

there has been no mixing or bioturbation of the sediments other than minor disturbance of the sediments in the top 5 cm of the core. Below 60 cm depth the ^{210}Pb activities are low and fluctuate around a vertical axis, strongly suggesting that they are at background level (Figure 3). The ages were calculated down to 55 cm depth using the 22.26 year half-life of ^{210}Pb and on the assumption that the top sample was deposited during the year that the core was collected (December 2002), with the rest of the core to 84 cm depth (c. 1813 AD) dated by extrapolating the derived ^{210}Pb sedimentation rate to the base of the core using the mean sedimentation rate is 0.445 ± 0.032 cm/year.

Organic matter elemental and isotopic geochemistry

The organic matter elemental and isotopic geochemistry varies considerably down core (Figure 4). Peak values for TOC occur at 5, 25 cm (15.7%) and 65 cm depth (17.9%), and a minimum value of 10% occurs at 30 cm (Figure 4). The TOC/TN ratio closely follows the TOC trend with minima of 5.4 and 7.4 at 30 cm and 75 cm depth

respectively. The TOC/TN peak of 14.1 at 65 cm depth is followed by an up core reduction in values until the minimum at 30 cm depth after which it increases and remains steady at c. 10 (Figure 4).

$\delta^{13}\text{C}$ in the bulk organic matter is also variable with relatively depleted $\delta^{13}\text{C}$ values of -25‰ at the base of the core increasing to a peak of -22.8‰ at 65 cm depth (Figure 4). A subsequent sharp depletion at 60 cm is followed by steady $\delta^{13}\text{C}$ enrichment of the bulk organic matter until 30 cm depth after which $\delta^{13}\text{C}$ depletion occurs with a minimum of -25‰ at 15 cm depth. The upper 15 cm of the core shows a trend to increasing $\delta^{13}\text{C}$ enrichment (Figure 4).

Sediment elemental geochemistry

The trace elements Pb, Zn and Cu varied throughout the core with the values for each increasing over the upper 40 cm of the sediment record (Figure 4). Pb levels remained low until 40 cm depth after which levels increased to a peak of 174 ppm at 5 cm depth before dropping back to 68 ppm just below the sediment-water interface.

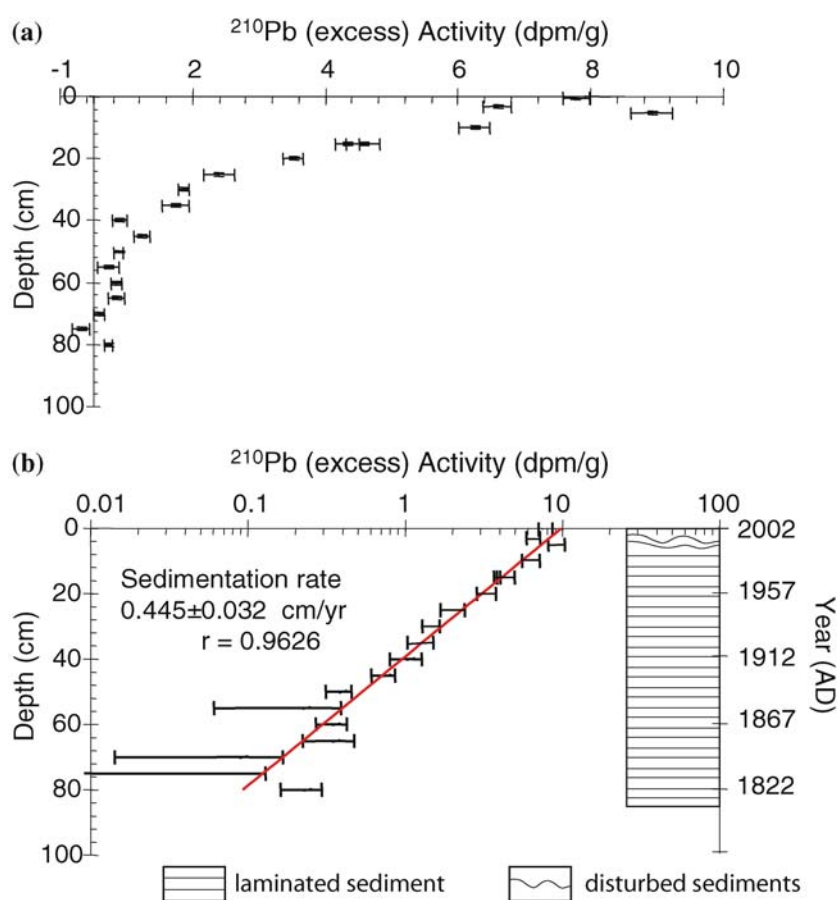


Figure 3. Unsupported ^{210}Pb profile for Lake Pupuke, with chronology and core log shown. The Cu peak at 30 cm depth is caused by copper sulphate addition to the lake in 1934.

