



NIWA

Taihoro Nukurangi

Lake Horowhenua sediment legacy

Prepared for Horizons Regional Council

November 2019

Prepared by:
Piet Verburg
Max Gibbs
Anathea Albert
Greg Olsen


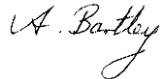

For any information regarding this report please contact:

Piet Verburg
Lake Scientist
Freshwater Ecology
+64-7-856 1787
piet.verburg@niwa.co.nz

National Institute of Water & Atmospheric Research Ltd
PO Box 11115
Hamilton 3251

Phone +64 7 856 7026

NIWA CLIENT REPORT No: 2018245HN
Report date: November 2019
NIWA Project: HRZ18204

Quality Assurance Statement		
	Reviewed by:	Chris Hickey
	Formatting checked by:	Alison Bartley
	Approved for release by:	Cindy Baker

© All rights reserved. This publication may not be reproduced or copied in any form without the permission of the copyright owner(s). Such permission is only to be given in accordance with the terms of the client's contract with NIWA. This copyright extends to all forms of copying and any storage of material in any kind of information retrieval system.

Whilst NIWA has used all reasonable endeavours to ensure that the information contained in this document is accurate, NIWA does not give any express or implied warranty as to the completeness of the information contained herein, or that it will be suitable for any purpose(s) other than those specifically contemplated during the Project or agreed by NIWA and the Client.

Contents

Executive summary	6
1 Introduction	7
1.1 Background	7
1.2 Objectives	7
2 Methods.....	10
2.1 Sediment sample collection.....	10
2.2 Analysis of P, N, Al, Fe and Mn	12
2.3 Sediment ages and sediment accumulation rates.....	12
2.4 Estimation of total N and P and C mass per unit area across the lake	13
2.5 Proportions of phosphorus.....	13
2.6 Determination of N and P accumulation rates	13
2.7 Determination of the sources of sediment by inflow stream and estimation of yields of sediment, N and P by sub-catchment	13
2.8 Stable isotopes of carbon and nitrogen.....	14
2.9 Heavy metals.....	14
2.10 Source proportion modelling using CSSI and bulk $\delta^{13}\text{C}$	14
3 Results and Discussion	16
3.1 Moisture and sediment density.....	16
3.2 Loss on Ignition: organic matter	19
3.3 Phosphorus and nitrogen	20
3.4 Al, Fe and Mn	27
3.5 Heavy metals.....	30
3.6 Core dating and sediment accumulation rates.....	32
3.7 CSSI source tracking.....	37
3.8 Bulk stable isotope signatures of organic matter in the lake sediment	40
3.9 Accumulation of N and P and cumulative N and P by depth.....	42
3.10 Sub-Catchment yields	44
3.11 Dissolved oxygen, DRP and algal chlorophyll <i>a</i>	45
4 Discussion	46
4.1 The sediment issue	46
4.2 Heavy metals.....	54

5	Conclusions and Summary	55
6	Acknowledgements	55
7	References.....	56

Tables

Table 1:	Positions of sediment core sites in the lake (cf. Figure 1).	10
Table 2:	Number of cores taken to collect the required amount of sediment of sections at indicated depths, using the 84 mm inner diameter gravity core.	12
Table 3:	Percent moisture downcore at each core site.	16
Table 4:	Sediment dry weight, per unit volume and per unit area.	18
Table 5:	Phosphorus contents (g kg^{-1} dry weight) at different depths in the sediment at four sites.	21
Table 6:	Phosphorus content (g m^{-2}) in the sediment in layers of 1 cm deep at different depths at four sites.	22
Table 7:	Nitrogen content (g kg^{-1} dry weight) at different depths in the sediment at four sites.	23
Table 8:	Nitrogen content (g m^{-2}) in the sediment in layers of 1 cm deep at different depths at four sites.	24
Table 9:	Nitrogen to phosphorus ratio (by weight) at different depths in the sediment at four sites.	25
Table 10:	Total aluminium (g kg^{-1} dry weight) in the sediment, at different depths at four sites.	27
Table 11:	Total manganese (g kg^{-1} dry weight) in the sediment, at different depths at four sites.	28
Table 12:	Total iron (g kg^{-1} dry weight) in the sediment, at different depths at four sites.	28
Table 13:	Concentrations (mg kg^{-1} dry weight) of heavy metals in the lake sediment at depths of 40-41 cm, 20-21 cm, and 0-2 cm (duplicates).	31
Table 14:	Depth-date table for cores from all four sites.	36
Table 15:	Carbon stable isotope data for the sources and sediment core from site 1.	38
Table 16:	Soil source proportions produced for different depths in the sediment from the core at site 1.	40

Figures

Figure 1:	Lake Horowhenua site map showing the three types of sampling sites.	10
Figure 2:	Percent moisture in the sediment at 4 sites.	17
Figure 3:	Dry weight of sediment per unit volume.	19
Figure 4:	Organic matter in the sediment.	20
Figure 5:	Depth profile of TP and TFe at site 1 in March 2011.	21
Figure 6:	Phosphorus and nitrogen concentrations in the sediment.	26
Figure 7:	The N:P ratio, by weight, in the sediment.	26

Figure 8:	Concentrations in the sediment of Al, Mn and Fe, and their ratios to P, by weight.	29
Figure 9:	Ratios by weight in the sediment of Fe:Mn.	30
Figure 10:	Sediment dating results.	32
Figure 11:	Sediment ages.	34
Figure 12:	Sediment accumulation rates in the central lake core (buoy core).	35
Figure 13:	Construction of a large shallow sediment trap beside the Arawhata Stream.	37
Figure 14:	Selection of the best isotopic tracers using polygons.	39
Figure 15:	Bar graph of soil proportions showing the relative proportion changes in soil sources contributing to the sediment at site 1.	40
Figure 16:	Bulk stable isotope signatures of organic matter in the lake sediment.	41
Figure 17:	Accumulation of P and N in the lake sediment.	42
Figure 18:	Nutrient accumulation in the sediment by year.	42
Figure 19:	Sub-catchment yields of P and N.	44
Figure 20:	Dissolved oxygen in water near the bottom, dissolved phosphorus and chlorophyll <i>a</i> .	45
Figure 21:	Spatial distribution of TP (g kg^{-1} DW) across Lake Horowhenua from surface sediment samples collected in 2017.	47
Figure 22:	Queen Street drain in flood September 1988.	48
Figure 23:	Spatial distribution of TP concentrations across Lake Horowhenua in A) 1988 and B) 2017 with stylised contours between iso-concentrations (g kg^{-1} dry weight).	51
Figure 24:	Map of Lake Horowhenua with a 1 ha grid overlay as used by Horizons Regional Council to plan weed harvesting areas.	52
Figure 25:	Trial dredging on Lake Horowhenua on 10th February 1989.	53

Executive summary

This report provides information for the Te Mana o Te Wai / Lake Horowhenua Trust report for MfE, and carries out a comprehensive scientific assessment of lake bed sediment state and extraction options, risks and opportunities to inform the next iteration of the Lake Accord Action Plan.

Included are 1) a review of the available data and information to identify gaps that need to be filled, and 2) an assessment of the legacy of sediment and nutrient inputs to the lake from sewage and other sources. We identify the opportunities to address these in response to the regular questions from iwi and the community about the legacy issue.

This project comes under the overarching project entitled Te Kakapa Manawa o Muaupoko – The heartbeat of Muaupoko and is part of the MfE funded contract for Te Mana o Te Wai / Lake Horowhenua.

Earlier core work suggested that the sediment around 40 cm depth may date from the end of the period during which sewage was being discharged into the lake (1952-1987) and thus would reflect 35 years of P accumulation in the lake sediments from the sewage effluent input. However, sediment core dating using radioisotopes Pb-210 and Cs-137 suggested that at a central lake site sediment of the period of sewage inputs to the lake is located at 12.5 – 28 cm depth, and that the P concentration (g kg^{-1}) was in fact lower at those depths than near the sediment surface. Sediment accumulation rates in the central area of the lake increased around 1960, to about 12 mm y^{-1} , from about 1 mm y^{-1} prior to 1960. After the 1960s sedimentation rates were about 4 mm y^{-1} .

Extrapolated to the lake wide surface area, the accumulation of P in the sediment was 0.5 t y^{-1} before 1960, about 4 t y^{-1} in the 1960s and 1.3 t y^{-1} from 1980 onward. The accumulation of N in the sediment was 5.5 t y^{-1} before 1960, about 65 t y^{-1} in the 1960s and declining from 23 t/y in 1980 to a present 12 t y^{-1} . However, these numbers are driven mainly by changes in the estimated sediment accumulation rate and not by concentrations in the sediment. The presence of a peak in P and N accumulation in the 1960s depends on whether or not a higher sediment accumulation rate is distinguished in the 1960s, based on evidence from limited data for such a higher sediment accumulation rate. When a single sediment accumulation rate is used since 1960 (sediment depths 0-30 cm in the centre of the lake) there was no pronounced peak in the 1960s in the accumulation per year of P and N, although from 1960 onward it was substantially higher compared with the low accumulation rates before the 1960s.

Analysis of the compound specific stable isotopes in a sediment core from the central lake site determined that the primary sources of sediment entering Lake Horowhenua are from the Arawhata Stream catchment, associated with horticulture and cropping, and from the Mangaroa Stream catchment associated with intensification of dairy farming in recent years.

Based on the depth distribution of nutrient concentrations in the sediment and other considerations, there is not much reason to expect a positive outcome from removal of sediment by dredging in the lake. The best strategy to improve the water quality in the lake is to reduce nutrient inputs as much as possible. It is to be expected that nutrient concentrations in the lake will slowly decline over time, as nutrients cycle from the sediment and are flushed out of the lake via the outlet.

1 Introduction

1.1 Background

This project comes under the overarching project entitled Te Kakapa Manawa o Muaupoko – The heartbeat of Muaupoko and is part of the MfE funded contract for Te Mana o Te Wai / Lake Horowhenua.

Legacy sediment is defined as the sediment that has been retained in the lake over time from land runoff. It includes the effects of land use change associated with forest clearance and conversion to pastoral farming as well as horticulture and cropping.

While the focus of this project is the sediment legacy in Lake Horowhenua, the sediment is closely linked to the nutrient legacy in the sediments, especially phosphorus (P). Of specific interest is the legacy of P in the sediments from the discharge of treated waste water effluent into the lake between 1952 and 1987, and how this P affects lake processes, such as blue-green algal blooms.

The legacy timeline does not preclude assessment of contemporary sources such as sediment and nutrients from horticulture and cropping, which have intensified in recent years.

A weir was installed on the outflow in 1956 which may have affected sedimentation rates.

Although there was some pollution before the 1950s from sewage effluent entering the lake by seepage, from 1952 to 1987 effluent from Levin's sewage treatment plant entered the lake in significant quantities (Waitangi Tribunal Report 2017). From 1969 to 1987, treated effluent was discharged directly into the lake (Waitangi Tribunal Report 2017), to the east of Makomako Road drain (Figure 1). The discharge of sewage into the lake ended in 1987, although on occasion sewage has spilled into the lake after 1987 (Waitangi Tribunal Report 2017). A sediment core taken in 2011 (Gibbs 2011) showed a maximum P concentration of around 1.7 g P kg^{-1} dry weight sediment at a depth of around 35 cm at the central lake site. This P concentration is comparable with the P concentration in an earlier core collected by Currie et al. (1978), which showed a maximum phosphorus concentration of around 1.9 g P kg^{-1} dry weight in the surface layer of a sediment core collected in 1977-1978. Gibbs (2011) considered this to suggest that the sediment P concentration observed at 35 cm depth most likely marked the end of the sewage input, and inferred an increase in sediment level by 35 cm over the period 1987 to 2011, or a SAR of 14 mm y^{-1} .

1.2 Objectives

This report 1) identifies what has been done and what needs to be done to complete the Te Mana o Te Wai / Lake Horowhenua report for MfE, and 2) carries out a comprehensive scientific assessment of lake bed sediment state and extraction options, risks and opportunities to inform the next iteration of the Lake Accord Action Plan.

Included are 1) a review of the data and information that has been already collected to identify gaps in the data that need to be filled, and 2) an assessment of the legacy of sediment and nutrient inputs to the lake from sewage and other sources. We identify the opportunities to address these in response to the regular questions from iwi and the community about the legacy issue.

We answer the following questions about the sediment legacy in Lake Horowhenua (as in the project brief):

(I) Collation and interpretation of existing data

Identify what has been done and what needs to be done to complete the Te Mana o Te Wai / Lake Horowhenua report for MFE.

(II) The sediment issue

The main questions to be addressed are:

1. What is the impact of sediment on the lake?
 - a) What are the infilling rates (SAR) across the lake?
 - Is there a difference in SAR spatially across the lake?
 - Have the SAR changed over time?
 - b) What is the effect of the sediment on the water quality in the lake?
 - Is turbidity increasing as the lake becomes shallower?

2. Should the sediment be removed or should it be left alone?
 - a) Why would the sediment need to be removed?
 - Is the rate of sediment accumulation sufficient to cause concern (turbidity issues)?
 - What are the benefits?
 - What are the disadvantages?
 - b) What is the risk to the lake ecosystem of disturbing the sediments during removal?
 - What is the risk of the lake becoming permanently turbid?
 - c) What chemicals would be released from the sediments during removal?
 - Would chemicals such as sulphides be released into the lake water?
 - d) What effect would sediment removal have on the benthic biota and plant communities in the lake?
 - How would the benthic habitat change affect benthic biota and aquatic plant communities in the lake?

3. If the sediment should be removed:
 - a) How much sediment should be removed and to what depth?
 - Would the sediment be removed as a layer across the whole lake or just a part of the lake?
 - How would the area of sediment to be removed be identified?
 - Would the sediment to be removed be the soft surface mud only without disturbing the buried P layer below 30cm?
 - Would a deeper layer of 50 cm depth be more effective by removing the buried P layer?

4. If the sediment is not to be removed:
 - a) Where does the sediment come from?
 - Identify soil sources in lake sediments using compound specific stable isotope (CSSI) and fallout radionuclide (FRN) techniques

b) What actions are required to reduce sediment inputs to the lake?

- Sediment trap efficiency?
- On farm mitigation / management plans?
- Drainage upgrade and maintenance?
- Others?

In addition, the following questions are addressed, either from the new data provided by the work carried out for this report, or from other, yet unpublished work:

- How much P is there in the lake sediment?
- How fast do sediment and nutrients accumulate in the sediment?
- Is the P concentration in the sediment and the P accumulation rate increasing or decreasing?
- How much of the P inputs are sequestered in the sediment?
- Where in the catchment are the sediment and the nutrients coming from?

2 Methods

Lake Horowhenua has a surface area of about 2.9 km² and a mean depth of 1.3 m.

2.1 Sediment sample collection

Sediment samples were collected from multiple locations in Lake Horowhenua (Figure 1) during July 2017 (sites A-R) and March 2018 (all other sites).



Figure 1: Lake Horowhenua site map showing the three types of sampling sites. Four core sites (1-4), 17 surface sediment sites (A-R), and the 7 inflow sediment sites (Pa drain was not sampled). The central site at the buoy (site 1) is indicated by the red circle. Sites A, C, and K correspond to sampling sites 2, 3 and 4 for the sediment cores.

Core samples were collected at the buoy site (site 1), and at sites A, C and K (Figure 1; Table 1). Sediment samples at seven inflow locations (Figure 1) was collected for compound specific stable isotope analysis (CSSI).

Table 1: Positions of sediment core sites in the lake (cf. Figure 1).

	Site 1 (at buoy)	Site 2 (A)	Site 3 (C)	Site 4 (K)
Latitude	-40.61069	-40.61699	-40.61416	-40.60621
Longitude	175.24904	175.24538	175.25466	175.25924

The depth into the lake sediment to which the 84 mm diameter gravity corer could be pushed was limited. At site 1 the corer collected sediment down to 51 cm, and at sites 2-4 down to 41 cm, with sections collected at specific depths (Table 2). To collect sediment below those depths, a 48 mm Livingstone corer was used, once at each of the four sites, to 100 cm depth. At site 2, sediment began to turn sandy from about 50 cm, and by 60 cm was completely sand, and it was not possible to collect sediment >66cm deep, because the sand was too solid to allow the corer to penetrate. Multiple cores were collected at each core site (Table 1) and combined to obtain enough sediment for the analyses. An additional core taken at site 1 with the 84 mm gravity corer down to 51 cm depth was sectioned every 1 cm. These 51 sections of the latter core were prepared and analysed only for radioisotope dating (section 2.3).

A surface sediment sample (0-2 cm thick) was also collected from each of the 4 core sites and from the mouth of each of the 7 main surface water inflows (Arawhata Stream, Hokio Sand Road drain, Makomako Road drain, Queen Street drain, Patiki Stream, Mangaroa Stream, Domain drain).

Apart from the upper 0-2 cm of sediment, the sediment cores were sectioned into slices of 1 cm thick (sections at 3-4, 5-6, 7-8, 10-11, and every 5 cm further down to 100 cm depth). Whole sections were weighed to determine wet weight and density. These sections were then freeze dried and subsample wet weights and dry weights determined. The sections from each depth in the site 1 core were processed for radiometric dating and analysed using alpha spectroscopy. Separate subsamples from each section of core 1 and the surficial sediments from the 7 inflow sites, were processed for sediment source determination using the CSSI technique. Additional analyses of the site 1 core sections included % carbon (C), % phosphorus (P) and % nitrogen (N) content. Stable isotopes of organic carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$). CSSI analyses were analysed in the sediment from the core collected at the centre lake position, and with the surface sediment samples collected in the lake inflows. All other analyses were performed on each of the four sediment cores.

The average moisture content in the near surface sediment expected from preliminary results was slightly over 90%, and the average dry weight per 1 cm section about 5 grams, using a sediment core pipe with 84 mm inner diameter. The total dry weight needed to carry out all analyses was about 140 grams for the centre lake core site and 90 grams for the remaining three core sites, per section. Therefore, it was necessary to collect about 30 sediment cores from the central site, and 20 sediment cores from each of the three remaining sites to provide sufficient dried sample mass for analysis, for a total of about 90 sediment cores. The sediment from the 15 depth sections in each of these cores were combined, separate for each core site, to get a total of 60 samples (15 depth sections from 4 core sites).

The proportion of organic matter was determined as loss on ignition (LOI) by combustion at 500°C of dried sediment, as the difference in weight before and after combustion.

Table 2: Number of cores taken to collect the required amount of sediment of sections at indicated depths, using the 84 mm inner diameter gravity core. In addition, a 48 mm inner diameter Livingstone corer was used down to 100 cm depth, 1 core per site. Note: top section is 2 cm, and deeper sections are 1 cm. Deeper into the sediment fewer cores were needed because of lower water contents and higher dry weights per section, providing more sample for analysis. An additional core taken with the 84 mm gravity corer down to maximum 51 cm depth was sectioned every 1 cm depth increment. See Figure 1 for site locations.

Section depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	12	6	6	6
3-4	15	6	6	8
5-6	15	5	5	8
7-8	10	5	5	8
10-11	12	5	5	8
15-16	10	4	4	8
20-21	10	4	4	7
25-26	9	3	3	6
30-31	8	3	3	6
40-41	7	3	3	6
50-51	2			

2.2 Analysis of P, N, Al, Fe and Mn

Sediment

Total recoverable phosphorus was analysed by Hill Laboratories using a dried and sieved sample, on an ICP-MS, after nitric/hydrochloric acid digestion (detection limit 0.04 g kg⁻¹ dry weight). Total nitrogen was analysed on a Thermal Conductivity Detector [Elementar Analyser], after catalytic combustion (900°C, O₂) and separation (detection limit 0.5 g kg⁻¹ dry weight). Total recoverable aluminium (detection limit 10 mg kg⁻¹ dry weight), total recoverable iron (detection limit 40 mg kg⁻¹ dry weight), and total recoverable manganese (detection limit 1.0 mg kg⁻¹ dry weight) were analysed using a dried and sieved sample, on an ICP-MS, after nitric/hydrochloric acid digestion.

