Waikato Peat Lakes Sediment Nutrient Removal Scoping Exercise

CBER Contract Report 78

Prepared for Environment Waikato

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Executive Summary

This report was commissioned by Environment Waikato to examine the available methods for internal (bottom sediment) nutrient removal and their suitability for application in the Waikato peat lakes. Lakes Ngaroto, Kainui, Rotomanuka and Cameron were chosen as focus lakes for the study, based on existing restoration objectives and recreational and conservation values. A range of methods designed to reduce internal nutrient loading was reviewed, including hypolimnetic aeration, hypolimnetic withdrawal and fish removal, with sediment removal, and additions of alum, Phoslock, zeolite, iron making slag and carbon examined in detail. Experimental and observational work was carried out to assess the feasibility of these methods in the target lakes:

- Alum was determined to be the least desirable of the options examined; as there is a high probability that soluble toxic forms of alum will be expressed or released due to the low alkalinity and pH of the target lakes.
- Sediment removal is the most expensive option, but may be appropriate in lakes with high ecological values. However, the external nutrient load must be reduced substantially to prolong benefits of dredging.
- Phoslock and zeolite both effectively reduced phosphate concentrations in the incubation cores. Zeolite was more effective than Phoslock in preventing nutrient release from the sediments following anoxia. However, Phoslock was more effective than zeolite in removing nutrients from the water column. Both substances should be applied with care and with careful documentation of chemical and biological effects as there may be hitherto undocumented effects on aquatic biota.
- The use of iron making slag to reduce internal nutrient load is not recommended, as nutrient concentrations were not reduced in the iron treated cores in an incubation study.
- Dissolved organic carbon addition may be useful in the naturally dystrophic peat lakes, and can be added naturally if measures are taken to conserve the surrounding peat substrate (e.g. riparian vegetation, maintenance of lake

levels). Further study is required to assess how humic substances would affect primary productivity and the availability of phosphate for algal growth.

- Hypolimnetic withdrawal is not a suitable nutrient reduction technique, as none of the Waikato peat lakes possesses a large anoxic hypolimnion, a long period of anoxia or a consistently large lake inflow.
- Hypolimnetic aeration may be useful in Lake Rotomanuka, as this is the only peat lake known to regularly stratify and become anoxic during summer. Hypolimnetic aeration can break down stratification and potentially reduce the abundance of cyanobacteria by disrupting their buoyancy.

Before a pilot study is carried out to reduce internal nutrient load, it is recommended the external nutrient load of the target lake(s) is reduced substantially, to the order of 50 % for most lakes where the catchment is highly modified and effects of restoration measures are not evident. On the basis of the evidence presented in this report, we recommend using fish removal and macrophyte re-establishment as part of an integrated strategy to improve water quality and transparency. Use of a flocculant could also be considered as part of an integrated strategy for reducing internal nutrient loads. The latter strategy should be undertaken under circumstances of mutual cooperation and communication amongst environmental managers, scientists and material suppliers, as optimising the timing and quantity of the flocculant applied will be an iterative process requiring adjustments for each waterbody application.

1.0 Introduction

This report was commissioned by Environment Waikato to review the current methods of reducing internal nutrient loads in lakes, with special reference to the Waikato peat lakes. Currently a high number of these unique lake ecosystems are classified as eutrophic. Varying degrees of restoration effort and methods to reduce external nutrient load have been applied to the Waikato peat lakes, however, few beneficial effects have been noted, and this lack of success has been attributed to the high internal nutrient load present within the lakes. Consequently, this report presents a review of the available methods for reducing internal nutrient loading, and the suitability of these techniques for use in the Waikato peat lakes.

The Waikato peat lakes are unique ecosystems that once belonged to a large peat wetland system. They are concentrated around the Waikato, Hamilton and Waipa Districts, where their association with peat formations has had a marked effect on their physical, chemical and biological nature. The lakes represent some of the few remaining areas of wetlands in the Waipa and Waikato Districts, and contain unique species of plants and animals that are adapted to live in the acidic conditions in association with the peat influence.