Zn increased gradually from the base of the core, although markedly a higher concentration of 94 ppm was encountered at 65 cm depth (Figure 4). Zn concentrations remained nearly steady from 60 to 35 cm depth after which Zn continues to increase, with this trend punctuated by two Zn concentration minima at 20 and 10 cm depth. Zn concentrations peak at 158 ppm at the top of the core just below the sediment-water interface. Cu concentrations in the Lake Pupuke sediments are generally low at less than 30 ppm, although there is a Cu spike (666 ppm) at 30 cm depth, and a trend to increasing Cu concentration in the sediment above 20 cm depth, with highest concentration (116 ppm) encountered in these sediments at the sediment water interface (Figure 4).

Variation in major element concentrations is represented by the trend in the ratios of K/Al and Na/Al in the sediment down core (Figure 4). This

ratio was used as a method to distinguish the fraction of metals related directly to anthropogenic impact by normalisation with respect to Al (Van Metre and Callender 1997; Tylmann 2005). This is necessary as heavy metals originate not only from anthropogenic sources but will also be supplied to the lake by the natural flux of elements from the catchment soils. The ratios are generally steady below 15 cm depth in the core after, above which the ratios increase markedly, especially in the top 5 cm.

Pollen record

In the lower part of the core, the pollen sum is dominated by *Pteridium* (bracken) and to a lesser extent *Coriaria* (tutu) (Figure 5). Values for these taxa decline in the upper core, largely due to

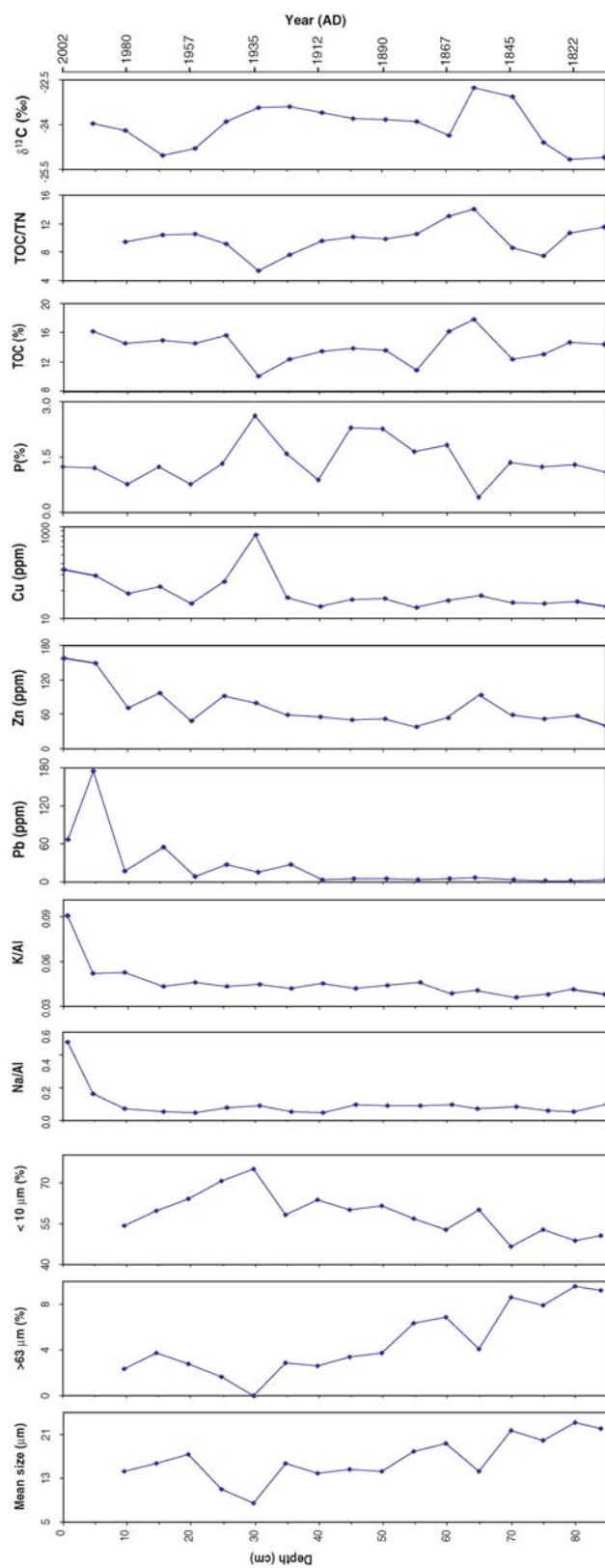


Figure 4. Down core variation in a range of physical and geochemical properties of the Lake Pupuke freeze core.