Macrophyte

A single sample of macrophyte material (*Potamogeton crispus*) was analysed by Hill laboratories for phosphorus content by ICP-OES, after nitric and hydrochloric acid micro digestion and filtration (detection limit 0.02 g kg⁻¹ dry weight), and for nitrogen content using Dumas combustion (detection limit 0.2 g kg⁻¹ dry weight).

2.3 Sediment ages and sediment accumulation rates

Sediment age and sediment accumulation rates were determined using radiometric techniques, with sediment cores collected at the 4 core sites. At site 1, the central lakes site, two cores were collected for analysis, one labelled as buoy core, the other as site 1. Sediment (2 grams) of the 51 sections from the sediment cores collected at the four core sites was submitted to the University of Ottawa for radiometric dating, using alpha spectroscopy to measure Pb-210 (²¹⁰Pb). Unsupported Pb-210 was reported by the laboratory. Total Pb-210, together with Cs-137 and Ra-226 data, was also obtained down core using gamma spectrometry (at the Environmental Radioactivity Laboratory, Institute of

Environmental Science and Research Limited) from the core collected at the central buoy site. Unsupported Pb-210 was estimated by deducting Ra-226 activity from total Pb-210. Sediment accumulation rates (SAR) were determined from linear regressions through semi-log plots of unsupported Pb-210 versus depth, following methods outlined by Pennington (1975), Appleby and Oldfield (1978), Appleby and Oldfield (1983), and Wren et al. (2016). Sediment age was estimated from the SAR for each core and sediment section depth.

2.4 Estimation of total N and P and C mass per unit area across the lake

The percent moisture content was determined, in each of the 15 core sections, from the ratio of dry weight to wet weight by freeze drying a subsample (5 grams), taken after thorough mixing of the complete sediment content of a core section. Loss on ignition (LOI) was then determined in the dried sample by combustion at 450°C to give the proportion of organic matter. The proportion of organic carbon was estimated as 47% of the weight of organic matter (Périé and Ouimet 2008).

Dried sediment samples (20 grams) were submitted to Hill Laboratories for analysis of % total N and total P. Total N and total P mass per unit area for each sediment core section were estimated as the percent N and P in each sediment core section multiplied by the total wet weight in each section multiplied by the subsample dry : wet weight ratio. The total N and P mass per unit area was then calculated by integration down to the deepest depth analysed in the sediment cores, and averaged between the four sediment cores to obtain the average across the lake.

Sediment was also analysed for concentrations of aluminium (Al), iron (Fe), and manganese (Mn) which affect binding of P in the sediment. Analysis of Al, Fe and Mn in the sediment was carried out by Hill laboratories.

2.5 Proportions of phosphorus

In July 2017 sediment was collected from the upper 1 cm at 17 sites (A to R) across the lake (Figure 1) and analysed for total P and total N.

2.6 Determination of N and P accumulation rates

N and P accumulation rates, and how they changed over time, were calculated from the SAR resulting from the radiometric data, by multiplying with the volumetric proportions of total N and P measured in the sediment from the sections in the cores at the 4 sites.

2.7 Determination of the sources of sediment by inflow stream and estimation of yields of sediment, N and P by sub-catchment

In order to determine the source proportions of the soil in the lake sediment, samples of surficial sediment from the lake and the deltas of the 7 inflow streams were analysed using the compound specific stable isotope (CSSI) technique. CSSI sample analysis was also carried out on each of the 15 selected sections from the site 1 core.

The sediment yield and proportional contributions of N and P to the lake from each sub-catchment were estimated from the CSSI results and the N and P concentrations in the sediment. These estimates were compared with output from the catchment model CLUES.

Wet sediments for CSSI extractions were homogenised, freeze dried and sieved at 500 µm. Each dried sieved sediment was extracted with dimethyl chloride (DMC) at 100°C at 2000 psi in a DIONEX ASE200 accelerated solvent extraction system using two 5 minute extraction cycles and combining the extracts. The extract was concentrated and methylated using 5% boron trifluoride (BF₃) catalyst in pure methanol to generate fatty acid methyl esters (FAMES) prior to analysis by GC-combustion-IRMS at the Environmental Stable Isotope Laboratory of the National Institute of Water and Atmospheric Research (NIWA) in Wellington. A subsample of the dried sediment was also acidified with 10% hydrochloric acid to remove inorganic carbonates and freeze dried prior to analysis for bulk δ¹³C. The bulk sediment analysis also produced %C, δ¹⁵N and %N values (section 2.8). A sample of the dominant macrophyte (*Potamogeton crispus*) was also prepared for CSSI analysis.

2.8 Stable isotopes of carbon and nitrogen

Aliquots (~10 mg) of dried sediment were analysed for stable isotopes of bulk organic carbon (δ¹³C) and nitrogen (δ¹⁵N) on a continuous flow, isotope ratio mass spectrometer (IRMS). Those to be analysed for δ¹³C were first acidified to remove inorganic carbonates. Isotope ratios are expressed in delta (δ) notation as δ¹³C or δ¹⁵N which have units of per mil (‰), relative to a standard, by $([R_{\text{sample}}/R_{\text{standard}}] - 1) \times 1000$, where R is the ratio ¹³C:¹²C or ¹⁵N:¹⁴N. The standard for carbon was referenced to PeeDee belemnite carbonate and the nitrogen isotopic ratio was referenced to atmospheric nitrogen gas (N₂). Analytical working standards (DL Leucine or flour) were inserted on average every three samples. Standard deviations for the standards were ±0.2‰ for δ¹⁵N and ±0.1‰ for δ¹³C. The stable isotope data also returned data on the %C and %N content of each sample.

2.9 Heavy metals

The concentrations of heavy metals, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), silver (Ag), nickel (Ni) and zinc (Zn), were determined in dried and sieved lake sediment from the central buoy site at depths 0-2 cm (in duplicate), 20-21 cm and 40-41 cm. These metals have atomic mass ranging from 52 (chromium) to 207 (lead). The metals with atomic mass heavier than 50 are regarded as heavy metals (Vodyanitskii 2016). The analysis was carried out by Hill laboratories on an ICP-MS (detection limits 0.010-0.4 mg kg⁻¹), after nitric/hydrochloric acid digestion, and expressed in mg kg⁻¹ dry weight. The reported uncertainty is an expanded uncertainty with a level of confidence of approximately 95 percent (i.e., two standard deviations, calculated using a coverage factor of 2). Reported uncertainties were calculated from the performance of typical matrices, and do not include variation due to sampling. However, to include some indication of sample variation, duplicate samples were analysed of the surface sediment (top 0-2 cm).

2.10 Source proportion modelling using CSSI and bulk δ¹³C

To determine the proportional contribution of land use soils in the sediment (the mixture) at different locations in Lake Horowhenua, the CSSI and bulk δ¹³C data from the inflow streams were used as the source data in a stable isotopic mixing model (SIMM) following best practices (Phillips et al. 2014).

Mixing models are statistical tools that use biotracers such as fatty acids and stable isotopes to probabilistically estimate the contribution of multiple sources to a mixture. They examine the data using a Monte Carlo simulation of mixing polygons to provide a quantitative basis for model rejection and exclusion for sediment samples which violate the point-in-polygon assumption i.e., the mixture must lie within the bounds of a polygon of straight lines drawn through and linking the extreme source values to be used in the SIMM. The simplest model is IsoSource (Phillips and Greg 2003),

which is a number-crunching process that multiplies all possible combinations of the source values, then selects the numerical combinations that are closest to the mixture values. Where there is sufficient data for statistical analysis (three or more replicates), a Bayesian model with a Markov chain Monte Carlo (MCMC) model fitting using “SIAR” (Stable Isotope Analysis in R) can be used. This type of SIMM (e.g., MixSIAR) produces simulations of plausible values, therefore representing a true probability density for the proportional contribution of source soils in the mixture tested (Stock and Semmens 2015).

Essentially there is no difference between the results from IsoSource and the Bayesian SIMMs and any of the SIMMs can be used to estimate plausible source contributions in the sediment mixture from the bed of the lake (Mabit et al. 2018). In this study we used IsoSource.

3 Results and Discussion

3.1 Moisture and sediment density

Moisture content was high, with especially fluid mud near the surface (Table 3; Figure 2). Only at site 2 below the depth where the sediment became sandy (>55 cm) moisture content dropped down to less than a third of that at the muddy surface. Sediment dry weights are in Table 4 and Figure 3.

Table 3: Percent moisture downcore at each core site. Site 2 began to turn sandy below 50 cm and by 60cm was completely sand, and because of difficulty to push in the corer no sediment was collected >66 cm deep at site 2.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	91.88	91.72	91.79	92.74
3-4	90.15	88.62	89.77	90.35
5-6	89.39	87.77	88.44	89.55
7-8	88.40	87.11	87.63	88.63
10-11	88.02	84.71	87.80	87.87
15-16	87.05	86.19	87.40	86.90
20-21	86.85	83.32	87.57	86.47
25-26	86.51	83.97	87.86	86.37
30-31	85.30	82.39	87.80	84.71
35-36	87.15	81.62	85.85	83.46
40-41	87.00	82.23	86.28	83.69
45-46	86.50	82.08	85.51	82.15
50-51	86.45	72.00	87.02	82.71
55-56	86.08	57.62	86.46	82.04
60-61	86.49	33.06	85.91	82.34
65-66	86.73	27.35	85.75	83.87
70-71	86.20		86.13	82.26
75-76	86.32		85.69	82.15
80-81	87.61		85.99	82.87
85-86	86.76		82.00	82.63
90-91	87.02		81.12	81.86
95-96	85.98		81.46	80.92
99-100	85.91		82.56	81.39

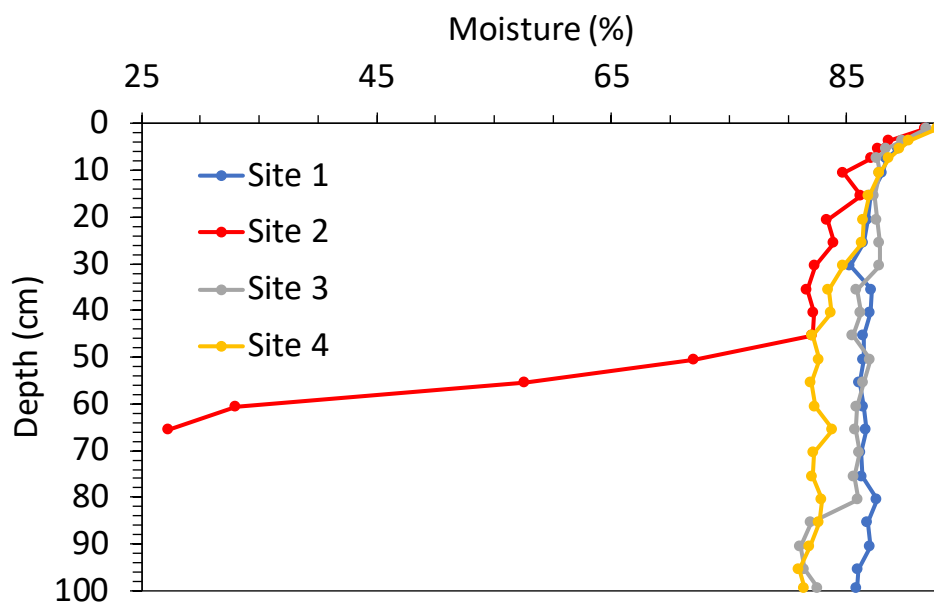


Figure 2: Percent moisture in the sediment at 4 sites.

In surface samples (0-2 cm) the densities (wet weights) were 0.81-0.89 g cm⁻³. Densities <1 g cm⁻³ suggest some material, likely mostly water, was lost during collection. The data of percent moisture, that feed into sediment aging models, were adjusted for these surface samples, assuming density = 1 g cm⁻³.

Table 4: Sediment dry weight, per unit volume and per unit area. Dry weight per unit area is per layer of 1 cm deep.

Depth (cm)	Dry wt (g cm ⁻³)	Dry wt (g cm ⁻³)	Dry wt (g cm ⁻³)	Dry wt (g cm ⁻³)	Dry wt (g m ⁻²)	Dry wt (g m ⁻²)	Dry wt (g m ⁻²)	Dry wt (g m ⁻²)
	Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
0-2	0.07	0.07	0.07	0.06	723	690	680	588
3-4	0.11	0.12	0.11	0.11	1087	1183	1089	1053
5-6	0.11	0.13	0.12	0.11	1113	1348	1182	1076
7-8	0.13	0.14	0.13	0.12	1276	1435	1332	1213
10-11	0.13	0.16	0.13	0.13	1322	1629	1312	1296
15-16	0.15	0.13	0.14	0.14	1455	1304	1369	1407
20-21	0.14	0.17	0.14	0.14	1410	1738	1358	1392
25-26	0.15	0.16	0.12	0.12	1459	1621	1222	1242
30-31	0.16	0.18	0.14	0.18	1560	1804	1367	1760
35-36	0.14	0.21	0.15	0.18	1366	2091	1468	1758
40-41	0.13	0.22	0.16	0.17	1316	2161	1637	1730
45-46	0.12	0.16	0.15	0.20	1197	1571	1461	2004
50-51	0.13	0.36	0.14	0.23	1287	3615	1429	2277
55-56	0.17	0.55	0.16	0.21	1680	5504	1634	2091
60-61	0.14	1.19	0.16	0.22	1391	11853	1562	2175
65-66	0.14	1.39	0.15	0.15	1446	13901	1533	1517
70-71	0.13		0.16	0.19	1329		1615	1886
75-76	0.14		0.16	0.22	1394		1593	2212
80-81	0.12		0.18	0.21	1152		1793	2052
85-86	0.14		0.24	0.17	1400		2371	1709
90-91	0.12		0.25	0.19	1153		2521	1937
95-96	0.16		0.23	0.25	1601		2250	2532
99-100	0.14		0.19	0.23	1416		1927	2255

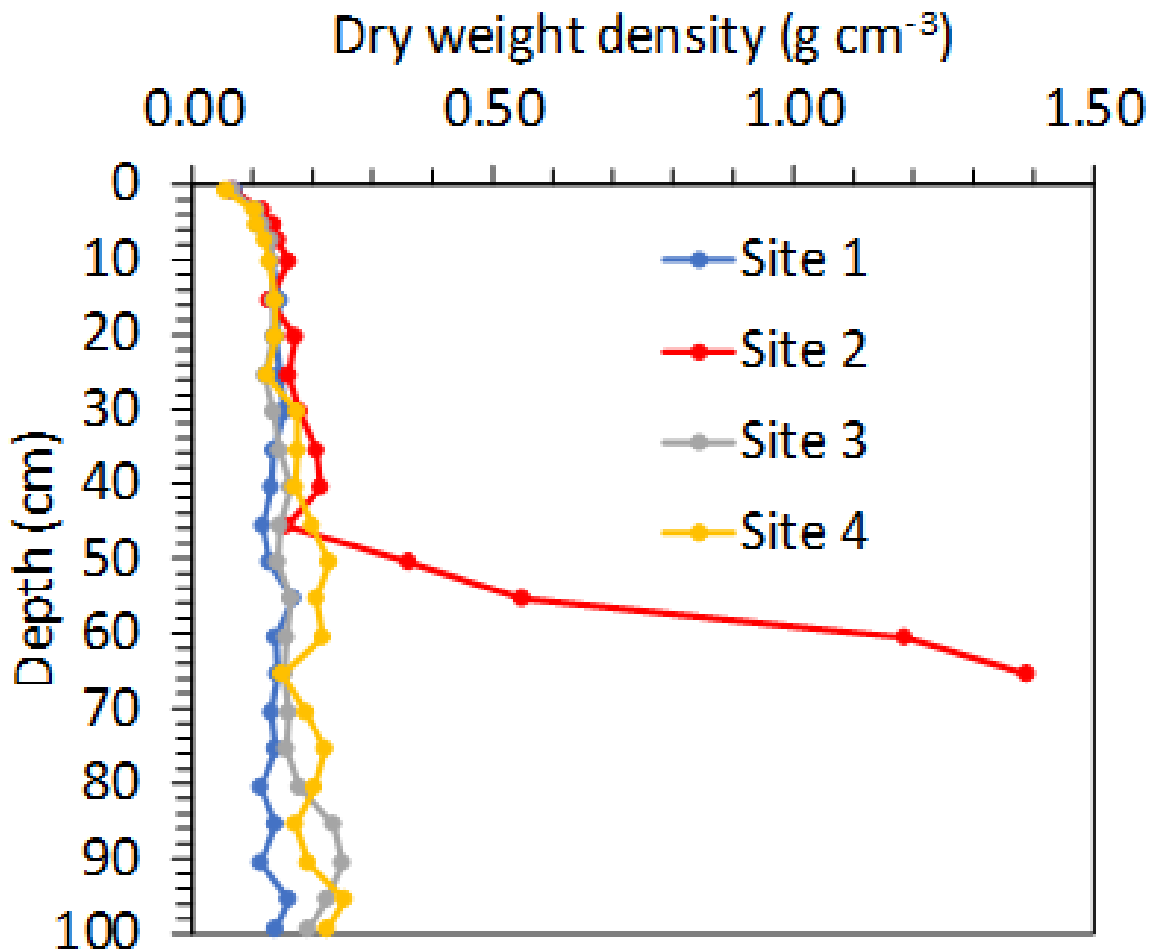


Figure 3: Dry weight of sediment per unit volume.

3.2 Loss on Ignition: organic matter

Loss on ignition was only determined to the depth to which the gravity corer could go. The sediment was highly organically enriched (Figure 4). Typically, 48% of LOI is assumed to be organic carbon. There was approximately 100 g carbon per kg sediment dry weight.