Before Europeans settled, most of the peat lakes in the Waikato Region had no inlets or outlets. Instead, seasonal influences (e.g. heavy rainfall and droughts) were responsible for variations in lake level. Water entered the lakes by subsurface flow from adjacent peat bogs and from rainfall, and was lost primarily through evaporation. Consequently, the Waikato Region’s peat lakes are vulnerable to the lowering of water levels, and drainage of the surrounding peat bogs has lowered water tables, and subsequent farming on peat soils has led to the shrinkage of the peat substrate. Seventy-five percent of the original peat bog area has been converted to farmland (Schipper & McLeod, 2002). Levels of most of the Waikato peat lakes have therefore been lowered substantially, and without a wetland buffer to filter nutrient runoff and trap silt eroding from surrounding farmland, the lakes have become eutrophic.

Restoration activities are currently being undertaken at a number of the Waikato peat lakes by management agencies or community groups. The priority sites for restoration to improve the ecological health of the lake as determined by Environment Waikato are Lakes Mangakaware, Serpentine, Ngaroto, Rotomanuka and Maratoto. The lakes we chose to examine in this study are Ngaroto, Kainui, Rotomanuka and Cameron (Fig. 1). These lakes were chosen to examine the feasibility of removing internal source of nutrients as a restoration method for the following reasons:

- High community interest (e.g. Lakes Ngaroto, Kainui, Cameron);
- Recreational values (e.g. Lakes Ngaroto, Kainui);
- Degree of modification – all lakes have been modified to some degree;
- Influence of peat (e.g. Lakes Cameron, Kainui, Rotomanuka);
- Serious algal bloom problems (e.g. Lakes Ngaroto, Kainui);
- Some effort to restore or preserve the lakes has been made, e.g. stock exclusion, weirs, sediment traps, esplanade reserves and native plantings.