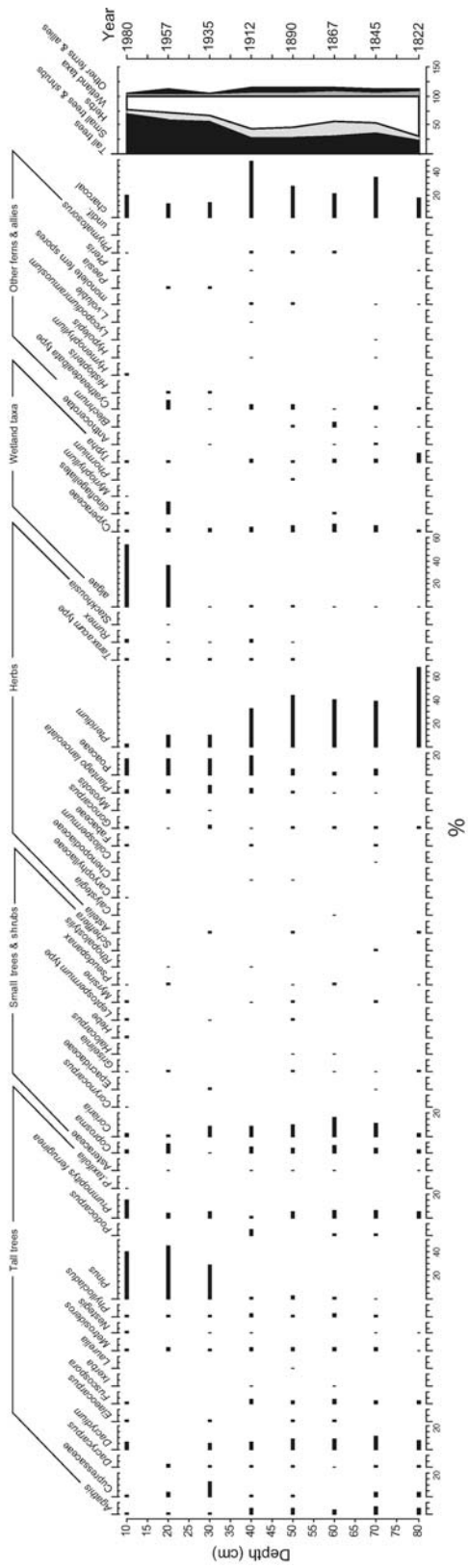


Figure 5. Pollen record from the lake Pupuke freeze core.

Table 1. Radiocarbon data for Lake Pupuke samples.

Depth (cm)	Lab number	$\delta^{13}\text{C}$ ‰	% Modern	^{14}C age (year BP)	Cal age (year BP)
81	NZA 17532 ^a	-26.5	83.28 ± 0.45	1419 ± 45	1343–1289
81	NZA 20368 ^b	-25.7	89.66 ± 0.41	824 ± 35	753–689

^aIndicates age from pollen extract.

^bIndicates age from plant detritus.

increases in pollen of *Pinus* (pine) and, to a lesser extent Poaceae (grasses). Except in the lowermost sample, indicators of European presence, namely pollen of *Plantago lanceolata* (plantain) and *Pinus* are present throughout the core. Tall indigenous trees generally record low values throughout. *Typha* (bulrush) is recorded in almost all of the samples and algal spores record very high values in the uppermost two samples. All samples have significant amounts of microscopic charcoal.

Diatom record

A total of 116 diatom taxa were identified in the core samples. Most of these were rare, and only 54 of these were present at greater than 1% relative abundance. The most abundant diatoms were the planktonic taxa *Aulacoseira ambigua* (including two morphotypes), *A. granulata* v. *angustissima*, *Cyclotella stelligera* and *Fragilaria crotonensis*, along with several facultative planktonic taxa, including *Pseudostaurosira brevistriata* (types 1 and 2), *Staurosira construens* and *S. construens* f. *venter* (including two morphotypes). Benthic taxa were less common and exceeded a third of the total assemblage in only one sample (80 cm). The most common benthic taxa were *Achnanthydium minutissimum*, *Cocconeis placentula*, *Encyonopsis microcephala* and *Epithemia sorex* (Figure 6).