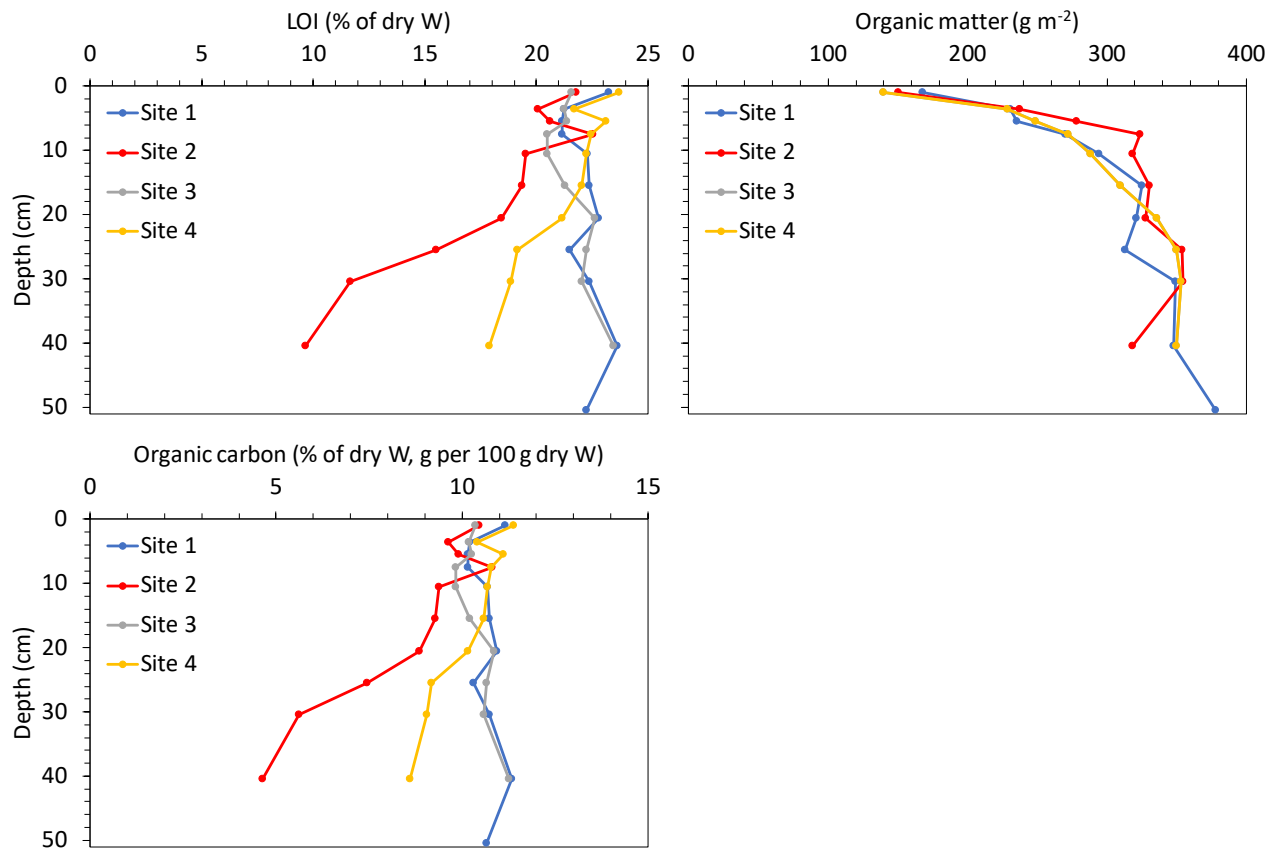


Figure 4: Organic matter in the sediment. As loss on ignition (LOI, top left), organic matter per unit area (right), and as organic carbon in g per 100 g sediment dry weight.

3.3 Phosphorus and nitrogen

The P content of the sediment at the four coring sites was highest in the near surface sediment and declined with increasing depth. Slightly higher content around 40 to 50 cm depth may be consistent with the burial of residual P from the discharge of sewage effluent between 1952 and 1987, which was shown at about 35 cm depth by Gibbs (2011; Figure 5). However, this appears to be contradicted by the dating results (section 3.6). Moreover, unlike in the data of Gibbs (2011), the P content at 30-50 cm depth was less than near the surface, at each of the 4 core sites (Figure 6), and P in the central lake site (site 1) was higher at 60 and 90 cm depth than at 30-50 cm depth.

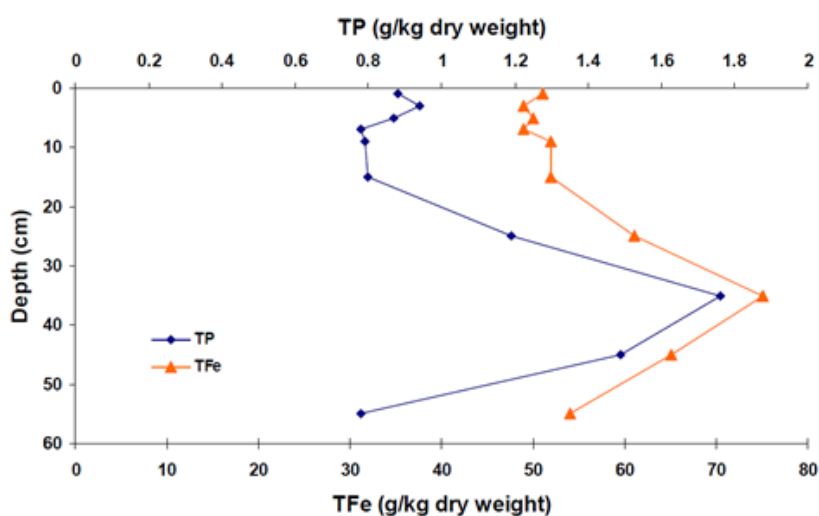


Figure 5: Depth profile of TP and TFe at site 1 in March 2011. This is Figure 31 from Gibbs 2011.

Tables 5-8 give the concentration per dry weight mass, and the amount present at each depth per unit area (m^{-2}), for N and P, and Table 9 gives the N:P ratios. The data are also in Figures 6 and 7. It should be noted that while at site 2 at the depth where the sediment became sandy, the concentration of P as a proportion of the dry weight declined, but P remained high as an amount per m^{-2} because of the increased dry weight density in the sandy sediment.

Table 5: Phosphorus contents (g kg^{-1} dry weight) at different depths in the sediment at four sites.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	1.27	1.24	1.21	1.45
3-4	1.00	1.00	0.91	1.15
5-6	0.95	0.89	0.90	1.08
7-8	0.92	0.90	0.82	1.10
10-11	0.79	0.74	0.74	1.09
15-16	0.71	0.54	0.74	0.85
20-21	0.74	0.45	0.94	0.78
25-26	0.83	0.38	0.68	0.65
30-31	0.96	0.31	0.87	0.62
35-36	0.69	0.37	0.69	0.59
40-41	1.19	0.26	0.63	0.74
45-46	0.87	0.36	0.74	0.70
50-51	0.91	0.28	0.84	0.74
60-61	1.58	0.14	0.73	0.45
70-71	1.26		0.58	0.38
80-81	1.06		0.47	0.35
90-91	2.80		0.33	0.36
99-100	0.70		0.36	0.39

Table 6: Phosphorus content (g m⁻²) in the sediment in layers of 1 cm deep at different depths at four sites. For the top 0-2 cm layer the average for a 1 cm layer is given.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	0.92	0.86	0.82	0.85
3-4	1.09	1.18	0.99	1.21
5-6	1.06	1.20	1.06	1.16
7-8	1.17	1.29	1.09	1.33
10-11	1.04	1.21	0.97	1.41
15-16	1.03	0.92	1.01	1.20
20-21	1.04	0.80	1.33	1.24
25-26	1.21	0.87	0.83	1.19
30-31	1.50	0.94	1.22	1.16
35-36	0.94	0.77	1.01	1.04
40-41	1.75	0.86	1.03	1.45
45-46	1.04	0.57	1.08	1.40
50-51	1.55	1.01	1.20	1.68
60-61	2.20	1.68	1.14	0.98
70-71	1.67		0.94	0.72
80-81	1.22		0.84	0.72
90-91	3.23		0.83	0.70
99-100	0.99		0.69	0.88

Table 7: Nitrogen content (g kg⁻¹ dry weight) at different depths in the sediment at four sites.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	14.1	12.0	12.4	13.9
3-4	12.8	11.2	11.1	12.5
5-6	12.0	12.0	10.4	11.6
7-8	12.1	11.4	10.8	11.8
10-11	12.6	10.2	11.2	11.5
15-16	12.7	10.2	11.8	11.4
20-21	12.7	9.4	11.4	10.9
25-26	13.0	8.3	11.2	9.6
30-31	12.8	6.7	12.8	9.4
35-36	12.0	8.2	12.5	9.5
40-41	13.2	4.8	13.0	9.2
45-46	12.2	7.7	12.4	8.6
50-51	11.8	3.6	12.4	8.6
60-61	13.4	0.6	12.2	8.8
70-71	12.5		12.2	9.9
80-81	13.1		11.2	10.6
90-91	11.4		7.1	10.1
99-100	11.0		8.8	10.0

Table 8: Nitrogen content (g m⁻²) in the sediment in layers of 1 cm deep at different depths at four sites.
 For the top 0-2 cm layer the average for a 1 cm layer is given.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	10.20	8.28	8.43	8.17
3-4	13.91	13.25	12.08	13.17
5-6	13.35	16.18	12.29	12.48
7-8	15.44	16.35	14.38	14.31
10-11	16.65	16.62	14.69	14.90
15-16	18.48	17.44	16.16	16.05
20-21	17.91	16.69	16.10	17.27
25-26	18.96	18.92	13.69	17.55
30-31	19.96	20.33	18.02	17.61
35-36	16.39	17.14	18.35	16.70
40-41	19.46	15.85	21.29	17.97
45-46	14.60	12.10	18.12	17.23
50-51	20.07	13.01	17.72	19.58
60-61	18.64	7.11	19.06	19.14
70-71	16.61		19.71	18.67
80-81	15.09		20.08	21.75
90-91	13.14		17.90	19.56
99-100	15.57		16.96	22.55

Table 9: Nitrogen to phosphorus ratio (by weight) at different depths in the sediment at four sites.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	11.1	9.7	10.2	9.6
3-4	12.8	11.2	12.2	10.9
5-6	12.6	13.5	11.6	10.7
7-8	13.2	12.7	13.2	10.7
10-11	15.9	13.8	15.1	10.6
15-16	17.9	18.9	15.9	13.4
20-21	17.2	20.9	12.1	14.0
25-26	15.7	21.8	16.5	14.8
30-31	13.3	21.6	14.7	15.2
35-36	17.4	22.2	18.1	16.1
40-41	11.1	18.5	20.6	12.4
45-46	14.0	21.4	16.8	12.3
50-51	13.0	12.9	14.8	11.6
60-61	8.5	4.2	16.7	19.6
70-71	9.9		21.0	26.1
80-81	12.4		23.8	30.3
90-91	4.1		21.5	28.1
99-100	15.7		24.4	25.6

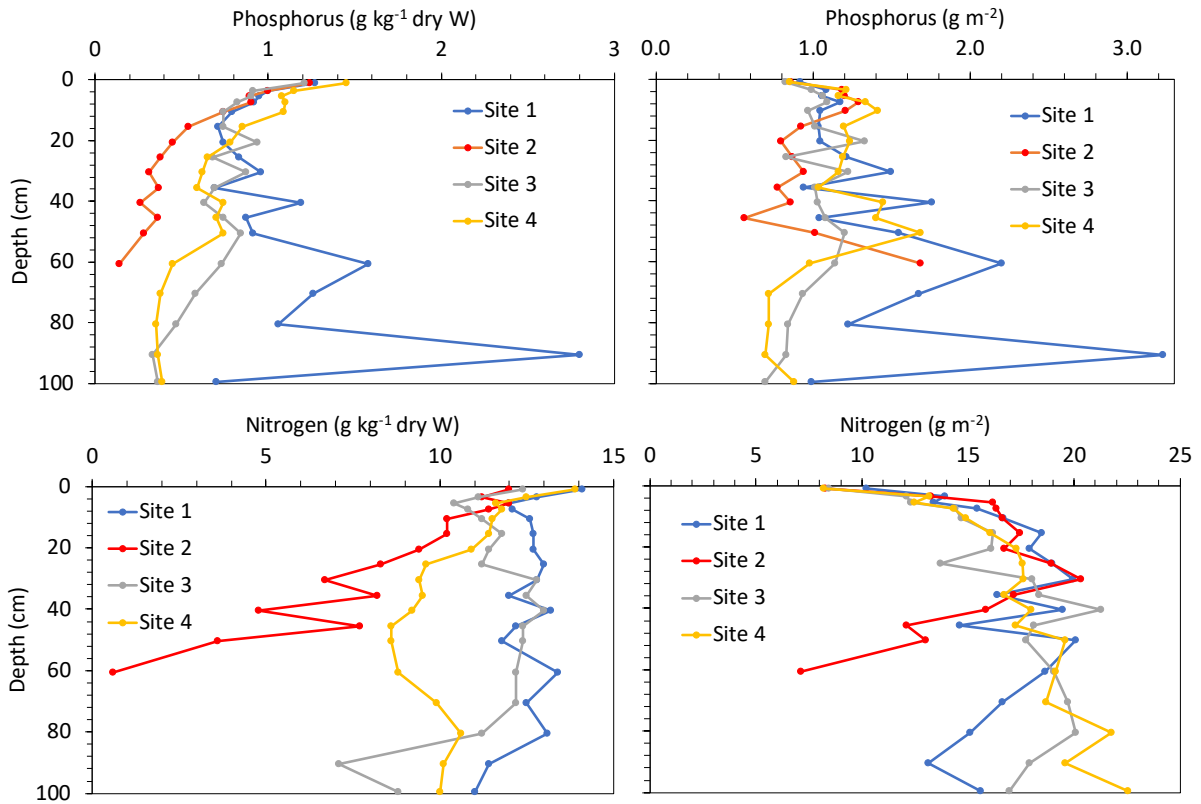


Figure 6: Phosphorus and nitrogen concentrations in the sediment. As a proportion of the sediment dry weight (left) and as the amount of phosphorus and nitrogen in a 1 cm thick layer, per unit area (i.e., g 10,000 cm⁻³, right).

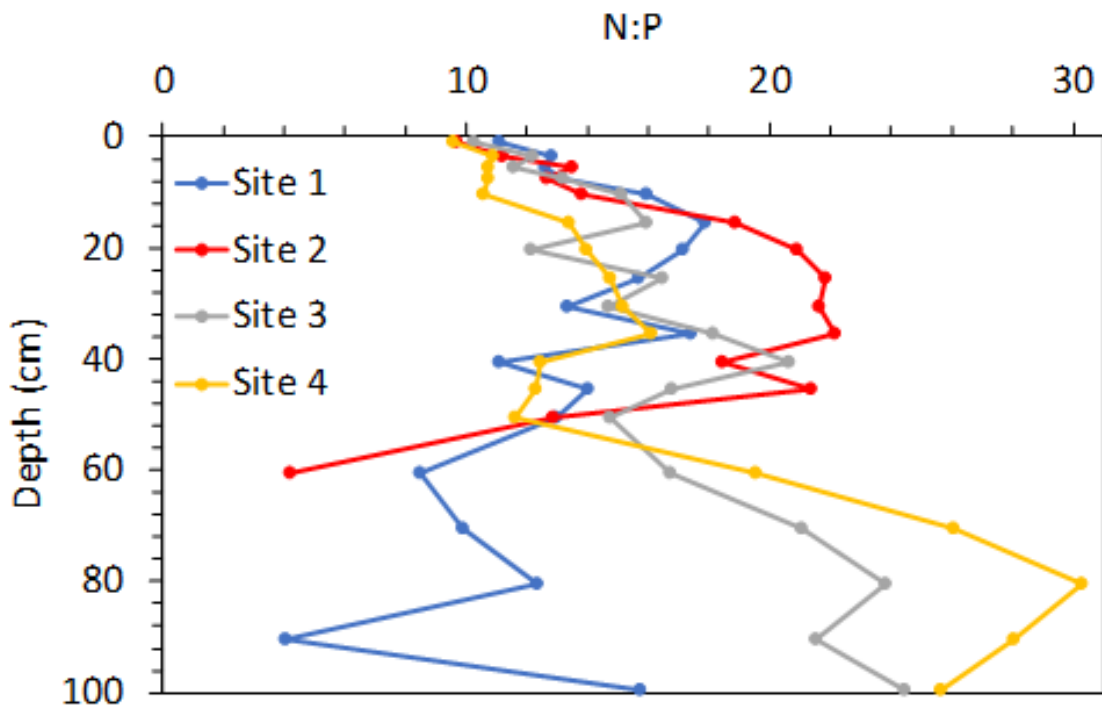


Figure 7: The N:P ratio, by weight, in the sediment.

Macrophyte (*Potamogeton crispus*) material recovered during the sampling contained 3.3 g N and 0.68 g P per 100 g dry weight (ratio 4.85).

3.4 Al, Fe and Mn

Aluminium and especially Mn decreased with depth in the sediment while Fe did not change much (Figures 8 and 9). The data of site 2 differ from the other three sites because of the different nature of the sediment, which is more sandy and has higher density at site 2 (Figures 2 and 3). The elevated near-surface Mn concentrations are indicative of micro-aerobic conditions which mobilise Mn and the associated P when DO is below about 3-4 ppm. Mn in deeper sediment is mobilized when bottom water DO is below about 3-4 ppm. Mn precipitates again in the near surface sediment because anoxic or low oxygen conditions in the bottom water do not last long in Lake Horowhenua (section 3.11), because it is shallow enough to be mixed quickly by the wind. This results in the increase in Mn toward the surface sediment. The same is not seen for Fe because mobilization of Fe from deeper sediment requires lower oxygen than Mn mobilization, and longer lasting anoxia events. There is not much Mn relative to Fe, and therefore the amount of Mn associated P released is probably low. The ratios of Al:P and Fe:P peaked at about 20 cm depth, while the ratio Mn:P decreased with depth. The data are in Tables 10-12.

Table 10: Total aluminium (g kg⁻¹ dry weight) in the sediment, at different depths at four sites. The average in the upper 8 cm was 22.5 g kg⁻¹ dry weight.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	21.0	23.0	21.0	22.0
3-4	22.0	24.0	22.0	23.0
5-6	22.0	23.0	22.0	24.0
7-8	23.0	23.0	21.0	24.0
10-11	20.0	20.0	22.0	22.0
15-16	21.0	16.9	20.0	22.0
20-21	20.0	16.0	21.0	22.0
25-26	19.0	15.8	21.0	19.9
30-31	18.3	13.2	19.1	18.9
40-41	17.1	11.1	19.4	17.0
50-51	17.7			

Table 11: Total manganese (g kg⁻¹ dry weight) in the sediment, at different depths at four sites. The average in the upper 8 cm was 1.53 g kg⁻¹ dry weight.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	1.91	1.69	1.96	2.30
3-4	1.72	1.27	1.67	2.20
5-6	1.25	1.03	1.32	1.72
7-8	1.10	1.00	1.01	1.32
10-11	0.93	0.87	0.91	1.20
15-16	0.94	0.68	0.89	1.00
20-21	1.00	0.60	0.98	0.96
25-26	0.98	0.49	0.95	0.89
30-31	0.97	0.37	0.81	0.84
40-41	0.95	0.30	0.82	0.87
50-51	0.96			

Table 12: Total iron (g kg⁻¹ dry weight) in the sediment, at different depths at four sites. The average in the upper 8 cm was 49 g kg⁻¹ dry weight.