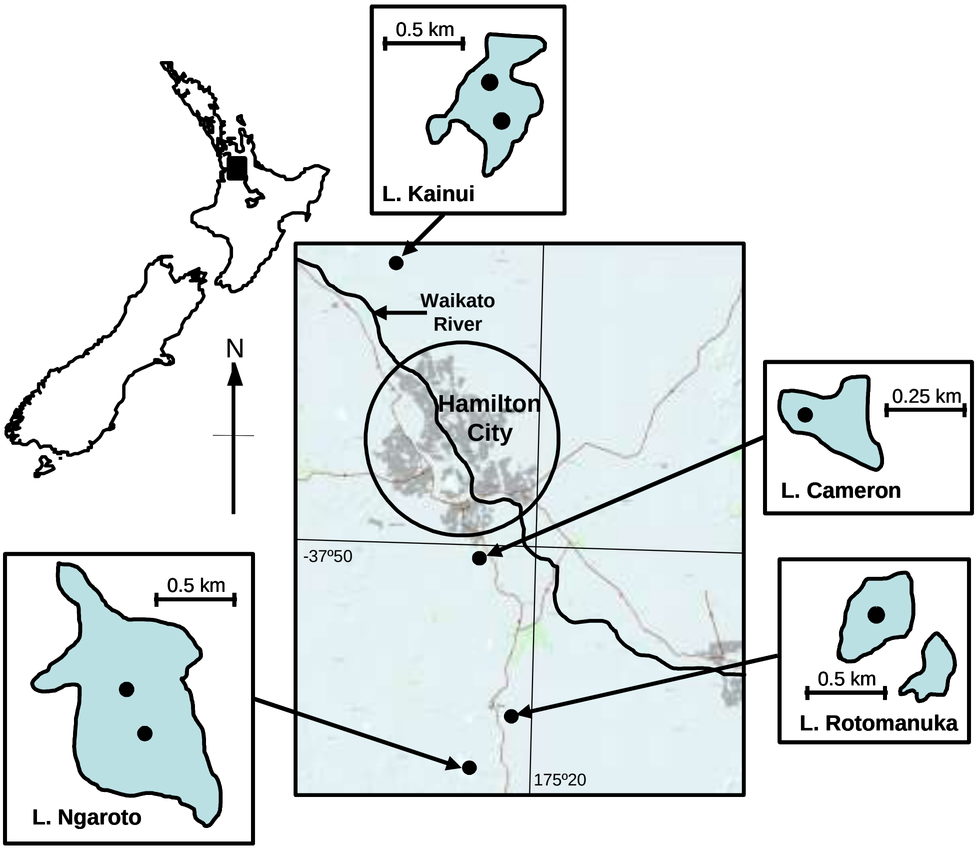

Figure 1. Location of the four lakes targeted in this study for internal nutrient reduction techniques. The circles located within the lakes represent the substrate coring sites

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1.1 Lake Ngaroto

Lake Ngaroto (area 108 ha, maximum depth 4 m) is not directly associated with the encroachment of peat bogs in the Waikato valley, but is instead affected by local wetland development around its margins (Selby & Lowe, 1992; Lowe & Green, 1987; Green & Lowe, 1985). Therefore it is incorrect to refer to Lake Ngaroto as a ‘peat lake’, although the lake could be influenced by humic substances from the surrounding reserve area and associated wetland (Boswell *et al*. 1985). Peat surrounding Lake Ngaroto extends to about 0.5 m deep at the lake margin and down to 2.5 m approximately 600 m from the lake edge. The peat associated with Lake Ngaroto tends to be lake peat, deposited when the lake area was larger and sedgy peat, which is comprised of marginal lake vegetation in a semi-decomposed state (Thompson, 1994).

Although the bottom sediments of Lake Ngaroto do not become anoxic in the summer, internal nutrient loading remains important. This occurs because in very productive lakes the sedimentation of organic material in summer is so high that bacterial consumption of oxygen reduces the oxic layer of sediment to a few millimetres. Thus the capacity of the sediment to bind phosphorus is reduced and phosphorus is released from decomposed organic matter or deeper parts of the sediment (Søndergaard *et al*. 2003).

Lake Ngaroto is used extensively for recreation, although recreational activities often become impaired during the summer months when cyanobacteria reach toxic levels in the lake. Current restoration activities include; placing a weir on the main outflow to regulate water levels, building sediment traps on the main inflows, riparian planting, spraying pest willow species and establishing a fenced reserve margin.

1.2 Lake Kainui

Lake Kainui (area 24.9 ha, maximum depth 6.7m) (also known as Lake D) is highly peat-influenced, as it is located within the Kainui peat bog, in the Horsham Downs area. Previously no submerged vegetation has been recorded in this lake (Champion *et al.* 1993), however, the presence of charophytes was recorded during a recent survey. Lake Kainui suffers from regular cyanobacterial blooms, which can become a hindrance to recreational activities such as power boating on the lake. Currently, the lake perimeter has been fenced and riparian planting is underway.

1.3 Lake Rotomanuka (North)

Lake Rotomanuka (area 17.1 ha) is the deepest of the Waipa lakes at 8.7 m. Sediment cores taken from the northern side of Rotomanuka by Thompson and Champion (1993) revealed that close to the lake there is a shallow peat deposit arising from marginal vegetation, which is overtopped by mineral soil. Further from the lake there is 1.5 m of oligotrophic (acid) peat overtopped the underlying mineral layer. These observations confirm that Lake Rotomanuka is associated with the edge of the Moanatuatua bog and deep peat deposits.

Stratification and anoxia of the hypolimnion in Lake Rotomanuka has been recorded during summer (Boswell *et al.* 1985). These conditions are likely to reduce binding of phosphorus to the sediments, resulting in phosphorus releases to the overlying water (Søndergaard *et al.* 2003). The perimeter of Lake Rotomanuka North and South and the wetland that adjoins the two lakes has been fenced to exclude stock.