Four zones can be identified based on the diatom assemblages. The first consists of the two lowermost samples taken from 84 to 80 cm. These samples are dominated by *Cyclotella stelligera*, a planktonic taxon typically associated with oligotrophic conditions. Reconstructed values for DRP, TP, pH and Chl *a* were all low in this zone. The second zone incorporates the four sediment samples taken from between 70 and 40 cm. These samples are dominated by a suite of facultative planktonic species belonging to the genera *Pseudostaurosira* and *Staurosira*. The planktonic taxon *Aulacoseira ambigua* is also relatively abundant

through this period. These taxa are typical of mesotrophic conditions, although *Pseudostaurosira* and *Staurosira* may tolerate a wide trophic range (Bennion et al. 2001; Sayer 2001) and it has been suggested that their abundance reflects the availability of suitable benthic habitat (Sayer 2001). Elsewhere in New Zealand these taxa have been found to be most common in mesotrophic lakes that retain high water clarity (Reid 2005). Reconstructed TP, DRP and Chl *a* values are all elevated from those in the underlying samples and also suggest mesotrophic conditions prevailed in the lake during this period. Similarly, reconstructed pH increases throughout this zone and can be construed as reflecting increased soil-derived bicarbonate into the lake waters.

The third zone includes the samples from 30 to 20 cm depth. The mesotrophic *Aulacoseira ambigua* and the eutrophic *Aulacoseira granulata* v. *angustissima* are both increased in abundance at 30 cm. *Aulacoseira granulata* v. *angustissima* and two other eutrophic to hypereutrophic taxa, *Cyclotella meneghiniana* and *Cyclostephanos tholiformis*, subsequently peak at 20 cm (Figure 6). Reconstructed values for DRP, TP and Chl *a* are again increased from values in underlying samples, whilst reconstructed pH is reduced. The final zone incorporates the two uppermost samples and is dominated by *Fragilaria crotonensis* (Figure 6), a planktonic taxon that is also an indicator of eutrophic conditions. Reconstructed TP and Chl *a* values remain high, while reconstructed DRP values are reduced. Reconstructed pH increases to its highest levels in zone 4.

Discussion

The ^{210}Pb CIC model allowed the development of a high-resolution chronology of changes in the various proxies over the past c. 190 years. Note that the ^{210}Pb method does not provide absolute ages but rather gives sedimentation rates. Indirectly, we