Depth (cm)	Site 1	Site 2	Site 3	Site 4
0-2	48	45	47	50
3-4	50	48	48	52
5-6	49	45	48	53
7-8	52	47	46	51
10-11	50	42	47	50
15-16	50	42	49	45
20-21	53	40	51	45
25-26	53	38	55	44
30-31	52	29	48	45
40-41	58	23	48	43
50-51	64			

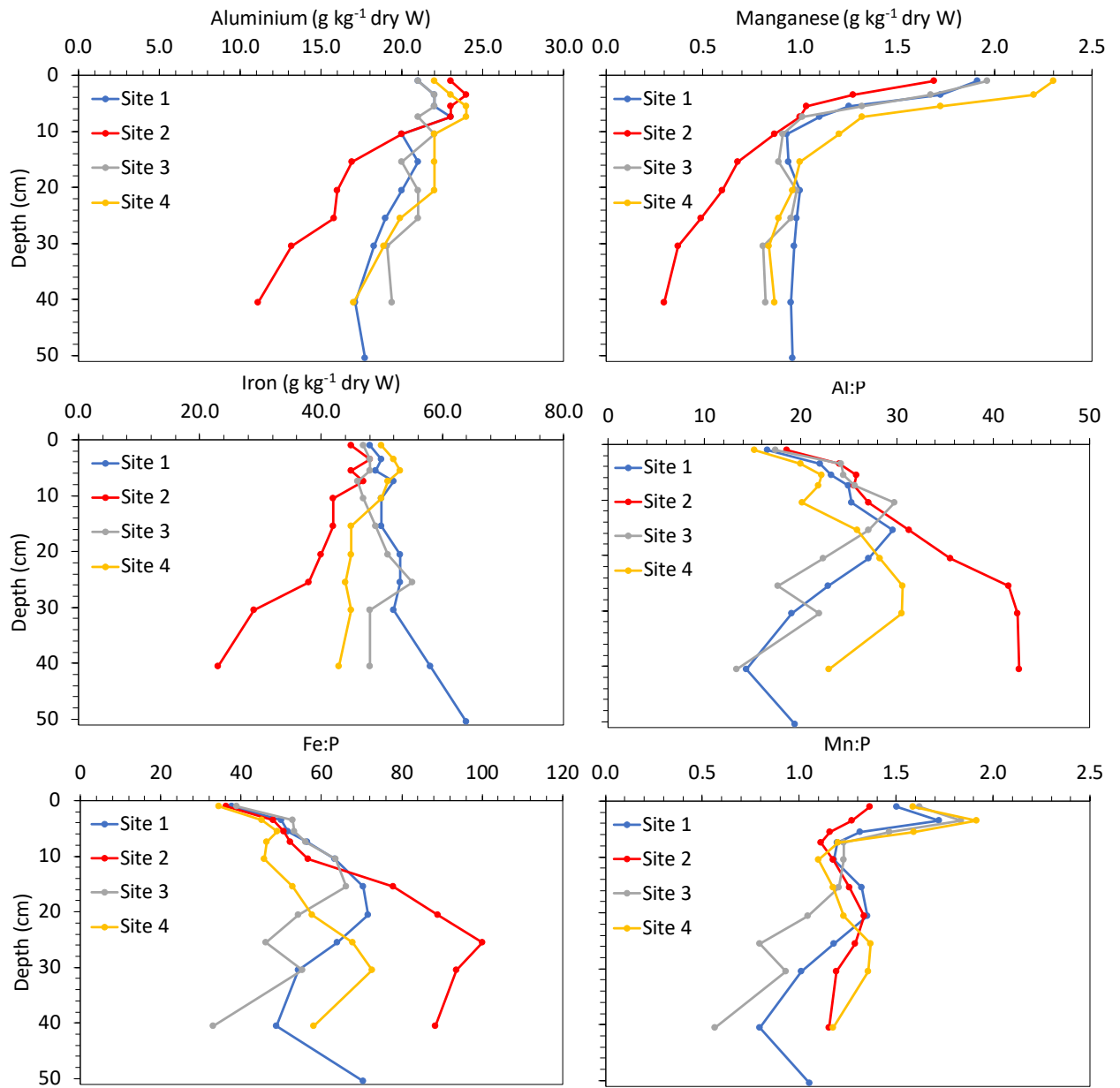


Figure 8: Concentrations in the sediment of Al, Mn and Fe, and their ratios to P, by weight.

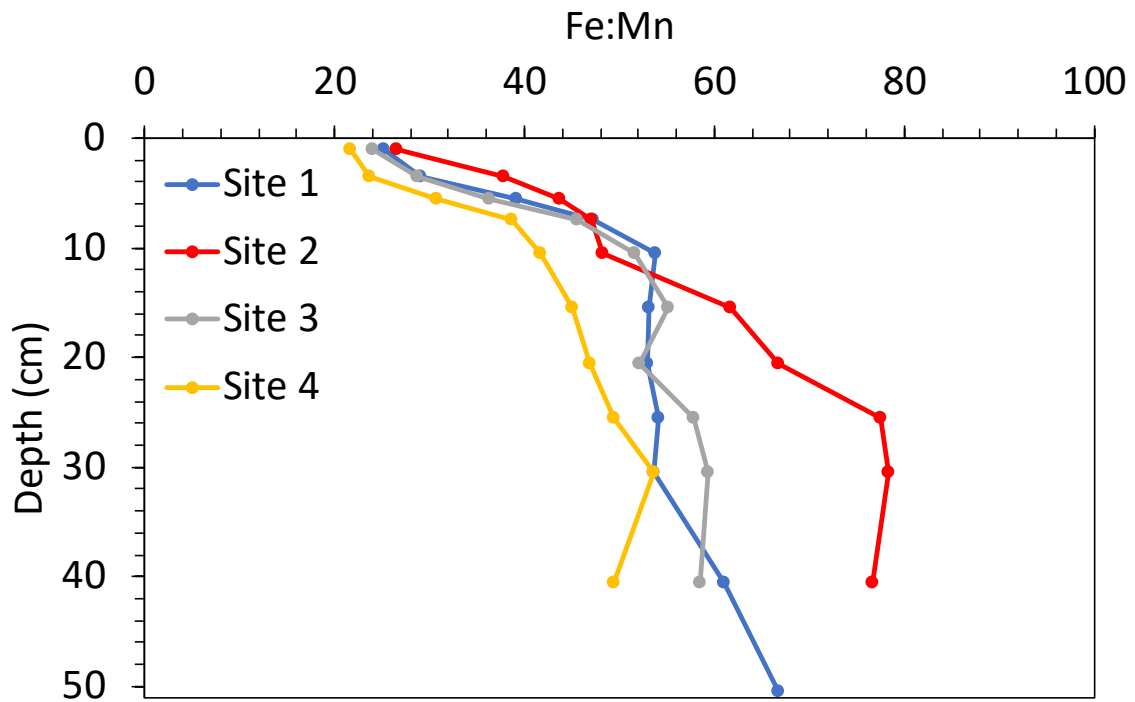


Figure 9: Ratios by weight in the sediment of Fe:Mn.

3.5 Heavy metals

None of the trigger values for sediment quality guidelines for heavy metals recommended by ANZECC (2000) were exceeded (Table 13). However, the mercury concentration at 0-2 cm was close to the ANZECC (2000) trigger value, and the mercury concentration at 20-21 cm slightly exceeded the ANZECC (2000) trigger value.

Concentrations of all metals at 20-21 cm deep in the sediment were similar to that in the surface sediment, except zinc which was 13% lower, and arsenic which was 28% higher at 20-21 cm into the sediment (Table 13). However, at 40-41 cm deep in the sediment, concentrations of almost all metals were about half of that in the surface sediment (range 39 to 75%, average 54% of the concentration in the surface sediment), the exception being chromium (95%) and arsenic with a concentration that was 40% higher than that in the surface sediment.

Table 13: Concentrations (mg kg⁻¹ dry weight) of heavy metals in the lake sediment at depths of 40-41 cm, 20-21 cm, and 0-2 cm (duplicates). The analytical uncertainty is indicated by a level of confidence of approximately 95 percent (i.e., two standard deviations, see methods). Included are, for comparison, the trigger values for sediment quality guidelines recommended by ANZECC (2000).

	40-41 cm	20-21 cm	0-2 cm#1	0-2 cm#2	ANZECC 2000
As	7.28±0.75	6.68±0.69	5.20±0.54	5.21±0.54	20
Cd	0.176±0.022	0.345±0.042	0.343±0.042	0.342±0.042	1.5
Cr	25.0±3.0	27.4±3.3	25.9±3.2	26.5±3.2	80
Cu	17.0±2.4	33.0±4.7	30.6±4.3	31.0±4.4	65
Pb	11.5±1.4	26.7±3.3	24.5±3.0	24.4±3.0	50
Hg	0.095±0.014	0.177±0.023	0.143±0.019	0.140±0.019	0.15
Ni	11.4±1.2	15.9±1.6	15.1±1.6	15.3±1.6	21
Zn	62±10	118±19	135±22	135±22	200
Ag	0.267±0.040	0.84±0.12	0.681±0.097	0.677±0.096	1

Concentrations of arsenic in near surface sediment is expected to be somewhat lower than in deeper sediment. Arsenic behaves in the same way as phosphorus in the sediment, it is subject to similar chemical reactions and arsenic near the surface in the sediment releases to the water column. This may explain the decrease in arsenic towards the surface of the sediment. For cadmium, copper, lead, mercury, nickel and zinc, their increases towards the surface of the sediment may indicate increased inputs of these heavy metals in recent years.

3.6 Core dating and sediment accumulation rates

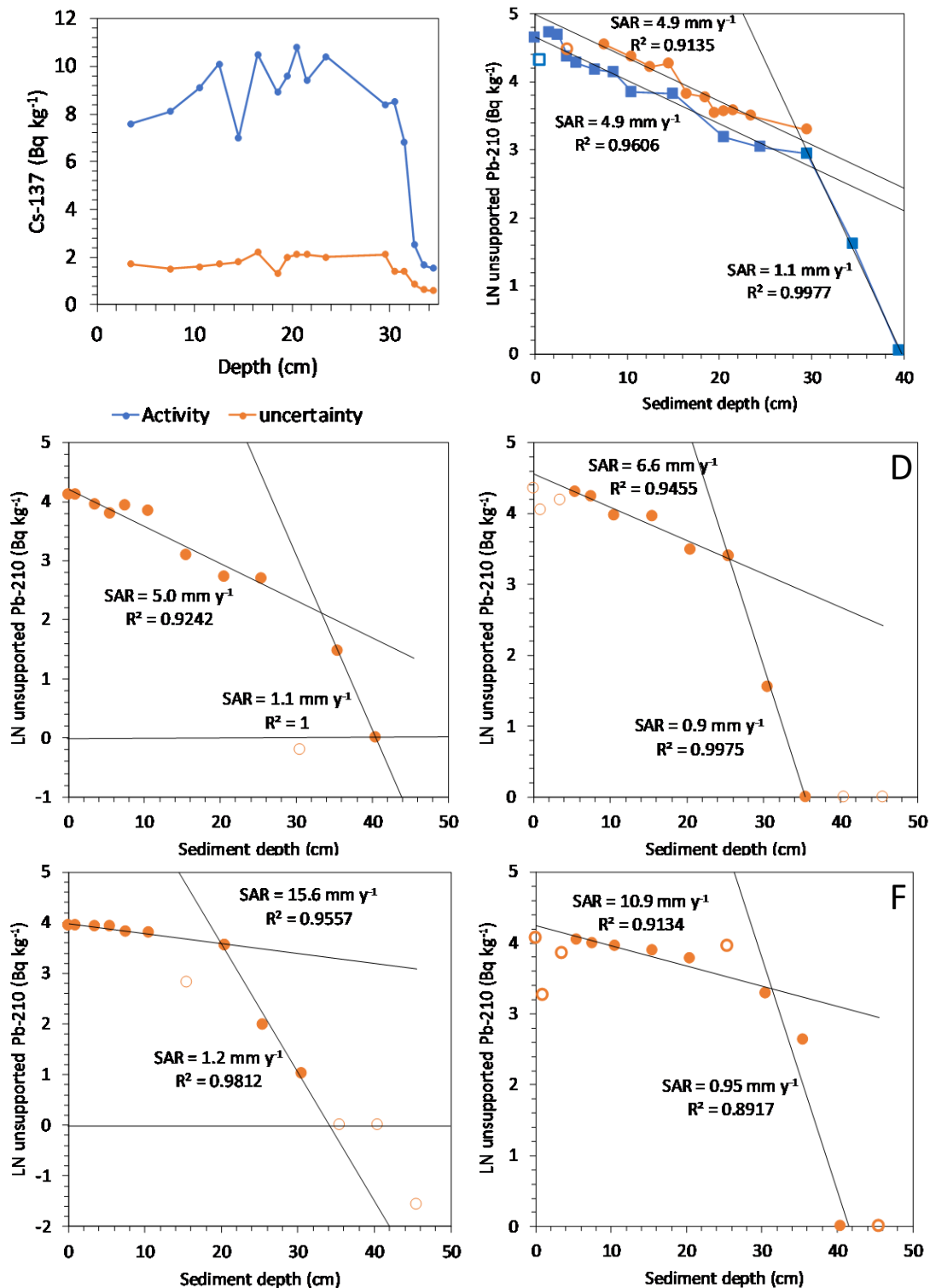


Figure 10: Sediment dating results. (A) Cs-137 in the buoy core. (B) Unsupported Pb-210 measured by alpha spectroscopy (blue squares) and gamma spectrometry (orange circles), with estimated SAR's, in the buoy core. Remaining panels: Unsupported Pb-210 measured by alpha spectroscopy in core 1 (C), core 2 (D), core 3 (E), and core 4 (F). Data where Bq kg⁻¹ = 0 were set at Ln(Bq kg⁻¹) = 0. Data not used in the fitting of SAR are indicated by open symbols (either outliers, data affected by surface mixing, or data below the depth with measurable excess Pb-210).

With a half-life of 22.3 years and an exponential decay to below detection in about 7 half-lives, the maximum age that can be determined using unsupported Pb-210 is about 150 years before present (BP). This means that Pb-210 data can only be used to estimate sediment accumulation rates (SAR) over the last 150 years, although it may be reasonable to extend sediment age estimates to depths further down core based on the SAR determined above these depths, especially when they can be verified against other measures of age. In the five cores analysed, the estimated ages of sediment at the deepest depths with measurable unsupported Pb-210 ranged from 1871 (buoy core), 1923 (core 3), 1925 (core 2), 1930 (core 1), to 1945 (core 4). However, it must be remembered that the deeper sections were typically only analysed 5 cm apart, which could account for more than 50 years of sediment accumulation. Radioisotope activities are expressed as concentration in S.I. units of Becquerel (disintegration s^{-1}) per kilogram ($Bq\ kg^{-1}$).

In each sediment core a change in SAR (Figure 10) occurred at about 20 to 30 cm depth, with slower sedimentation in the deeper segment than in the near surface segment. The SAR in the shallow segment was almost the same in the buoy core ($4.9\ mm\ y^{-1}$) and core 1 ($5.0\ mm\ y^{-1}$). As these cores were from the same site this gives confidence in the results. The estimated SAR of the upper segment was also the same between the samples analysed by ESR and those analysed by MyCore (both $4.9\ mm\ y^{-1}$, Figure 10B). The SAR in the deeper section in the buoy core was about $1.1\ mm\ y^{-1}$. This deeper SAR is close to the estimate of $0.8\ mm\ y^{-1}$ below 60 cm depth of Bevins (2019), based on three radiocarbon samples from about 85, 205 and 300 cm depth at approximately the same site. The change in sedimentation rate makes a difference for the estimation of ages of the sediment. For instance, the top circa 30 cm took about 60 years to deposit, and the next 10 cm, at 30 to 40 cm depth, took about 100 years, with a total of 160 years for the top 40 cm. The estimated date when the switch down core to lower sedimentation rates occurred was 1955 in the buoy core, and 1951 in core 1. While similar, as expected, the former had more data and is therefore more reliable.

The SAR in the deeper section was similar in all cores, on average $1.0\ mm\ y^{-1}$. However, the four core sites varied in SAR estimated in the top layer, from $5.0\ mm\ y^{-1}$ in core 1 to $15.6\ mm\ y^{-1}$ in core 3. Therefore, the year in which a change in sedimentation occurred differed between sites, ranging from 2005 in core 3, 1989 in core 4, 1980 in core 2, to 1955 in the buoy core. Sediment ages were the least well defined by Pb-210 data in the core from site 4.

Ages in the second segment down core (Figure 11), the segment with the slower sedimentation rates, are more uncertain than in the upper segment, for a number of reasons: lower Pb-210 activity with a proportionally higher uncertainty for each measurement, fewer data points for fitting, and uncertainty arises from not knowing exactly when or at what sediment depth the shift in sedimentation rates occurred. The latter source of uncertainty has a substantial impact on the deeper age estimates because of the large decrease in SAR below that depth.

Our SAR results at the central lake buoy core site agree with the average of Bevins (2019) for the upper 60 cm. The mean sedimentation rates in the upper 60 cm in the buoy core ($3.0\ mm\ y^{-1}$) and in core 1 ($3.2\ mm\ y^{-1}$) were similar to the $3.4\ mm\ y^{-1}$ in the upper 60 cm determined by Bevins (2019) with an age-depth model using four radiocarbon dates, sampled between 2 to 300 cm depth from approximately the same site in the lake. Our results present a refinement, with higher SAR in the upper 30 cm and lower SAR between 30 and 60 cm (Bevins 2019 had only a single radiocarbon sample above 85 cm depth, from combined sections between 2 and 12 cm depth). Mean sedimentation rates in the upper 60 cm were also similar at core site 2 ($3.3\ mm\ y^{-1}$), but higher at core sites 3 ($6.2\ mm\ y^{-1}$) and 4 ($6.1\ mm\ y^{-1}$). These 2 core sites with higher sedimentation rates were in the mid-south and east side of the lake, respectively (Figure 1).

The Pb-210 derived sedimentation rate estimate was verified with Cs-137 data of sediment from the buoy core. First measurable Cs-137 occurred in the 34-35 cm section. This suggests a date of about 1954 for this section, and an average SAR of 5.3 mm y⁻¹ above it. This is in reasonable agreement with the estimate derived from Pb-210 (4.9 to 5.0 mm y⁻¹). There was no obvious peak in the Cs-137 (Figure 10A) to correspond with the year 1963, when atmospheric deposition of Cs-137 was maximum. This peak can appear soon after first measurable Cs-137 (Wren et al. 2016). It is possible that the 1963 peak was missed by our analysis and occurred between 23 and 29 cm sediment depth. We therefore agree with Bevins (2019), who analysed Cs-137 samples in sections 15-17 cm and 28-30 cm but not between these sections, and who assumed the 1963 peak occurred in the non-sampled interval. According to our Pb-210 chronology 1963 would correspond to 27 cm sediment depth (26.8 cm and 27.2 cm in the buoy core and core 1 respectively). It would be useful in future research to sample Cs-137 in the intervening layer (23 to 29 cm) at greater resolution than presented here. However, the 1963 peak in Cs-137 can be difficult to detect in the Southern Hemisphere (Sanchez-Cabeza et al. 2012).

Sedimentation rates between about 20 to 30 cm depth at the central buoy core may have been above the average of the top 30 cm (Figure 12). This is suggested by both the ESR and MyCore data sets, and although core 1 (Figure 10C) has fewer data in this region it is apparent in that core as well. Regressing the data between 20 to 30 cm in the buoy core separately, the estimated SAR is 11.2 to 11.9 mm y⁻¹. This SAR corresponded with dates from 1960 to 1968, when sewage inputs to Lake Horowhenua occurred. It may also be explained by a temporary increase in sedimentation following the construction of a weir on the outflow in 1956. Observations of changes in land use in the lake catchment around this time include substantial intensification of horticulture (cropping) in the Arawhata Stream catchment, including the straightening and clearance of drains, as well as the development of dairy farming in the Mangaroa Stream catchment. These activities have the potential to increase soil erosion and thereby the SAR in the lake. As a result of accepting a higher SAR at 20-30 cm, the estimated SAR at 0-20 cm becomes smaller, about 4 mm y⁻¹, but still substantially higher than it was before 1960. The chronological division in three sections with different SAR makes virtually no difference for the estimate of the likely position in the sediment of the 1963 peak in Cs-137. According to the Pb-210 chronology 1963 would correspond to 26.7 cm sediment depth.