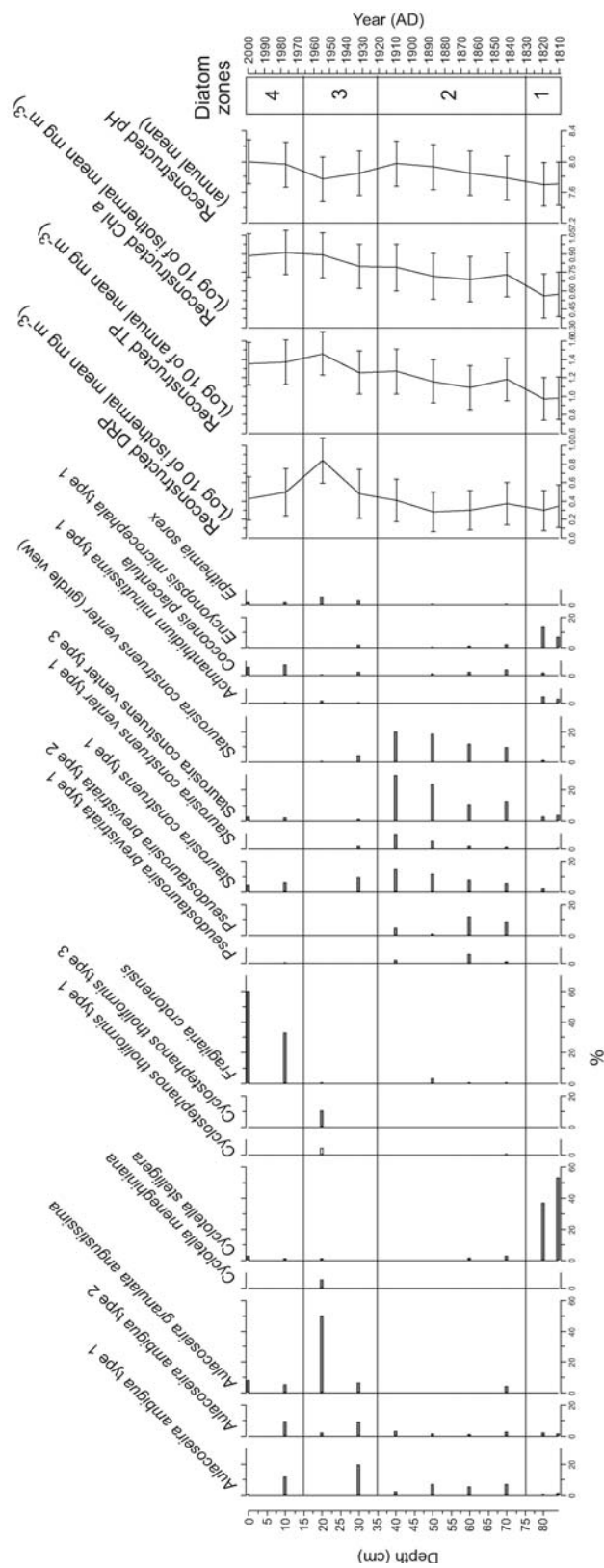


Figure 6. Diatom record and transfer function-based reconstructions of DRP, TP, Chl α and pH from Lake Pupuke freeze core.

can then determine from the sedimentation rate how much time has elapsed between samples at different depths, which can in turn, be used to calculate ages. However, the method assumes that the age of the top sample in the core sediment sequence is known, which is usually based on the assumption that the top sediment was deposited in the year the core was collected. Consequently it is critical that the coring technique used is capable of capturing the topmost sediment. Lake Pupuke is a deep lake with limited fetch and minimal fluvial input and output so it is unlikely to experience erosion or sediment disruption associated with drying or current-induced reworking. This lack of disturbance of the sediment is supported by the well-laminated nature of the record (Figure 2). Furthermore, the lake floor sediments are unlikely to have been subject to bioturbation given the deep, anoxic nature of the bottom waters.

The extrapolation of the sedimentation rate of 0.445 ± 0.032 cm/year down to the base of the freeze core at 84 cm depth suggests a basal age of c. 1813 AD, which is incompatible with the AMS ^{14}C ages on pollen and bulk organic matter from 81 cm depth of 1419 ± 45 and 824 ± 35 ^{14}C year BP respectively. These ages are clearly too old, a situation which mirrors the anomalously old ages obtained from pollen concentrations taken from a Mackereth core from Lake Pupuke (Horrocks et al. 2005). In this case, the ages were 850–2700 ^{14}C years too old given that the dated samples were collected from horizons located between the known age Taupo (1800 ± 15 ^{14}C year BP) and Rangitoto Tephra (760 ± 50 ^{14}C year BP). These anomalously old ages were explained as either due to reworking of old pollen into the younger sediments, or, the high bicarbonate content of the lake sourced from soil influx which is then taken up into aquatic algae and macrophytes during photosynthesis (Horrocks et al. 2005). Furthermore, examination of pollen exines from all samples in the present study indicates that they display little evidence of corrosion as would be expected in the case of the reworking (Wilmschurst and McGlone 2005), so that reworking is unlikely to be the explanation for the anomalously old ^{14}C ages obtained from sediment collected from 81 cm depth in the Lake Pupuke freeze core.

Consequently, the ^{210}Pb -based CIC chronology is used here to constrain the timing of the changes in the proxies rather than the ^{14}C ages, and this is

further supported by the known timing of copper influx events into Lake Pupuke. During the 1920s and 1930s Lake Pupuke was used as a water supply and suffered from blooms of toxic algae. In an attempt to end the blooms, the Auckland Water Board dumped copper sulphate into the lake in 1933, 1934 and 1939 (Vant et al. 1990). The addition of copper sulphate to the lake is reflected in the Cu spike (lowermost black layer) encountered in the core at 30 cm depth. The sediments above the black lamina are almost pure diatoms and chrysophyte cysts, and indicate that the CuSO_4 addition was successful in reducing the toxic algae. Given the ^{210}Pb based sedimentation rate of 0.445 ± 0.032 cm/year, then the age of the Cu spike at 30 cm depth is c. 1934, an age that is a close match for the initial (1933) copper sulphate addition, and adds support to the reliability of the CIC model for the sedimentation rate and derived sediment ages. The black layers immediately above the basal Cu-rich layer are also Cu-rich and probably reflect the CuSO_4 additions in 1934 and 1939.

Vegetation history

The absence of European pollen indicators from the lowermost samples (80 and 84 cm depth) strongly suggests deposition prior to significant European settlement of Auckland which commenced in the early 1840s. The remainder of the sediment sequence appears to have been deposited in the European era, with the very high *Pinus* values in the uppermost three samples probably reflecting late European times and expansion of pine plantations in western Auckland in the early 1930s. During the late Polynesian and early European eras, *Pteridium* and *Coriaria* scrub would have comprised a major part of the local landscape, partially deforested by repeated Polynesian fires. Forest remnants would have included trees of *Agathis* (kauri) and *Metrosideros* (rata/pohutukawa) (both local pollen dispersers). The presence of *Typha* pollen throughout the core suggests eutrophication associated with human presence, and the very high values of algal spores in the uppermost two samples (past 40 years) reflects intensification of eutrophication in late European times.

The ^{210}Pb based chronology suggests an age of c. 1845 at 70 cm depth and given the initial

settlement and planting of *Pinus* in Auckland at around this time, provides further support for extending the ^{210}Pb chronology to the base of the freeze core.

Major and trace element geochemistry

The sediments contain high but variable concentrations of elemental Pb, Zn and Cu in the samples from the upper 40 cm of the core, with the concentrations of these elements above expected background concentrations given by the concentrations in the lowermost samples that range from 2–6 ppm (Pb), 38–58 ppm (Zn) to 17–31 ppm for Cu. The measured concentrations of Pb are significantly above the background levels in the upper 35 cm of the core and the sharp concentration increase above 40 cm depth in the freeze core (c. 1912) supports an anthropogenic source for these higher than background concentrations. The Pb level increases above background levels at 35 cm (c. 1923) and then continue to rise before a peak of Pb at 10 cm depth (c. 1990). The initial increase is probably due to the introduction of leaded petrol in New Zealand in the mid 1920s and relates to the development of roads in the catchment at that time, with runoff from the slopes and roads flowing into the lake. New Zealand had one of the highest levels of Pb in petrol in the world (0.84 g/l) prior to 1986, when it was reduced to 0.45 g/l (Taylor 1993). Unleaded petrol was introduced in 1987 and leaded petrol has now been phased out. Another possible source is Pb from old house paints, but whatever the source, urbanisation of the catchment is the factor controlling the Pb increase since the 1920s.

The Zn levels start to rise above background levels at c. 1923 and can be explained by the urbanisation of the catchment and introduction of anodised Al roofing. The degradation and rusting of Zn-plated roofing iron is an important source of Zn pollution. Zn is also found in pesticides and fertilisers (Abraham and Parker 2002) and may be a significant component of this Zn influx to the lake. The Cu spike in the sediments at c. 1934 relates to the influx of CuSO_4 in an attempt to stop the nuisance algal blooms. The cause of the increase in Cu content of the sediments since c. 1957 is unknown but may relate to Cu-based agrochemicals used in surrounding parkland and urban gardens that back onto the lake.

The elemental Na/Al and K/Al ratios suggest that although there is a slight increase in K addition to the lake that may be due to accelerated erosion associated with land use change from forest to farmland after c. 1855, a marked increase in K/Al only occurred after c. 1968 and in Na/Al (and K/Al) after c. 1990. These trends suggest that accelerated erosion due to anthropogenic causes is at most only a minor contributor to the sediment record that has accumulated in Lake Pupuke over the past c. 190 years.

Organic matter geochemistry

The proportion of sedimentary organic matter derived from terrestrial plants and that derived from within a lake can be identified from the difference between TOC/TN ratios of vascular land plants and algae (Meyers 1994, 2003). Increased influx of land plant derived organic matter is recorded as increased TOC/TN ratios, because vascular land plants have TOC/TN ratios >20, whilst algae typically have TOC/TN ratios between 4 and 10. Values between 10 and 20 usually relate to a mixed terrestrial-aquatic source for the organic matter. This difference is likely to be a consequence of the absence of cellulose in algae and its abundance in vascular plants (Meyers 1994; Meyers and Lallier-Vergès 1999). Consequently, increased dominance of autochthonous algal-derived organic matter would result in reduced TOC/TN ratios, whilst elevated TOC/TN ratios would indicate an increased proportion of allochthonous terrestrial organic matter.

The TOC/TN ratio minima at 70 and 30 cm depth (Figure 4) are a reflection of increased algal productivity, probably associated with lake eutrophication. The range in TOC/TN values of between 10 and 14 at most sample intervals in the Lake Pupuke core indicates a mixed terrestrial-aquatic source for the organic matter at most sample depths.

The TOC values also reflect changes in *in situ* lacustrine and terrestrial organic matter biomass, with the peaks of TOC at 65 and 25 cm possibly reflecting increased influx of terrestrial organic matter. The lower TOC percentages at 70 (c. 1845), 55 (c. 1878) and 30 cm depth (c. 1935) indicate the increased dominance of algal

production in the organic matter inventory at those times associated with algal blooms.