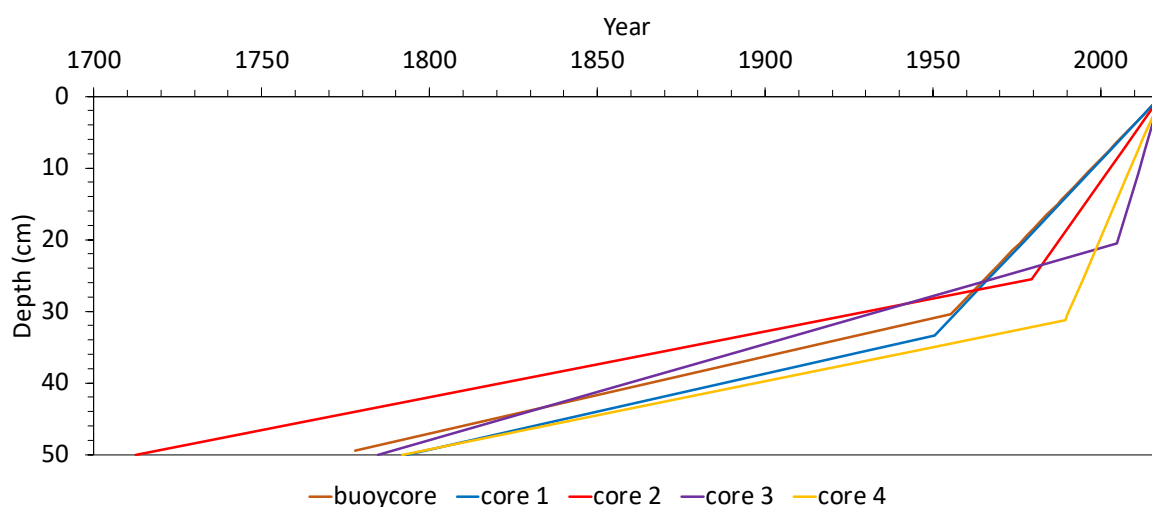


Figure 11: Sediment ages.

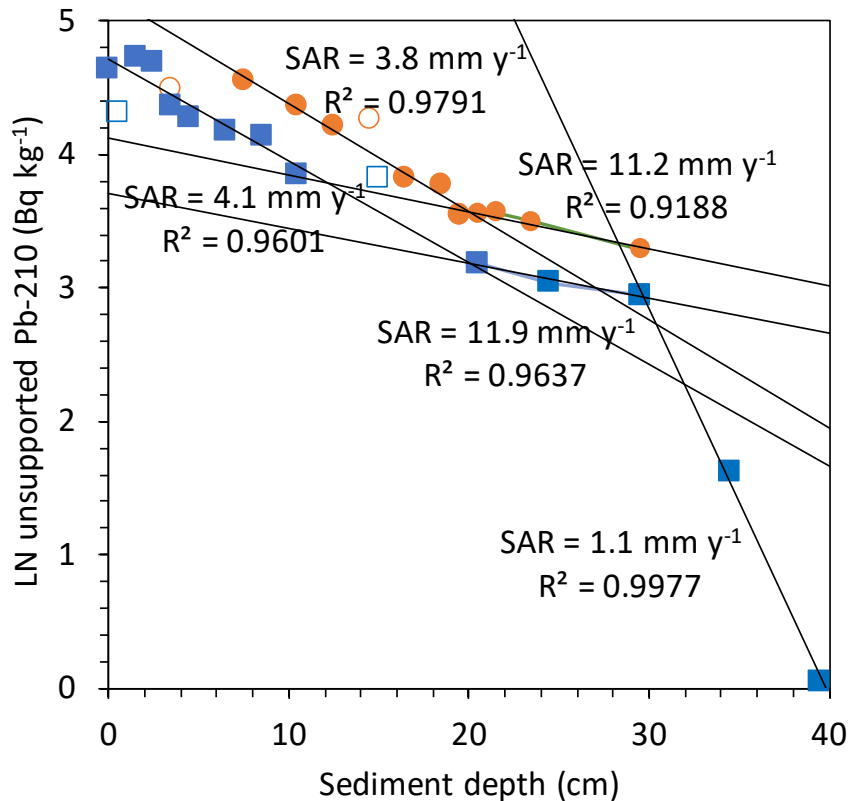


Figure 12: Sediment accumulation rates in the central lake core (buoy core). Greater sedimentation rate between 20 to 30 cm sediment depth.

Currie et al. (1978, page 34) reported the volume of silt in the lake as 3.7 million m^3 (also cited by the Waitangi Tribunal Report, 2017). This would amount to a mean depth of sediment of about 1.3 m. Therefore, most of this sediment is not the result of recent anthropogenic sediment inputs, as appears to be suggested by the Waitangi Tribunal Report (2017). The bottom of that layer of sediment would be more than 1000 years old. In contrast, Currie et al. (1978, page 34) estimated the inputs of suspended solids as $150 \text{ m}^3 \text{ y}^{-1}$. Currie et al. (1978) concluded a rate of filling of 0.05 mm yr^{-1} . That estimate is about 100 times too small, and even taking into account a 90% water content in the sediment it still is 10 times too small.

Cunningham et al. (1953) found maximum depth in Horowhenua to be 2 m in January 1949. Six macrophyte surveys between 2014 and 2018 (see de Winton (2014) for the first survey in January 2014) found maximum depths varying from 1.76 m to 2.12 m, average 1.95 m. Maximum depth was lowest in summer, 1.76 m in January 2014 and 1.78 m in January 2018. Sediment accumulation from 1949 until 2018, as derived from Pb-210, is estimated as 29.6 cm ($11 \text{ year} \times 1.1 \text{ mm} + 58 \text{ year} \times 4.9 \text{ mm}$, see Figure 10B). This agrees well with the 22 cm lower maximum depth in 2018 compared with 1949. The difference between the estimated sediment accumulation and the reduction of depth since the survey by Cunningham is probably explained by interannual differences in maximum depth, and by the measurement error of the maximum depths, in particular that of Cunningham et al. (1953) which was reported without decimals.

Table 14: Depth-date table for cores from all four sites. Note: only in the buoy core could 3 SAR segments be distinguished, which especially affects the depth-age estimates around 1970-1990 (Compare with Figure 11, where only 2 SAR segments are distinguished in the buoy core, resulting in dates being virtually the same as in core 1). Estimated sediment dates between 1962-1987, the main period of sewage inputs, are in bold.

Depth cm	Buoy core Year	Core 1 Year	Core 2 Year	Core 3 Year	Core 4 Year
0.0	2018	2018	2018	2018	2018
1.0	2016	2016	2016	2017	2017
2.5	2012				
3.5	2009	2011	2013	2016	2015
5.5	2005	2007	2010	2014	2013
7.5	2000	2003	2007	2013	2011
10.5	1992	1997	2002	2011	2008
12.5	1987				
14.5	1982				
15.3		1987			
15.5	1980	1987	1995	2008	2004
16.5	1978				
18.5	1973				
19.5	1970				
20.5	1968	1977	1987	2005	1999
21.5	1967				
22.7				1987	
23.5	1966				
24.5	1965				
25.5	1964	1966	1980	1964	1995
25.8				1962	
27.1			1962		
27.7		1962			
27.8	1962				
29.5	1961				
30.5	1953	1956	1925	1923	1990
31.5					1987
33.9					1962
34.5	1916				
35.5	1906	1930	1870	1883	1945
39.5	1869				
40.5	1860	1883	1816	1842	1892
44.5	1823				
45.5	1813	1836	1761	1801	1839
50.0	1771	1793	1712	1764	1792

The unusual reduction in ^{210}Pb activity between 2013 and 2018 in cores 2 and 4 and perhaps in the top of the buoy core (Figure 10) requires a sediment source with a lower radioactivity than the sediment below it. Normally this would not be possible in a low sloping catchment where slips and earth flows, that could release subsoils with lower radioactivity, are unlikely to occur. However, in 2017 work began on a sediment trap beside the Arawhata Stream (Figure 13). Sediment from this

source is up to 1 m deeper than the surface soil and therefore will have unsupported Pb-210 older (i.e., with much lower activity) than recent sediment. Some of that sediment may have been transported into the lake by the Arawhata Stream and blended with the sediment from other inflows to produce the lower activity signal observed.



Figure 13: Construction of a large shallow sediment trap beside the Arawhata Stream. The Arawhata Stream flows along the eastern side of the trap and will flow into it when the water levels are high, allowing the sediment to settle in the slower moving water inside the ponding area. [Photo montage by Max Gibbs 22/06/2017].

3.7 CSSI source tracking

Stable isotope data, both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the bulk sediment and $\delta^{13}\text{C}$ of fatty acids (i.e., CSSI data) have been compiled and correlated with depths and dates (Table 15). The Suess correction (Verburg 2007) needed because of the change in the $\delta^{13}\text{C}$ signature of CO_2 in the atmosphere as a result of fossil fuel emissions, has been applied to the carbon isotope data, using the ^{210}Pb dating for assessing the time BP.

The source data also includes the isotopic data for the dominant aquatic macrophyte, *Potamogeton crispus*. It is notable that the isotopic values for this plant (-27‰) are much more depleted in $\delta^{13}\text{C}$ than aquatic macrophytes typically are (around -10‰). The stream sediment delta isotopic values have come from terrestrial plants labelling the soil carried in the stream water. Both terrestrial and aquatic plants use CO_2 during photosynthesis to produce the fatty acids they exude through their roots and which bind to the soil or sediment particles. However, because of the nature of the terrestrial versus aquatic environment, isotopic fractionation by macrophytes tends to be less because CO_2 availability is more limiting in water than in air, resulting in less depleted $\delta^{13}\text{C}$. The relatively depleted $\delta^{13}\text{C}$ signature of macrophytes in Lake Horowhenua suggest an inorganic carbon source for photosynthesis other than atmospheric carbon, such as methane.

Because Lake Horowhenua is a hypereutrophic lake, the anaerobic sediments likely produce methane, which is known to have highly isotopically depleted $\delta^{13}\text{C}$ values (e.g., -40‰ to -60‰ or lower). These depleted values may also appear in the CO_2 released from the sediment and may be utilised by the aquatic macrophytes thereby causing isotopic depletion in the fatty acids (FAs) produced by the macrophytes.

Table 15: Carbon stable isotope data for the sources and sediment core from site 1. $\delta^{13}\text{C}$ of bulk organic matter and of fatty acids. The sources are the streams which deliver sediment to the lake and the dominant aquatic macrophyte in the lake (*Potamogeton crispus*). The core data are for each 1-cm thick slice at the specified depth taken as the middle of each slice. The dates are derived from ^{210}Pb dating and the time is given in years before present (BP). The core isotopic data have been corrected for the Suess effect (Verburg 2007).

Sources			$\delta^{13}\text{C}$	C16:0	C18:0	C18:1w9c	C22:0	C24:0	C26:0
Mangaroa Stream			-28.05	-35.8	-35.3	-34.8	-33.9	-31.5	-30.4
Patiki Stream			-28.92	-32.4	-31.9	-33.6	-35.2	-34.8	-33.9
Domain drain			-29.42	-34.9	-36.1	-34.2	-36.3	-35.8	-35.5
Queen St drain			-25.83	-32.5	-32.3	-32.1	-34.0	-32.3	-32.4
Makomako Rd drain			-26.87	-33.1	-31.9	-31.8	-34.4	-32.6	-32.1
Arawhata Stream			-30.93	-43.0	-39.5	-40.7	-36.9	-36.7	-36.0
Sand Rd Stream			-29.90	-36.8	-36.5	-35.0	-36.5	-35.9	-36.2
Macrophytes			-26.72	-39.3	-34.9	-36.3	-36.4	-36.3	-35.4
Core site 1 data									
Depth (cm)	Date	Time BP (y)	Suess corrected CSSI data						
1.5	2016	2	-27.86	-35.15	-31.18	-31.04	-33.25	-31.09	-28.73
3.5	2009	6	-28.48	-35.36	-31.07	-31.30	-32.48	-31.97	-30.14
5.5	2005	11	-28.68	-34.38	-29.76	-31.06	-32.24	-32.41	-31.05
7.5	2000	14	-28.54	-38.50	-32.82	-31.25	-33.78	-32.28	-31.50
10.5	1992	18	-28.66	-34.44	-35.35	-30.67	-32.20	-32.78	-32.46
15.5	1980	27	-28.60	-39.76	-29.82	-34.39	-32.04	-32.98	-32.57
20.5	1968	38	-28.84	-37.71	-33.49	-33.11	-32.60	-32.70	-32.48
24.5	1965	46	-29.06	-34.73	-35.79	-32.88	-32.73	-32.60	-32.36
29.5	1961	56	-29.00	-35.10	-37.38	-33.26	-32.64	-32.97	-32.86
39.5	1869	76	-29.36	-35.12	-34.89	-32.52	-36.69	-36.25	-33.26
50.5	1771	96	-30.46	-37.38	-37.55	-37.05	-39.05	-36.30	-36.03

Another feature of Lake Horowhenua is its history of extensive swarms of lake flies (non-biting midges – chironomids) that were common while the sewage effluent was being discharged into the lake between 1952-1987. During the 1988-89 study, gauze face masks were sometimes needed to enable breathing while working around the shore line (M. Gibbs, NIWA, pers. comm.). The chironomid larvae live in the sediments and feed on the bacteria and other detritus (bits of decomposing plant material). Since the presence of methane requires methanogenic bacteria in the sediment and these also take on the highly isotopically depleted $\delta^{13}\text{C}$ values from methane, chironomid larvae which consume them also have highly isotopically depleted $\delta^{13}\text{C}$ values (Jones and Grey 2004; Deines et al. 2007). These chironomid larvae can also exhibit highly isotopically depleted FA $\delta^{13}\text{C}$ values (Makhutova et al. 2017).

While macrophytes and chironomids are not normally regarded as sources of sediment, their isotopic signatures could add to the complexity of the isotopic signatures in the sediment, making discrimination of external sediment sources difficult.

3.7.1 Polygons to distinguish organic carbon sources

In order to select the best tracers for modelling the proportional contribution from soil sources at each depth in the core, the isotopic data were plotted as a series of X-Y graphs and polygons were drawn surrounding the values of the sources (Figure 14). The best tracers were the fatty acids C18:0, C24:0 and C26:0. Bulk C ($\delta^{13}\text{C}$) could also have been used as it made no significant difference to the proportions output from the model but did significantly increase the run time for the model. Consequently, a judgement call was made to use only the three fatty acids as tracers in the sediment source modelling.

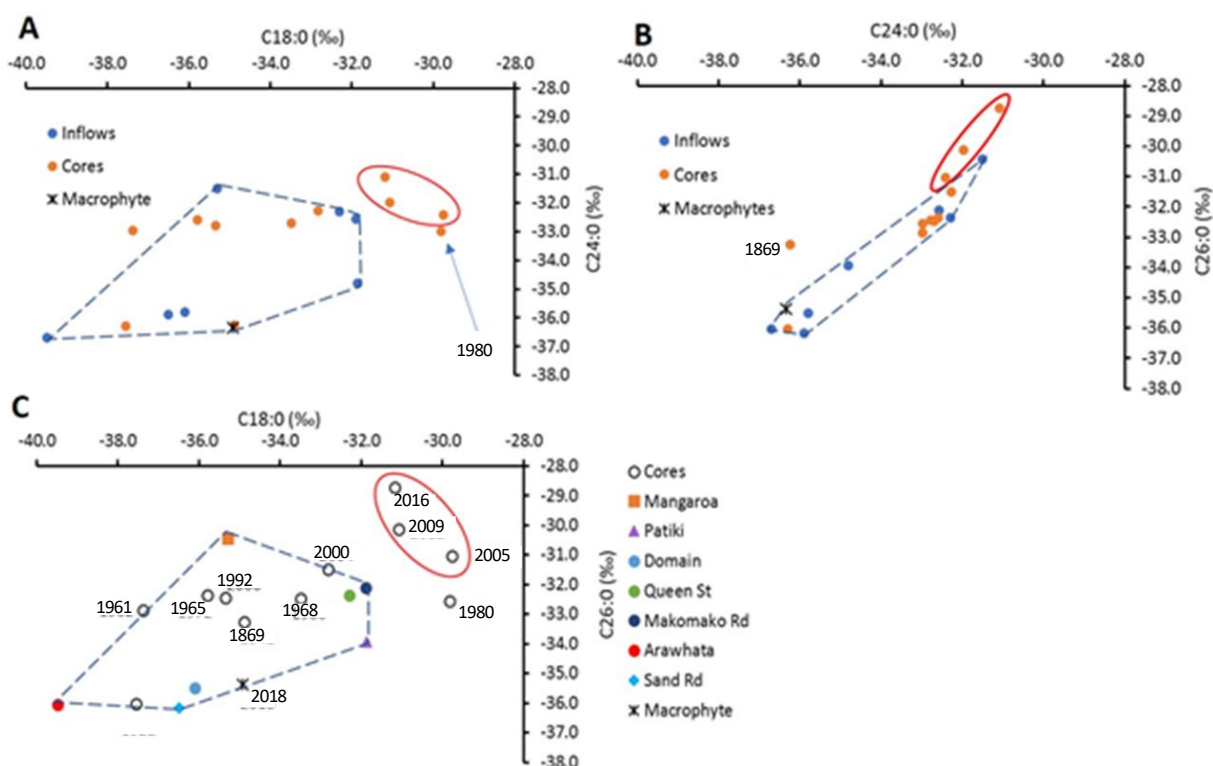


Figure 14: Selection of the best isotopic tracers using polygons. The fatty acids that traced organic carbon sources best were C18:0, C24:0 and C26:0. Polygons A) C18:0 vs C24:0, B) C24:0 vs C26:0, and C) C18:0 vs C26:0 show the inclusion of core data within the source polygon (dashed blue line). Core data excluded from the polygons are explained in the text. The points circled in red are the most recent data points. Part C shows the relationship of the 7 source inflows with the dates down the core at site 1. The macrophyte data show how different their isotopic signatures are compared with recent terrestrial signatures from 2005 to 2016.

To meet the best-practice protocols for modelling (Phillips et al. 2014), the core sample isotopic values should lie within the polygon drawn around the inflow sediment data. Clearly some of the core points do not comply with this requirement (Figure 14). Of the non-compliant samples (Figure 14C), the three samples from the surface mixed layer (0-6 cm; 2005-2016) are all more enriched than the deeper (older sediment) layers and much more enriched than the macrophyte values. This pattern was consistent for all polygons and implies a recent input from an enriched source such as a swamp (soil spilled from the construction of the sediment trap on the Arawhata Stream could be a source as it has lower ^{210}Pb activity (see section 3.6) and is likely to have enriched isotopic signatures due to the higher carbon turnover rates in wetlands. The other non-compliant sample was from 1980.

3.7.2 Source proportions

The stable isotope data was modelled using SIMM IsoSource and the most efficient tracers identified from the polygons. The macrophyte data was not included in the modelling (Table 16). The model output includes a parameter 'n' which is the number of feasible solutions. As the value of n decreases, the reliability of the result increases with a value of 1 indicating a unique solution. Values of $n < 100$ are excellent, from 100 – 1000 are good, from 1000 – 2500 are acceptable but need caution in their use or need to be remodelled, and for values > 2500 the data needs to be remodelled with different tracers. In this study, remodelled failed to reduce the value of n substantially and, consequently, the original modelling results are reported.

The results for most core slices were valid, but two depths – 5-6 cm (2005) and 15-16 cm (1980) – produced results which were not interpretable, and these have been excluded from the model output. The isotopic proportions from the modelling were converted to soil proportions using a linear regression equation (Gibbs 2008) and are presented as percent composition in Table 16 and in a bar graph (Figure 15) to visualise the changes in sediment source over time.

Table 16: Soil source proportions produced for different depths in the sediment from the core at site 1. Data for 2005 and 1980 were not interpretable and have been omitted. Standard deviations given in brackets. The parameter ‘n’ reflects the reliability of the results, with lower numbers suggesting greater reliability. Locations shown in Figure 1.