Sedimentary organic matter $\delta^{13}\text{C}$ values are affected by rates of algal production in lakes which are controlled by dissolved nutrient availability. Runoff of soil-derived nitrates and phosphates enhances aquatic productivity which selectively removes ^{12}C -rich dissolved inorganic carbon and leads to enriched $\delta^{13}\text{C}$ values in the organic matter produced by the remaining inorganic carbon (Meyers 2003). Hence, the zone of $\delta^{13}\text{C}$ enrichment at 65–60 (c. 1856–1867) and gradual enrichment from 55 to 30 cm (c. 1890–1935) – after which $\delta^{13}\text{C}$ depletion occurs – could reflect phases of enhanced algal productivity as a consequence of anthropogenic nutrient input into the lake. However, the factors that influence the $\delta^{13}\text{C}$ values of lacustrine organic matter are complex with productivity only one of several possible controls that could be involved. Others include: (1) proportion of organic matter from different source organisms, (2) $\delta^{13}\text{C}$ of the carbon substrate used by each source, and (3). post-depositional $\delta^{13}\text{C}$ changes (Street-Perrott et al. 2004). Furthermore, lacustrine organic matter is a complex mix of compounds synthesized by terrestrial plants, aquatic macrophytes, algae and bacteria each of which may differ substantially in their $\delta^{13}\text{C}$ values.

Consequently, bulk organic matter $\delta^{13}\text{C}$ analysis on its own is limited because it does not distinguish between different sources of organic matter entering a lake so that other organic indicators such as TOC/TN or pollen analysis need to be used to identify the organic matter sources (Lamb et al. 2004). In the case of Lake Pupuke, the catchment changed from forest to farmland (mainly dairy farms) in 1850s after the initial settlement of the area in 1845. This change in landuse resulted in accelerated release of soil nutrients and their influx (as well as dairy effluent) into the lake. Subsequent expansion of urban development and livestock populations further increased nutrient delivery to the lake system, enhancing algal growth and forcing the utilization of soil derived HCO_3^- in the lake waters to generate the $\delta^{13}\text{C}$ enrichment during the high aquatic productivity phases.

The increased aquatic productivity apparent from TOC/TN ratios and $\delta^{13}\text{C}$ at c. 1833–1845 and at and after c. 1935 was not accompanied by greater influx of clastic sediments as is indicated by the reduction in mean grain size at those depths as

well as the reduction in percentage of sediment $> 63\ \mu\text{m}$ and increase in sediment $< 10\ \mu\text{m}$ size (Figure 4). The finer grain size of the sediment is consistent with increased algal productivity and minimal inwash of both clastics and terrestrial-sourced organic matter. The reduction in sediment grain size from 70 to 30 cm depth in the core is consistent with the increased algal productivity and increase in lake eutrophication, with the dominance of sediment $< 10\ \mu\text{m}$ size at c. 1935 a direct consequence of the algal blooms associated with copper sulphate addition to the lake.

Diatom changes

The inferred increase in algal productivity is further supported by the diatom record which shows a dramatic change from the *Cyclotella stelligera*-dominated flora prior to c. 1845 to one dominated by increasingly eutrophic taxa after this time. Similarly, the diatom-inferred reconstructed DRP, TP, pH and Chl *a* values all increase after c. 1845, with DRP and TP peaking at c. 1950, while Chl *a* peaks during the mid 1970s (Figure 6). Interestingly, elemental P measured in the sediments shows a similar pattern to that of the diatom-inferred reconstruction, although the peak for elemental P occurs earlier at c. 1935. This difference may be a consequence of the high resolution sampling for the geochemical analyses, that is, the peak is not ‘captured’ by the diatom-inferred P records. It is also possible that the elemental P record under-estimates water column P after c. 1935 as a result of post-depositional mobility of P, a common process in stratified eutrophic systems when hypolimnetic anoxia develops (Engstrom and Wright 1984; Boyle 2001). We also note that disparities between elemental P measurements and diatom-inferred P may reflect errors in the reconstructions. Estimates of model performance for diatom-inferred TP and DRP (Reid 2005) showed that these models performed only moderately well compared with those for Chl *a*.

Increased nutrient loadings associated with changing land use in the catchment after European settlement in the Auckland region appears to be the dominant control on the diatom assemblages. The lake was used as the North Shore Auckland’s water supply from 1895. However, by 1924 it proved to be inadequate with many houses

discharging sewerage into the lake (Cassie 1989). In particular, high ammonia and sulphide values were recorded between 1925 and 1940, whilst large amounts of oil contaminating the water supply, as well as taste and odour problems associated with the dinoflagellate *Ceratium hirundinella*, prompted the authorities in 1933, 1934 and 1938 to use large doses of copper sulphate to control noxious algal blooms (Vant et al. 1990).