Slice depth (cm)	Year (AD)	Catchment Sources						n
		Mangaroa	Patiki	Domain drain	Queen St	Arawhata	Sand Rd	
1.5	2016	45.0(0.6)	3.6(0.5)	0.0(0)	3.2(2.4)	48.2(2.6)	0.0(0)	22
3.5	2009	20.2(0.5)	2.3(0.4)	0.0(0)	1.9(2.3)	75.6(2.1)	0.0(0)	11
5.5	2005	-	-	-	-	-	-	-
7.5	2000	25.9(0)	0.0(0)	0.0(0)	0.0(0)	74.1(0)	0.0(0)	1
10.5	1992	52.8(1.3)	12.9(1.2)	3.3(1.8)	10.0(2.4)	7.3(3.5)	13.7(1.9)	1160
15.5	1980	-	-	-	-	-	-	-
20.5	1968	12.7(1.8)	17.1(1.6)	6.5(3.6)	47.5(4.3)	13.5(4.1)	2.7(3.7)	2546
24.5	1965	72.1(1.4)	0.0(0)	0.0(0)	1.9(2.1)	2.0(0.7)	24.0(1.4)	2
29.5	1961	28.8(1.1)	1.3(0.4)	1.0(1.1)	0.3(0.8)	68.2(1.1)	0.4(1.1)	116
39.5	1869	0.7(3.7)	86.0(9.3)	0.3(1.6)	0.1(0.6)	12.9(6.2)	0.0(0.7)	866
50.5	1771	1.1(2.4)	1.9(0.5)	5.3(4.7)	10.4(3.3)	68.2(4.4)	13.0(6.7)	1162

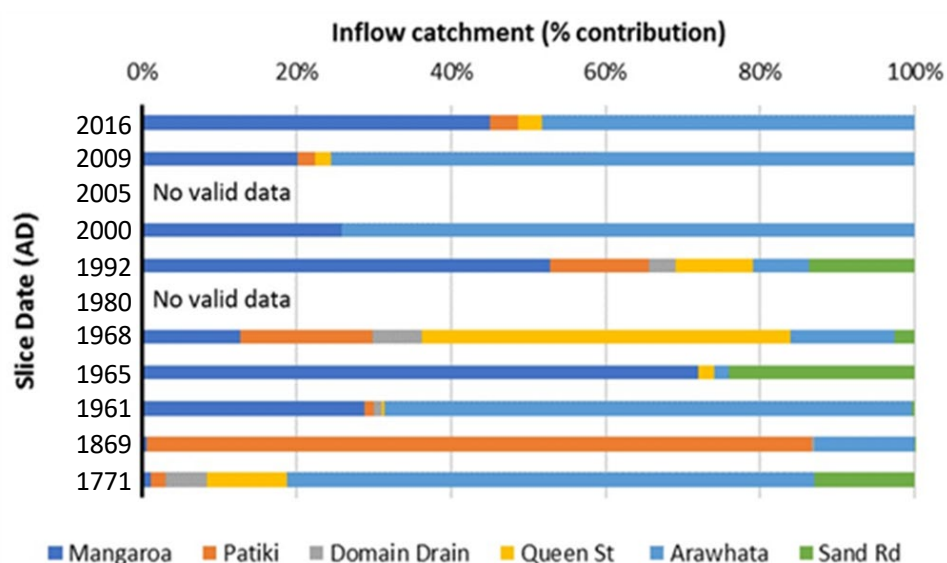


Figure 15: Bar graph of soil proportions showing the relative proportion changes in soil sources contributing to the sediment at site 1. Data from 2005 and 1980 have been omitted because they were not interpretable.

3.8 Bulk stable isotope signatures of organic matter in the lake sediment

Stable isotope values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Figure 16) decreased steadily down the sediment core to 40 cm depth. The increase in $\delta^{15}\text{N}$ towards the present was large, about 4‰. High values of $\delta^{15}\text{N}$ suggests anthropogenic inputs of N, such as sewage and fertilizer, which have high $\delta^{15}\text{N}$ signatures. The point of the sewage input (indicated on the map in Figure 22) was closest site 3, but this site is not highest in $\delta^{15}\text{N}$ at the sediment depth corresponding to 1952-1987 (12.5 – 30.6 cm). However, also denitrification can increase the $\delta^{15}\text{N}$ signature of the remaining nitrogen. $\delta^{15}\text{N}$ in lake sediment is

typically expected to be similar to that of bulk phytoplankton in the water column. If the $\delta^{15}\text{N}$ signature in the sediment is representative for phytoplankton in Lake Horowhenua, then it is much higher than what is usual in lakes (about 0 – 5 ‰). As a result, the consumers in the food web are expected to be elevated in $\delta^{15}\text{N}$ as well.

Increasing $\delta^{13}\text{C}$ may suggest increasing eutrophication towards the present. When eutrophication increases, and photosynthesis in the water column increases, the demand for CO_2 is enhanced and the strong isotopic fractionation that occurs during assimilation of CO_2 is diminished.

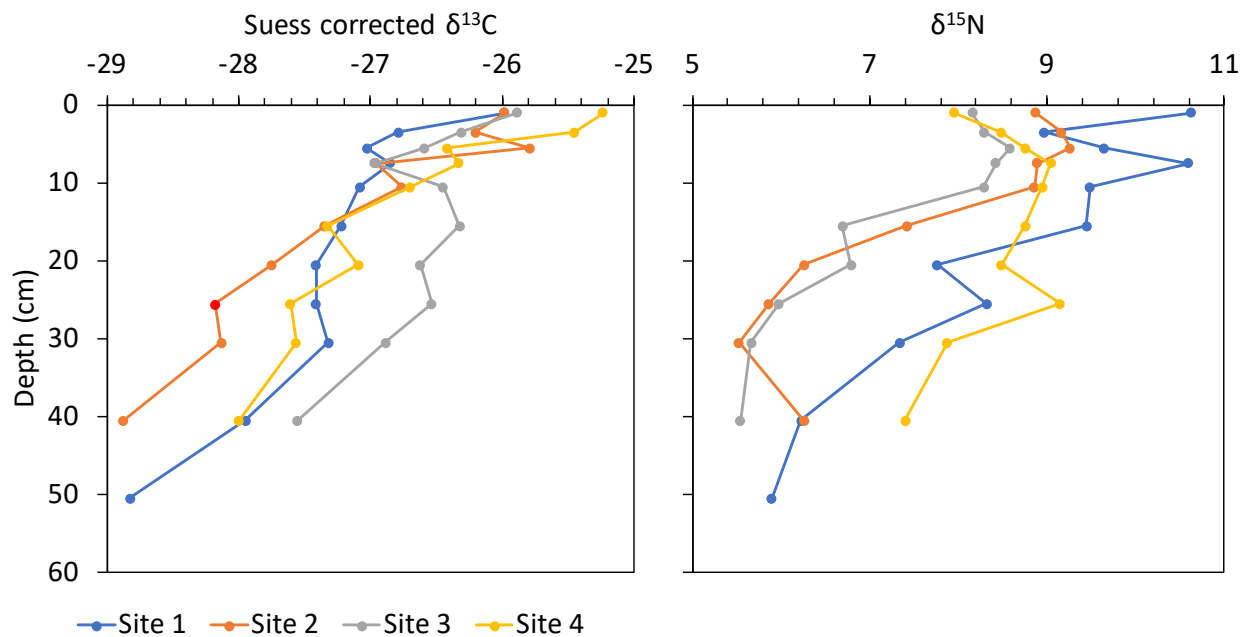


Figure 16: Bulk stable isotope signatures of organic matter in the lake sediment. Sediment was acidified to remove inorganic carbon before determining $\delta^{13}\text{C}$. Samples for $\delta^{15}\text{N}$ analysis were not acidified. $\delta^{13}\text{C}$ values were corrected for the Suess effect (Verburg 2007).

3.9 Accumulation of N and P and cumulative N and P by depth

The lake sediment down to 1 m depth (2,900,00 m³ or 0.0029 km³), assuming the means of accumulated N and P in the sediment cores (Figure 17) are representative for the lake, contains about 360 tonne P and 5200 tonne N.

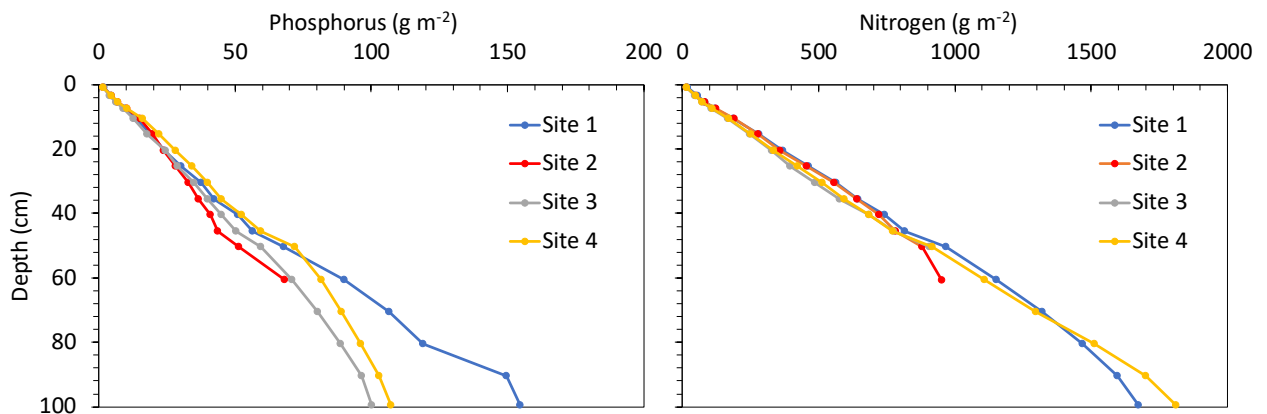


Figure 17: Accumulation of P and N in the lake sediment. Cumulative with depth.

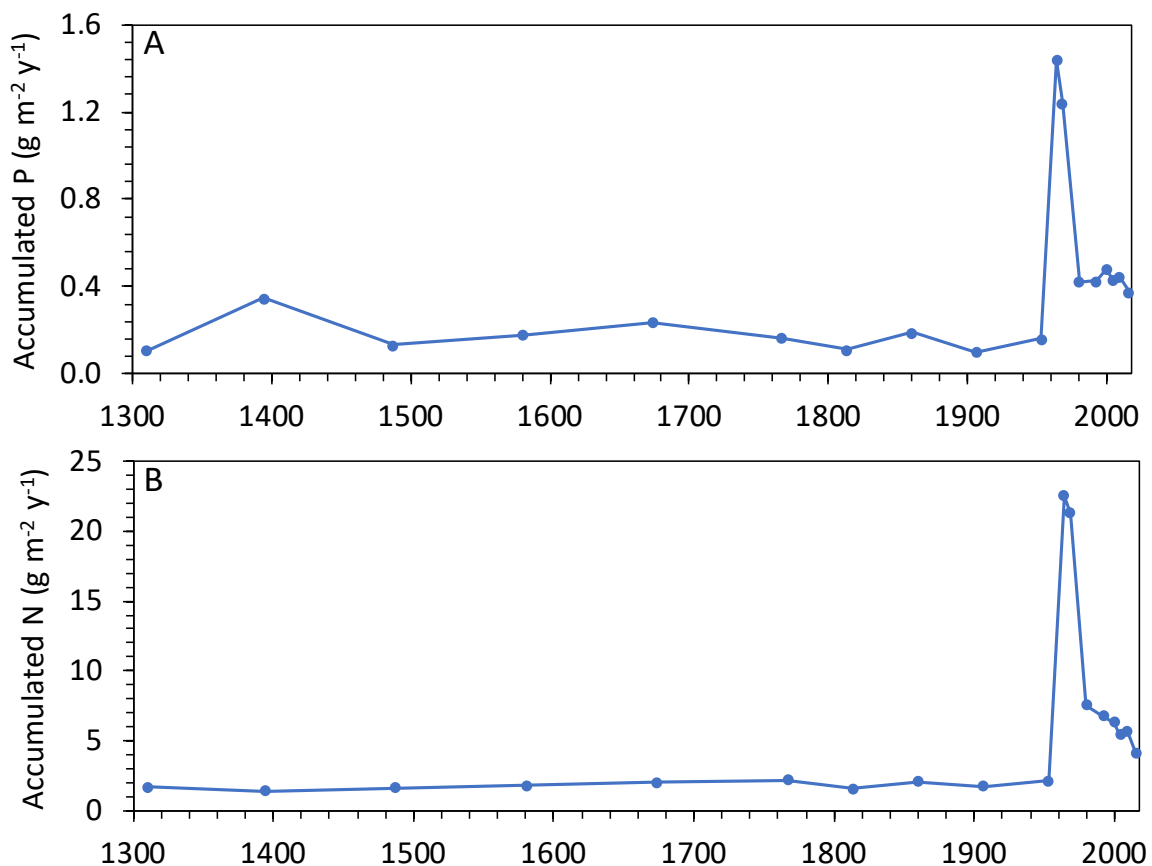


Figure 18: Nutrient accumulation in the sediment by year. (A) Phosphorus (B) Nitrogen.

Accumulation of P in the sediment per year at the central lake site is shown in Figure 18, estimated from the product of P concentrations per unit volume (Figure 6) and SAR (Figure 12). If extrapolated to the lake wide surface, the accumulation of P was 0.5 t y^{-1} before 1960, about 4 t y^{-1} in the 1960s and 1.3 t y^{-1} from 1980 onward. This compares with a present load from the catchment of about 3 t P y^{-1} . However, it must be kept in mind that in recent decades P accumulation in the sediment has actually been negative, in other words there is strong evidence that more P leaves the lake via the outlet than enters the lake (unpublished data). Therefore, P in the near surface sediment may represent P that has been mobilised from deeper depths and re-precipitated closer to the sediment-water interface. This would increase the apparent accumulation rate near the surface sediment while reducing the apparent accumulation rate deeper in the core. Nevertheless, a pronounced signature of sewage inputs in the 1960s remains. The peak in P accumulation in 1964 (Figure 18) is mostly driven by the SAR, with the SAR being highest in 1962 and 1964 (P concentrations were not estimated in other years during the period of enhanced SAR in the 1960s), as P concentrations in the sediment were more similar in the upper 50 cm. In the remaining cores, cores 2 to 4, there is probably too little resolution in the SAR results for a comparable analysis. In these cores only 2 periods with different SAR were distinguished, while there were 3 different periods in the central lake core. In cores 2-4 no clearly different SAR could be distinguished in the 1960s.

The pattern for N accumulation in the sediment (Figure 18B) is similar to that of P, except that N accumulation has continued to decrease, after the peak in the 1960s, from 1980 to the present. This is a result of the decrease in volumetric sediment contents of N towards the present from a peak in the 1950s (Figure 6). If extrapolated to the lake wide surface, the accumulation of N was 5.5 t y^{-1} before 1960, about 65 t y^{-1} in the 1960s and declining from 23 t y^{-1} in 1980 to a present 12 t y^{-1} . This compares with a present load from the catchment of about 200 to 250 t N y^{-1} , much of which is lost by denitrification or flushed by the outflow. The sewage inputs may have had a relatively high N:P ratio, in view of the N:P ratio in the sediment being highest around 1960-1980 at site 1 (Figure 7).

Two observations are of importance: 1) in spite of sewage inputs for 35 years the P concentrations in the sediment, an average 1.1 g kg^{-1} dryw in the upper 1 m and 1.3 g kg^{-1} dryw near the surface, are not particularly high (compared for instance with the range in Bay of Plenty lakes, $0.5 - 3.5 \text{ g kg}^{-1}$ dryw, with about 3 g kg^{-1} in several deep oligotrophic lakes, Trolle et al. 2008), and 2) the average concentration of P in the sediment (0.8 g P kg^{-1} dryw) in the period with enhanced SAR, identified as the 1960s, was actually below average. At 12.5-30.6 cm depth, corresponding to 1952-1987 when sewage inputs occurred, average P concentrations were 0.8 g P kg^{-1} dryw and 0.11 kg m^{-3} , less than the average in the upper 1 m (1.1 g kg^{-1} dryw and 0.14 kg m^{-3}). It would appear that while P inputs were enhanced during the sewage inputs, total sediment inputs were enhanced at least as much. While P concentrations in the sediment are naturally relevant for internal loading and eutrophication, at least as important is whether conditions exist that are conducive to internal loading such as low oxygen concentrations in the bottom water. Also Lake Horowhenua's shallow depth plays a role: a sediment legacy that would pose no problem in deeper lakes, results, once release occurs, in far greater concentrations in the shallow water column than it would in a deeper lake.

Currie et al. (1978) reported losses of P through the outlet that exceeded the amount of P that entered the lake in November 1975 to November 1977, just as has been the case in recent years (see above). This would suggest there was no storage of P in the sediment in the lake during the sewage input years, no build-up of a legacy load. However, Currie et al. (1978) likely missed a significant portion of the P budget by not accounting for groundwater inputs. During the 1970's, P loading to

the lake was very high by sewage inputs (Vant and Gilliland 1991) and this must have resulted in a nutrient legacy build-up in the sediment. For P losses from the lake to exceed P inputs there must have been a prior period where the reverse was the case, and clearly that must have been the case during the years of sewage inputs.

3.10 Sub-Catchment yields

The estimates of sub-catchment yields of P and N, using the catchment model CLUES, suggested high yields both of P and N in the south and north areas of the catchment (Figure 19). These sub-catchments are drained by the Arawhata Stream and Mangaroa Stream, respectively. Therefore these modelling results are consistent with the CSSI results of surficial sediments (Table 15).

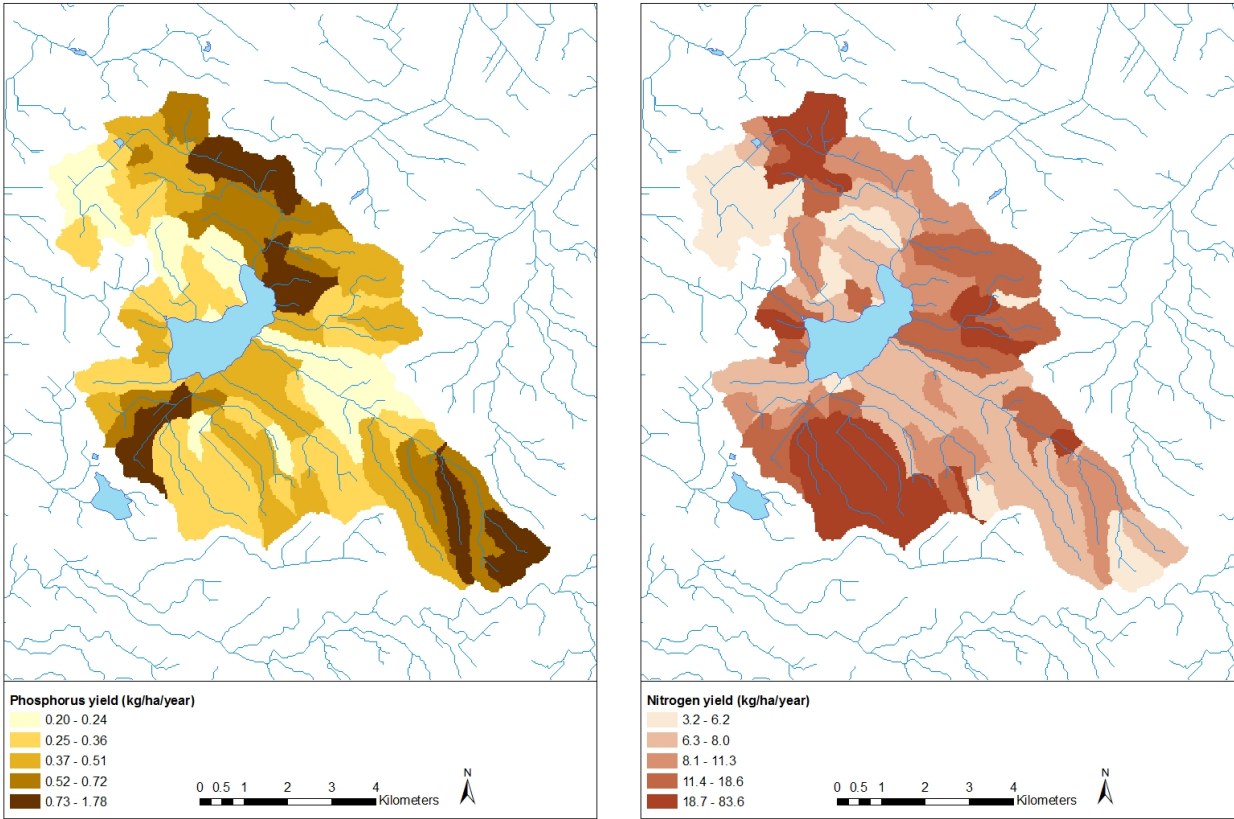


Figure 19: Sub-catchment yields of P and N. Estimated using CLUES.

3.11 Dissolved oxygen, DRP and algal chlorophyll *a*

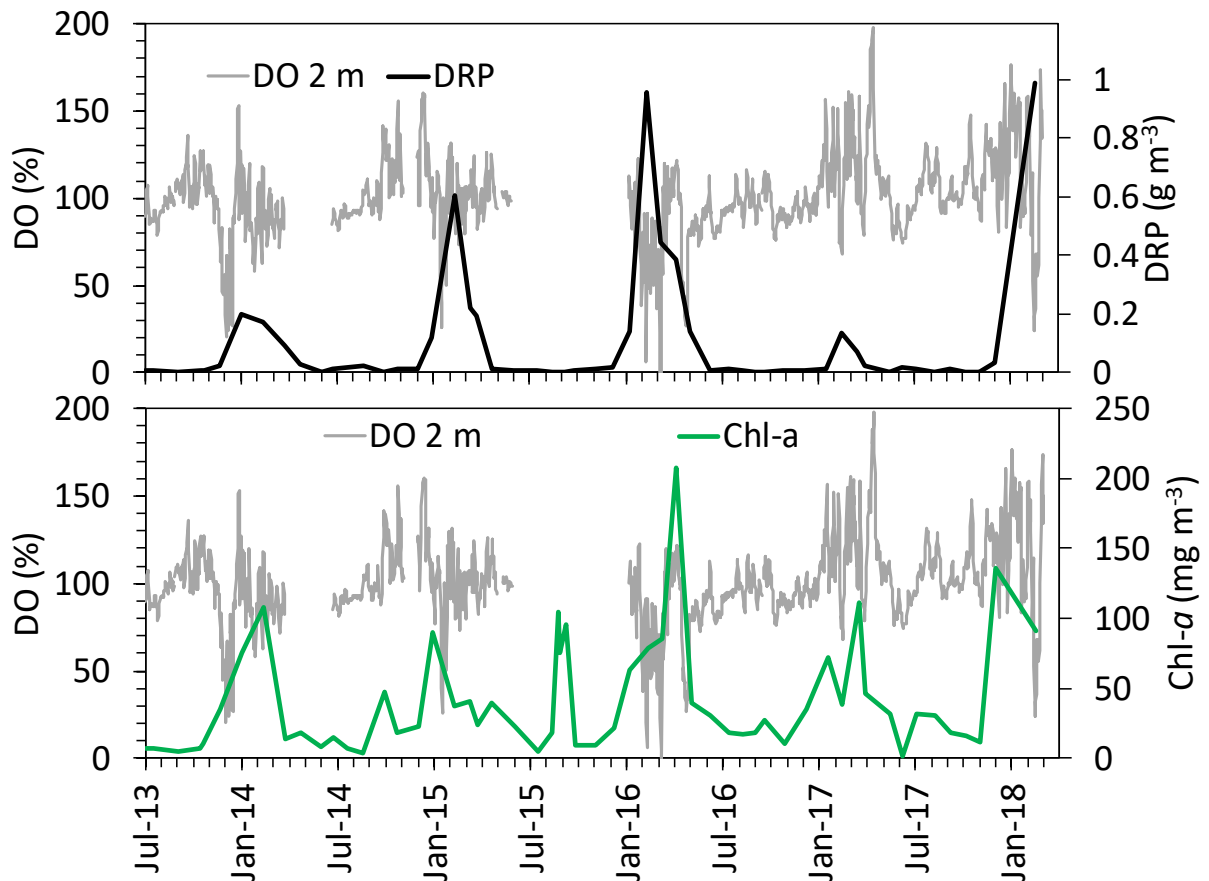


Figure 20: Dissolved oxygen in water near the bottom, dissolved phosphorus and chlorophyll *a*. Dissolved oxygen (DO, measured near the bottom, daily means computed) are data from the automatic buoy monitoring station, and dissolved reactive phosphorus (DRP) and chlorophyll *a* are near surface sample data from the monthly monitoring program maintained by HRC.

Typically, dissolved oxygen becomes low every year during summer, followed by a large increase in dissolved reactive phosphorus (DRP) and algal chlorophyll *a*. During summer phytoplankton is dominated by cyanobacteria, mostly *Microcystis* which is the non-diazotrophic, i.e., it does not fix nitrogen (unpublished data). The summer increase in DRP must be explained by in-lake processes, such as internal loading from the sediment, because it does not reflect seasonal patterns in the inputs from the tributaries (unpublished data).

4 Discussion

4.1 The sediment issue

The main questions to be addressed in this report are:

1. *What is the impact of sediment on the lake?*
2. Should the sediment be removed or should it be left alone?
3. If the sediment should be removed, how much sediment would be removed and to what depth?
4. If the sediment is not to be removed, where does the sediment come from and what actions are required to reduce sediment inputs to the lake?

Question 1: *What is the impact of sediment on the lake?*

The sediment is a repository of nutrients and minerals, including heavy metals, that get trapped in the lake from multiple external sources including streams, stormwater, groundwater and discrete discharges. The proportion of these inputs that do not get flushed out of the lake, or in the case of nitrogen, removed by denitrification, accumulates in the sediments as a legacy load. It is possible for the natural biogeochemical cycles associated with temperature and oxygen dynamics to mobilise key elements such as phosphorus, arsenic, iron and manganese and other trace elements as well as soluble forms of nitrogen from the sediments into the water column. The levels of trace elements and heavy metals in Lake Horowhenua sediments are below the trigger values for sediment quality guidelines recommended by ANZECC (2000) (Table 13) and are therefore unlikely to be a concern for the lake (except perhaps mercury). Conversely, the concentrations of P in the surficial sediments (Table 5, Figure 6), may continuously replenish P concentrations in the overlying water, thereby sustaining algal growth and the poor water quality in the lake under low oxygen conditions in summer.

In shallow lakes wind-wave action during storm events can also disturb the sediment and the water column can become turbid, reducing the light climate at the lake bed thereby affecting the potential regrowth of native aquatic macrophytes to the advantage of exotic weed species, which can tolerate lower light levels (e.g., *Potamogeton crispus*). While aquatic macrophyte biomass can be high in spring and early summer in Lake Horowhenua, these exotic weed species can remove P and N from the water column and a management strategy that balances the pros and cons is needed for lake Horowhenua.

The aquatic macrophytes in a shallow lake protect the lake bed from wind-wave erosion thereby reducing potential turbidity events. Because of their leaf structure these plants act as natural sediment traps enhancing the rate of suspended solids removal from the water column after an event.

Specific questions include:

- a) *What are the infilling rates (SAR) across the lake?*

The total sediment accumulation since 1960 was estimated as 30 cm, as a measure of infilling. Data from this study show that sediment accumulation rates ranged from about 1 mm y⁻¹ to 11 mm y⁻¹ at different times BP in the core at the buoy location. It is likely that spatially there are

also differences in SAR across the lake, as was suggested by the data of cores 2 to 4, although the Pb-210 data of these cores were sparser than for the core at the buoy location. TP concentrations in the surface sediment (Figure 21) may give an indication of spatial differences in SAR. The spatial distribution of surficial TP concentrations is consistent with the soil source contribution data (Figure 15) which indicated that the majority of the sediment entering Lake Horowhenua in recent times came from the Mangaroa catchment in the north and the Arawhata catchment in the south.

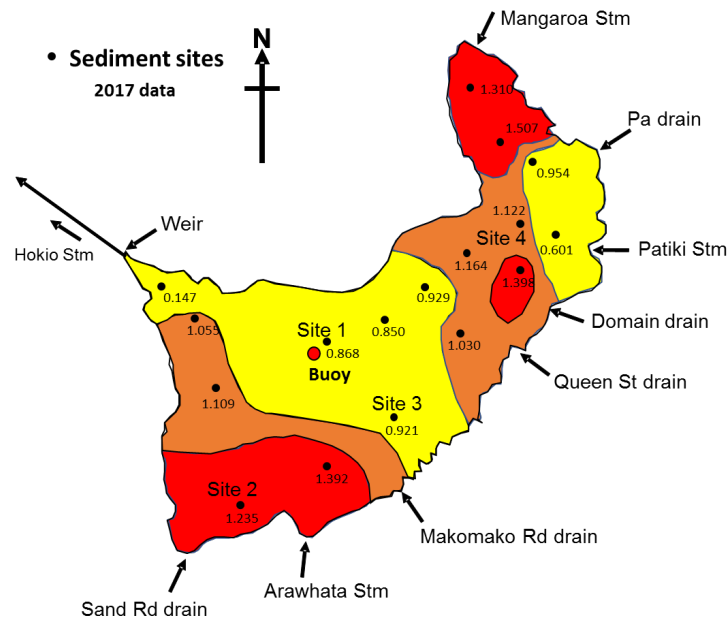


Figure 21: Spatial distribution of TP (g kg^{-1} DW) across Lake Horowhenua from surface sediment samples collected in 2017. The contour boundaries are tentative and are only intended to draw the eye to groupings of similar concentrations.

- o *Is there a difference in SAR spatially across the lake?*

The surficial TP data (Figure 21) suggest it is highly likely that there are differences in the SAR across the lake.

- o *Has the SAR changed over time?*

The lake sediment core data (Figure 10) show that there have been changes in SAR over the last 100 years. SAR increased in general to the present. Prior to the 1960s, the SAR was estimated to be about 1 mm y^{-1} . This historic level of sediment accumulation is comparable with other locations around New Zealand at that time (Trolle et al. 2008) and reflects the low slope of the land and influence of coastal forests on stabilising the soil. Based on the CSSI isotopic proportions, in the early 20th century the sediment came from the southern inflows (Arawhata Stream and Sand Road drain) and the Queen Street drain. In the 1940s the sediment originated from the Arawhata Stream and Patiki Stream catchments, but by 1962 the sediment originated from the Arawhata Stream and Mangaroa Stream catchments, at opposite ends of the lake (Figure 15). The large proportion of soil from the Patiki Stream catchment around 1942 may be consistent with the relatively large proportion of that catchment in cropping on the rolling hills and the possibility of erosion following rainfall events at that time.

During the period that sewage effluent was being discharged into the lake, this may have been an additional source of sediment, but it would seem unlikely to have been a major source. The CSSI isotopic proportions indicate that, in 1972, the sediment originated from the Mangaroa Stream at the northern end of the lake and the Sand Road drain at the southern end of the lake. In 1980 the sediment was coming from the Queen Street Drain which is consistent with observations by Gibbs and White (1991; 1994) of very high flows of turbid water in the Queen Street drain (Figure 22) and the Arawhata Stream. At that time, the Queen Street drain flow was augmented with water from the Ohau River and also received water from hydroponics (M. Gibbs, NIWA, personal observations).



Figure 22: Queen Street drain in flood September 1988. The high sediment load at that time came from runoff from unsealed roads, open drains and land tillage in the catchment of the headwater stream feeding the Queen Street drain. [Photo by Max Gibbs].

b) *What is the effect of the sediment on the water quality in the lake?*

Fine sediment is the major vector for P between the catchment and a lake. The sediment is deposited on the lake bed where P can be released into the water column under reducing (low oxygen) conditions. The P can then be used by algae including cyanobacteria for growth. The immediate effect of fine sediment on lake water quality is the reduction in light levels that can reduce the growth range of native macrophytes, and the interference in feeding by freshwater mussels. This is especially an issue in shallow lakes because of the vulnerability to wind disturbance. The low light levels favour the growth of *Potamogeton crispus* in Lake Horowhenua as this aquatic macrophyte species can tolerate much lower light levels than the native macrophyte species.

- o Is turbidity increasing as the lake becomes shallower?

Analysis of a set of turbidity data for Lake Horowhenua from the period 2013 to 2016 suggests that water depth may affect turbidity. Higher turbidity was somewhat more likely to occur when water levels were low although the correlation was small ($R^2 = 0.08$, $n = 1007$ daily means, $p < 0.00001$). However, under the present lake conditions with aquatic plant cover across much of the lake bed, strong winds may nevertheless cause turbidity events even when water levels are relatively high. Increases in turbidity may be the result of lake bed disturbance by wind waves or the input of fine sediment eroded from the catchments and discharged into the lake via stream inflows.

The correlation of turbidity and algal chlorophyll fluorescence ($R^2 = 0.03$, $n = 960$, $p < 0.00001$, daily means of data recorded by automatic buoy station) was even less than of turbidity and lake level. Wind is probably the main cause of turbidity in Lake Horowhenua.

Question 2: *Should the sediment be removed, or should it be left alone?*

There needs to be very good reasons before deciding to remove sediment. The main reason for removal would be to reduce the internal P load in the lake and thereby to reduce the incidence of summer blooms of cyanobacteria, which are driven by the release of P from the sediment after the collapse of the exotic weed beds around January each year.

However, the removal of a surface layer of the lake sediment could well expose deeper lake sediment that is higher in P per unit volume than the sediment near the surface (Figure 6), although P concentrations per kg sediment dry weight generally decrease with depth (Figure 6), especially in the upper 20 cm. In addition, as mentioned (section 3.9), the P concentration in the sediment is not particularly high compared with other lakes. Moreover, the P load in the sediment may be reducing naturally. Internally loading returns sedimented P back to the water column and a substantial part of this will be flushed from the lake via the outlet. As long as external loading does not increase this should result in a slow decrease in the sediment nutrient legacy. Comparing the spatial surficial P data from 1988 with the recent data from 2017 (Figure 22) suggests that the concentration of P in the surficial sediment (upper 2-cm in 1988 and upper 1 cm in 2017) has decreased by 32% over the last 30 years. This represents an estimated loss of 1.2 tonnes of P from the surficial sediments in the lake.

Removing the surface sediment would also remove residual seed banks for aquatic macrophytes, leaving the lake bed bare and more vulnerable to wind-wave disturbance (i.e., at risk of increasing turbidity).

The removal process would also be very expensive and socially disruptive as the operation of equipment (noise and dust from the dredge and truck movements) would continue for many months. It would require a large area of land on which to store the sediment. This last issue could be resolved by spreading the nutrient and organically rich sediment after dewatering on poor quality land as a 'conditioning treatment' to improve the quality of that land for agriculture.

Removing the sediment would release nutrients, including $\text{NH}_4\text{-N}$, DRP and heavy metals, from the dredged area into the lake water (Dunn et al. 2017). These nutrients could stimulate cyanobacteria blooms and could adversely impact the aquatic biota close to the dredging point at that time. However, the concentrations may not be high as Dunn et al. (2017) observed that only 0.58%–5.50% of the bioavailable $\text{NH}_4\text{-N}$ present in the sediment contributed to the water column concentration during dredging. Similarly, disturbance and resuspension events are unlikely to have a significant

effect on water column DRP concentrations, other than locally where, in the short term, there may be a temporary “spike” in concentrations until phosphates mobilised from sediment porewaters re-associate with suspended sediment particles and newly formed FeOOH minerals, before settling out (Dunn et al. 2017).

Disturbing the sediments may pose a risk to the lake ecosystem through the release of toxic gases such as hydrogen sulphide (H₂S) and methane into the water column. These gases may impact lake biota, including fish, and may be released into the atmosphere where odorous properties could become a public nuisance down-wind of the dredging site. However, in Lake Horowhenua, which is rich in iron, the H₂S should react rapidly and bind with soluble iron, also released from the sediment, to form the insoluble iron sulphide (FeS) (Lohrer and Wetz 2003; Morgan et al. 2012). This would rapidly settle out, potentially mitigating the effect of H₂S.

While the removal of the sediment will obviously remove some benthic organisms as well, because the complete sediment removal is not instantaneous the lowered lake bed will be recolonised from the undisturbed adjacent areas within the lake. A possible exception are kākahi, the freshwater mussel (*Echyridella menziesii*), which have limited mobility except during their parasitic larval stage (the glochidia). Other benthic organisms such as koura and polychaetes will also migrate and colonise the dredged areas (Thrush et al. 1996; Dernie et al. 2003), if there are undisturbed areas of habitable lake bed adjacent to the dredged area.

When sediment is removed, turions, propagules of *Potamogeton crispus*, will drift around the lake and settle onto the newly exposed sediment and grow. Because this plant species can tolerate low light levels and the water column will become turbid during the dredging, it is highly likely that *Potamogeton* will remain dominant in the lake. The sequential recolonisation of the dredged lake bed by aquatic macrophytes will provide a similar level of protection from wind-wave disturbance as is currently afforded by these plants. Consequently, there is unlikely to be a high risk of the lake becoming permanently turbid. There will be increased turbidity during the dredging but this would be expected to occur only in the general area of the dredging.

The mitigation of in-lake dredging effects could be managed by designing a dredging pattern that removed small areas and amounts of sediment from selected areas across the lake so that recolonisation from neighbouring undisturbed areas had maximum chance of success. These undisturbed areas would be dredged in turn, at a later time, rather than having a large area of lake bed being systematically dredged to enhance the chance of recolonisation from adjacent undisturbed areas.

In summary, it is probably best to not remove the sediment. This conclusion is based on the disturbance of areas of cultural significance to owners, the cost of removal and public disruption, the likelihood of exposing sediment that is at least as high in P as the removed sediment, and the observation that the lake is likely to slowly recover as previously predicted (Gibbs 2011). However, if permission were sought and granted to remove the sediment, an important option to consider would be the development of a management strategy for the dredging to allow recolonisation of the newly exposed lake bed thereby mitigating the dredging effects.

Question 3: If the sediment should be removed, how much sediment would be removed and to what depth?

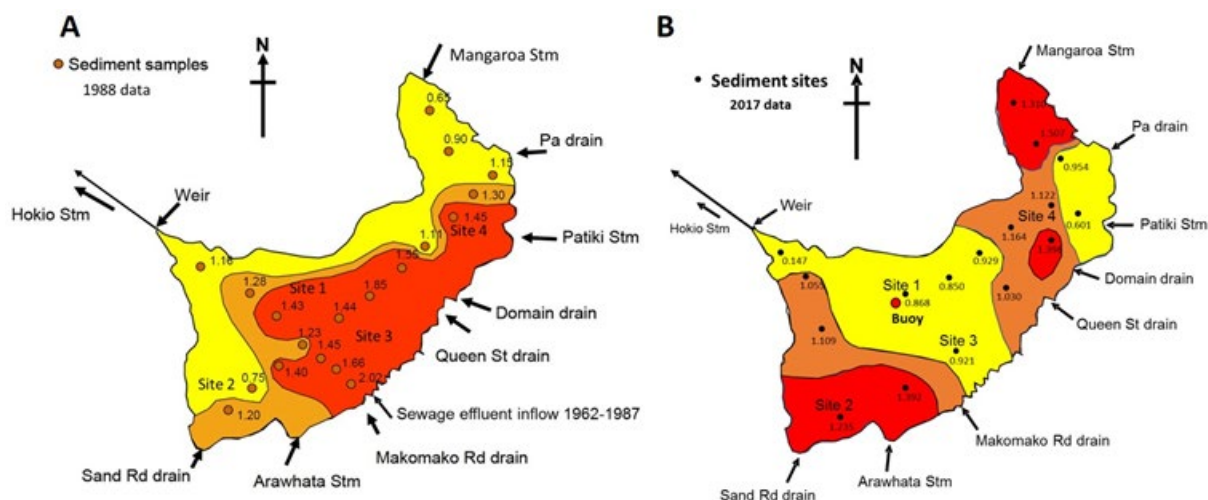


Figure 23: Spatial distribution of TP concentrations across Lake Horowhenua in A) 1988 and B) 2017 with stylised contours between iso-concentrations (g kg^{-1} dry weight). The discharge point for treated sewage effluent into the lake from 1969 to 1987 is shown in part A.