The lake water quality measurements also indicate that the lake is now less eutrophic than it was in 1966–1967 and that it is probably in better condition than it was in the 1930s when domestic and agricultural wastewaters were uncontrolled and nuisance outbreaks of phytoplankton occurred (Vant et al. 1990). The concentration of Chl *a* in near surface waters for example, fell from 22 mg/m³ in 1966–1967 to less than a third of this in 1982–1990 (average 5.7 mg/m³) (Vant et al. 1990), although measurements taken over the period from 1992 to 1996 show Chl *a* increased slightly to average 6.1 mg/m³ (Burns and Rutherford 1998). In the case of nutrients, dissolved nitrogen species (NO₃, and NH₄) levels in the near surface waters have fallen from 45 to 16 mg/m³ from 1966 to 1990 and have fluctuated around this level until the present (Burns and Rutherford 1998; M. Reid, unpublished data). Dissolved reactive P (DRP) and total P averaged 3 and 15 mg/m³ respectively and varied with no trend apparent over the period 1976–1990 (ARWB 1990). However, slight declines are apparent since 1990, with the five-year averages for 1992–1996 being 1.4 and 11 mg/m³ for DRP and TP respectively (Burns and Rutherford 1998). The improvement in lake water quality is also indicated by reduction in the rate at which dissolved oxygen is consumed in the bottom waters in the summer in the layer of water 20–30 m deep during 1984–1986 was less than half of that observed in 1966–1967. At the same time plant nutrient concentrations may have decreased – nitrate and ammonia were apparently 3–12 times higher in 1966–1967 than 1976–1990 (Vant et al. 1990).

Hence, the historical data available for the period covered by the two upper-most core samples (Barker 1967, 1970; Burns and Rutherford 1998; Vant et al. 1990; M. Reid unpublished data) are largely in accord with the diatom record and the diatom-inferred estimates for phosphorus and Chl *a* (Figure 6). According to the historical data,

productivity in Lake Pupuke peaked around the mid-1960s and declined thereafter up until 1990 (Vant et al. 1990) after which time DRP and TP have further declined while Chl *a* increased slightly from 1992 to 1996 (Burns and Rutherford 1998). These trends match well those evident in the reconstructed records. Moreover, measurements taken during 1995–1996 show that DRP (2.0 mg/m³), TP (11.3 mg/m³), Chl *a* (8.3 mg/m³) and pH (8.7) compare well with reconstructed DRP (2.7 mg/m³), TP (22.5 mg/m³), Chl *a* (7.7 mg/m³) (all back-transformed) and pH (8.0). However, without higher resolution sampling of the sediments deposited during this recent period it is difficult to judge the accuracy of the diatom-inferred Chl *a* and phosphorus records except in very general terms. Thus, the use of these quantitative measures to infer baseline pre-European Chl *a* and phosphorus concentrations in Lake Pupuke awaits further testing of the models.

Conclusions

Changes in sediment geochemistry and paleoecology inferred from sediments, sedimentary organic matter and microfossil remains deposited since c. 1813 AD in Lake Pupuke directly reflect the late Polynesian environment, and subsequent changes in landuse in the catchment following European settlement in the 1840s. The onset of European impacts on the lake and catchment was clearly indicated by the appearance of European pollen types and diatom assemblages, with oligotrophic conditions apparent in the lake pre-1840. Clearing in the catchment, accompanied by phosphorus and nitrate influx to the lake associated with farming and uncontrolled addition of animal effluent, generated eutrophic conditions and high levels of algal productivity as indicated by diatom, pollen, TOC/TN ratios, TOC and $\delta^{13}\text{C}$ changes. In particular, the proxies identify high productivity phases from c. 1935 to c. 1957 after which algal productivity commensurate with lake nutrient status reduced and the lake returned to a mesotrophic state.

Anthropogenic Pb and Zn are only detected after c. 1923, and closely reflect the progressive development of the catchment with development of the roading network and expansion of housing. The diatom-derived transfer functions, sediment

geochemistry and organic matter geochemistry described in this study reflect sensitively changes in Lake Pupuke and its catchment. Similar multiproxy studies of anthropogenic impacts on lacustrine environments should be undertaken on other New Zealand lakes as long-term lake monitoring data is rarely available, and this information is essential for informed management of the lake ecosystems.

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