Differences between the 1988 spatial plot of surficial P concentrations and a similar plot drawn from the 2017 data (Figure 23) suggest that there has been a substantial reduction in P in the central part of the lake where the treated sewage was discharged between 1952 and 1987. This may be associated with burial by low P sediments and is consistent with there being low ongoing P input in this area of the lake. In contrast, the increases in P content at the northern end of the lake is consistent with the intensification in dairy farming in the Mangaroa Stream catchment while the increase in the amount of P in the sediment at the southern end of the lake is consistent with intensification of horticulture in the Arawhata Stream catchment. Since P is typically attached to fine sediment, these increases are likely to be associated with sediment runoff. These spatial data are consistent with the source tracking data which indicate that most of the sediment currently entering the lake is from the Arawhata Stream catchment with a lesser amount from the Mangaroa Stream catchment. Also catchment yield per ha y^{-1} results from CLUES modelling are consistent with most N and P entering the lake through the Arawhata Stream and the Mangaroa Stream.

The area of sediment to be removed can be identified using GPS coordinates and tracking on the dredge. In order to remove sediment in patches between zones left undisturbed, as suggested above to facilitate maximum recolonisation of the dredged areas, a work schedule could use a grid coordinate system to identify the area of sediment to be removed in a particular pattern on each day. For example, a 1 ha grid overlay (Figure 24) was developed by Horizons Regional Council to locate weed harvesting areas and this could be a basis for designing the dredging strategy.

From the data presented in Figure 6, the best option for sediment removal appears to be to remove just the soft surface mud, the upper 10 or 20 cm. This would expose a sediment layer that is lower in P kg^{-1} dry sediment. Below 20 cm depth the concentration (g kg^{-1}) was variable but generally decreased further with depth down to 1 m at sites 2 - 4, although slower than in the upper 20 cm,

but not at site 1 where it increased down to 1 m depth. Volumetric concentrations tended to increase with depth but this increase was associated with increasing sediment density. Dredging has been considered in the past (e.g., Gilliland 1989) with a small trial conducted on 10th February 1989. The physical size of the dredge head at that time would have precluded its use for selective sediment removal as shallow as the upper 20 cm (Figure 25A).

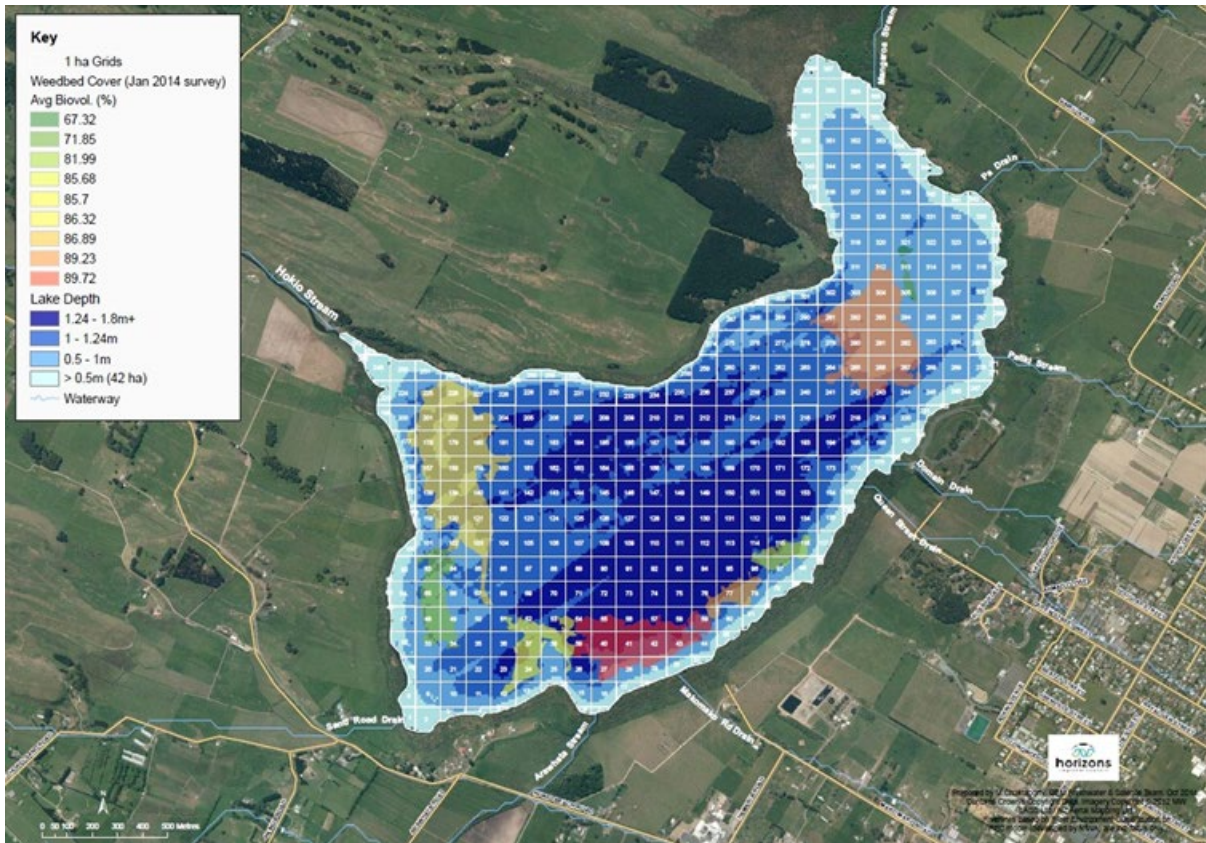


Figure 24: Map of Lake Horowhenua with a 1 ha grid overlay as used by Horizons Regional Council to plan weed harvesting areas. Blue coloured backgrounds indicate depth, while reds to green indicate the density of weed beds in average biovolume (%).

The main issues with dredging are the delivery of the dredged sediment to shore, in the 1989 trial a pipeline was used (Figure 25B), and the dewatering of the sediment (Figure 25C) to enable drier sediment (Figure 25D) to be trucked away to its final destination.

An upgraded dredging system would improve sediment removal efficiency but would still result in similar issues found during the trial. The sediment is about 85% water (Figure 2) and there will be a proportion of lake water mixed with the dredged sediment to allow the dredge pump to work.

This water must be removed in the dewatering ponds before the sediment can be trucked away. Because this water includes the porewater, which will be rich in DRP, NH₄-N and heavy metals, the water draining from the dewatering ponds is likely to stimulate algal (cyanobacteria) growth in the shallow edge waters of the lake.



Figure 25: Trial dredging on Lake Horowhenua on 10th February 1989. Showing A) the dredge used, B) the pipeline delivery to shore, C) the on-shore dewatering pond and bund, and D) the dewatered sludge. [Photos by Max Gibbs].

Question 4: *If the sediment is not to be removed, where does the sediment come from, and what actions are required to reduce sediment inputs to the lake?*

CSSI data (Figure 15, Table 16) show that the main soil sources to Lake Horowhenua are in the Arawhata Stream catchment, which has been contributing between 48% and 75% of the sediment over the last 5 years, and the Mangaroa Stream catchment, which has been contributing between 20% and 45% over the same period.

The construction of a sediment trap on the Arawhata Stream was a first step in reducing the sediment load on the lake from this source. The trap is predicted to reduce the total sediment load from this source by about 50%. Other mitigation strategies that could be considered is the binding of the tilled soil on cropped land with an anionic polyacrylamide to reduce sediment erosion during irrigation and heavy rainfall. This technique is standard practice in the USA and China. On-site sediment retention bunds could also reduce the direct runoff from agricultural land, while constructed wetlands associated with the drainage network could also be beneficial.

In the Mangaroa Stream catchment, land use is dominated by dairy farming on flat to rolling country. Here the options are to prevent stock access to the stream and main drainage channels with appropriate stock exclusion fences, and the development of farm management plans to target specific sediment sources on each farm. Fall back positions for each farm would be a constructed or enhanced natural wetland on the outflow end of the drainage ditches. Spraying or mowing the

grasses and weeds on the sides of the drainage ditches instead of scooping them out with a digger bucket would also leave the banks more stable and thereby reduce the risk of erosion.

The actions required to reduce sediment inputs to the lake include:

- o Sediment trap on the Arawhata Stream. The efficiency is expected to be around 50% but that needs to be confirmed.
- o Developing on-farm mitigation / management plans.
- o Upgrading drainage and maintenance of drains without the use of excavators.
- o Others include the enhancement of natural wetlands or construction of wetlands on the outlets of the main farm drains, the exclusion of stock from all permanent flowing streams and drains with appropriate fencing, investigation of the use of polyacrylamide flocculants on tilled crop land to reduce soil erosion, and the installation of on-side sediment detention bunds on outlets from tilled cropland.

4.2 Heavy metals

High mercury concentrations in the sediment may have repercussions in the food web in the lake (Verburg et al. 2014). Mercury is a contaminant that biomagnifies in the food web. Mercury can be absorbed by phytoplankton and is passed on to consumers in the food web, with mercury concentrations increasing with every step in the food web. As a result, mercury concentrations are typically highest in top predators, especially when these are long lived, such as tuna.

In Lake Horowhenua, mercury concentration in the near surface sediment was $143 \mu\text{g kg}^{-1}$ dry weight. Verburg et al. (2014) found 28 to $343 \mu\text{g mercury kg}^{-1}$ dry weight in the sediment of lakes Rotorua, Tarawera and Rotomahana (Bay of Plenty Region). This resulted in mercury concentrations in trout that were above the international marketing limit for fish ($500 \mu\text{g kg}^{-1}$ wet weight) in two of the lakes (Verburg et al. 2014).

Further work to measure the tissue mercury concentration in tuna and other resident fish species in Lake Horowhenua is recommended.

5 Conclusions and Summary

Earlier core work suggested that the sediment around 40 cm depth may date from the end of the period during which sewage was being discharged into the lake (1952-1987) and thus would reflect 35 years of P accumulation in the lake sediments from the sewage effluent input. Sediment core dating in this report suggests sediment of this period is located at 12.5 – 30.6 cm depth at a central site in the lake, and that the P concentration (g kg^{-1}) was lower at those depths than near the sediment surface. Sediment accumulation rates in the centre of the lake increased to about 12 mm y^{-1} in the early 1960s, from about 1 mm y^{-1} before the 1960s, and dropping to about 4 mm y^{-1} from about 1970 onward. Analysis of the compound specific stable isotopes in the sediment core from site 1 determined that the primary sources of sediment entering Lake Horowhenua are from the Arawhata Stream catchment, associated with horticulture and cropping, and from the Mangaroa Stream catchment associated with intensification of dairy farming in recent years.

6 Acknowledgements

We thank Horizons Regional Council for arranging the required permissions to work on Lake Horowhenua, David Feek for his help with the collection of sediment cores from the lake and sediment from the inflows, Jonathan Procter and Logan Brown for facilitating the fieldwork, and Andrew Kingston for carrying out the CSSI sample analysis. Dating of the sediment cores was done by MyCore Scientific Inc, Ontario, and by the Environmental Radioactivity Laboratory, Institute of Environmental Science and Research Limited (ESR), Christchurch. Johan Wiklund (University of Waterloo) and Andrew Swales provided advice regarding interpretation of Pb-210 and Cs-137 data to estimate the sediment accumulation rate. The proportions in the lake sediment of N, P, Al, Fe, Mn and heavy metals were determined by Hill laboratories. Bulk sediment stable isotope analysis (^{13}C and ^{15}N) were carried out by the NIWA isotope laboratory in Wellington. Funding was provided by the Te Mana o te Wai fund administered through the Ministry for the Environment which went towards the Te Kakapa Manawa o Muaūpoko project led by the Lake Horowhenua Trust, Horizons Regional Council and MBIE grant UOWX1503 (Enhancing the Health and Resilience of New Zealand Lakes).

7 References

- ANZECC (2000) Australian and New Zealand guidelines for fresh and marine water quality. *National Water Quality Management Strategy Paper*, No. 4. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.
- Appleby, P.G., Oldfield, F. (1978) The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, 5: 1–8.
- Appleby, P.G., Oldfield, F. (1983) The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. *Hydrobiologia*, 103: 29-35.
- Bevins, C. (2019) *A record of natural and human induced environmental change from Lake Horowhenua*. Master of Science thesis, School of Agriculture and Natural Environment, Massey University, Palmerston North, New Zealand: 142.
- Cunningham, B.T., Moara, N.T., Torrie, A.W., Parr, P.J. (1953) A survey of the western coastal dune lakes of the North Island, New Zealand. *Australian J. Mar. Freshw. Res.* 4: 343-388.
- Currie, K.J., Dee, K.T., Millson, D.B.E., Walker, W.A., Ferrier, D., Brown, B., Hughes, H., McColl, R.H.S. (1978) Lake Horowhenua, Current condition, nutrient budget and future management. *Report from the Lake Horowhenua technical committee to the Lake Horowhenua Steering committee, Manuwatu Regional Water Board*: 49.
- de Winton, M. (2014) Delimitation of submerged weed bed areas in Lake Horowhenua. *NIWA report HAM2014-015*, prepared for Horizons Regional Council. Horizons Report No. 2014/EXT/1360, ISBN 978-1-927250-61-7: 20.
- Deines, P., Grey, J., Richnow, H-H., Eller, G. (2007) Linking larval chironomids to methane: seasonal variation of the microbial methane cycle and chironomid $\delta^{13}\text{C}$. *Aquatic Microbial Ecology*, 46: 273–282.
- Dernie, K.M., Kaiser, M.J., Warwick, R.M. (2003) Recovery rates of benthic communities following physical disturbance. *Journal of Animal Ecology*, 72(6): 1043-1056.
- Dunn, R.J.K., Waltham, N.J., Teasdale, P.R., Robertson, D., Welsh, D.T. (2017) Short-term nitrogen and phosphorus release during the disturbance of surface sediments: A case study in an urbanised estuarine system (Gold Coast Broadwater, Australia). *Journal of Marine Science and Engineering*, 5: 16. doi:10.3390/jmse5020016.
- Gibbs, M.M., White, E. (1991) Lake Horowhenua and its restoration. Taupo Research Laboratory. *DSIR Marine and Freshwater Report*, No. 127.
- Gibbs, M.M., White, E. (1994) Lake Horowhenua: a computer model of its limnology and restoration prospects. *Hydrobiologia*, 275/276: 467–477.
- Gibbs, M. (2011) Lake Horowhenua review: Assessment of opportunities to address water quality issues in Lake Horowhenua. *NIWA Client Report HAM2011-046*, to Horizons Regional Council: 117.

- Gilliland, B. (1989) *Lake Horowhenua Steering committee – dredging display*, File: 9/6/1: 21.
- Jones, R.I., Grey, J. (2004) Stable isotope analysis of chironomid larvae from some Finnish forest lakes indicates dietary contribution from biogenic methane. *Boreal Environment Research*, 9: 17–23.
- Lohrer, A.M., Wetz, J.J. (2003) Dredging-induced nutrient release from sediments to the water column in a south-eastern saltmarsh tidal creek. *Marine Pollution Bulletin*, 46(9): 1156-1163.
- Mabit, L., Gibbs, M., Mbaye, M., Meusburger, K., Toloza, A., Resch, C., Klik, A. Swales, A., Alewell, C. (2018) Novel application of Compound Specific Stable Isotope (CSSI) techniques to investigate on-site sediment origins across arable fields. *Geoderma*, 316: 19–26.
- Makhutova, O.N., Borisova, E.V., Shulepina, S.P., Kolmakova, A.A., Sushchik, N.N. (2017) Fatty acid composition and content in chironomid species at various life stages dominating in a saline Siberian lake. *Contemporary Problems of Ecology*, 10: 230–239.
- Morgan, B., Rate, A.W., Burton, E.D. (2012) Water chemistry and nutrient release during the resuspension of FeS-rich sediments in a eutrophic estuarine system. *Science of the Total Environment*, 432: 47-56.
- New Zealand Water & Wastes Association (2003) *Guidelines for the safe application of biosolids to land in New Zealand*, Volume 1: guidelines.
https://www.waternz.org.nz/Folder?Action=View%20File&Folder_id=101&File=biosolids_guidelines.pdf
- Pennington, W., Cambray, R.S., Eakins, J.D., Harkness, D.D. (1975) Radionuclide dating of the recent sediments of Blelham Tarn. *Freshwat. Biol.*, 6: 317-331.
- Périé, C., Ouimet, R. (2008) Organic carbon, organic matter and bulk density relationships in boreal forest soils. *Canadian Journal of Soil Science*, 88: 315-325.
- Phillips, D.L., Gregg, J.W. (2003) Source partitioning using stable isotopes: Coping with too many sources. *Oecologia*, 136: 261–269.
www.epa.gov/wed/pages/models/stableisotopes/isotopes.htm
- Phillips, D.L., Inger, R., Bearhop, S., Jackson, A.L., Moore, J.W., Parnell, A.C., Semmens, B.X., Ward, E.J. (2014) Best practices for use of stable isotope mixing models in food-web studies. *Canadian Journal of Zoology*, 92: 823–835.
- Sanchez-Cabeza, J.A., Ruiz-Fernandez, A.C. (2012) ²¹⁰Pb sediment radiochronology: An integrated formulation and classification of dating models. *Geochimica et Cosmochimica Acta*, 82: 183–200.
- Stock, B.C., Semmens, B.X. (2015) *MixSIAR User Manual*, Version 3.0.
<https://github.com/brianstock/MixSIAR/>
- Thrush, S.F., Whitlatch, R.B., Pridmore, R.D., Hewitt, J.E., Cummings, V.J., Wilkinson, M.R. (1996) Scale-dependent recolonization: the role of sediment stability in a dynamic sandflat habitat. *Ecology*, 77(8): 2269-2572.

- Trolle, D., Hamilton, D.P., Hendy, C., Pilditch, C. (2008) Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. *Marine and Freshwater Research*, 59: 1067–1078.
- Verburg, P. (2007) The need to correct for the Suess effect in the application of $\delta^{13}\text{C}$ as a productivity proxy in sediment of autotrophic Lake Tanganyika in the anthropocene. *J. Paleolimnology*, 37: 591–602. DOI 10.1007/s10933-006-9056-z.
- Verburg, P., Hickey, C.W., Phillips, N. (2014) Mercury biomagnification in three geothermally-influenced lakes differing in chemistry and algal biomass. *Science of the Total Environment*, 493: 342–354. doi:10.1016/j.scitotenv.2014.05.097.
- Vodyanitskii, Y.N. (2016) Standards for the contents of heavy metals in soils of some states. *Annals of Agrarian Science*, 14: 257-263.
- Waitangi Tribunal Report (2017) *Horowhenua: The Muaūpoko Priority Report*. Pre-publication version. Downloaded from www.waitangitribunal.govt.nz.
- Wren, D.G., Rigby, J.R., Davidson, G.R., Locke, M.A. (2016) Determination of lake sediment accumulation rates in an agricultural watershed using lead-210 and cesium-137. *Journal of Soil and Water Conservation*, 71: 137-147.