1.4 Lake Cameron

Lake Cameron (area 3.4 ha, maximum depth 1.5 m) (also known as Lake Kareaotahi) is highly influenced by peat formations. The northern margin of the lake is surrounded by mineralised soil and shallow peaty deposits. The south-western margin faces the Rukuhia peat bog and the depth of eutrophic marshy peat exceeds 3 m (Thompson, 1994). No submerged macrophytes have ever been recorded in this lake, which has been attributed to low water clarity due to peat staining and an apparent high level of turbidity (Champion *et al*. 1993). Champion *et al*. (1993) and Thompson (1994) estimated that the edge of the Rukuhia peat bog would subside below present lake levels by 2003 if drainage continued at the rate observed in 1993. Currently the maximum lake depth is 1.5 m and a minimum lake level has been set, although there is no water control structure present. Extensive native plantings and a small recreational area have been established on the northern lake edge of Cameron and the perimeter of the lake has been fenced.

1.5 Outline of report

The control of sediment and nutrient inputs entering the lakes is a high priority for most lake restoration projects, but these external controls may not be enough to produce the desired changes. The purpose of this report is to determine what options are available for removing nutrients from within the Waikato peat lakes in order to help achieve existing restoration objectives.

This report reviews current methods for removing nutrients from within lake systems: sediment removal, phosphorus inactivation, including the capping or sealing of nutrients, hypolimnetic discharge, hypolimnetic aeration and biomanipulation (fish removal). For each method the technical and political issues are outlined along with examples of field trials undertaken world-wide and in New Zealand, where available. From these methods sediment removal and phosphorus inactivation using flocculants were chosen for more detailed examination, to determine if they would be appropriate in-lake nutrient removal techniques for the Waikato peat lakes. This was done by collecting new and previously published chemical and physical data from the target peat lakes and assessing the biological, chemical, physical and long-term effects of alum treatment and sediment removal in the peat lakes.

In addition, to gain further insight on the effects of phosphorus inactivation using Phoslock, modified zeolite, iron making slag and carbon addition, a laboratory incubation core study was conducted using cores obtained from Lake Ngaroto. The technical factors and case studies for these methods are reviewed in section 4 of this report, and the methods, results and discussion and conclusions of the laboratory study are presented in Section 5.

The aim of this study was to determine the feasibility of current methods for controlling internal nutrient loads within the peat lakes. Based on this aim, four lakes were chosen to specifically test at a small scale – by laboratory and field mesocosms – the feasibility of applying some of the more promising techniques. Section 9 of this report presents the methodology, equipment requirements and possible monitoring programme for a field trial designed to reduce internal nutrient loading within a target lake, based on the conclusions obtained from the literature review, and laboratory studies.

2.0 Sediment Removal

2.1 Literature Review

Sediment removal is recommended in cases when the internal nutrient load needs to be reduced, recreational activities are impaired due to sediment build-up, for macrophyte control or to remove toxic substances present in the lake bed (Cooke *et al.* 1993). Sediment removal for reduction of the internal nutrient load is only recommended in lakes where all possible efforts have been made to reduce external nutrient inputs, and where, because of cycling of nutrients from internal sources, there has been no improvement in water quality (Jorgensen, 1980).

Where dredging is intended, concurrent reductions of 50–75% of the external nutrient load are recommended in order to prolong the benefits of sediment removal (Kleeberg *et al.* 2001; Kleeberg & Kohl, 1999). A single lake dredging, however, may not be a permanent solution. Due to sedimentation and ongoing external nutrient inputs, dredging will most likely have to be repeated on a regular basis or augmented with other biomanipulation techniques such as fish removal (Cockshoot Broad, England: Moss *et al*. 1996; Lake Trummen, Sweden: Cooke *et al*. 1993).

There are several factors that must be considered before deciding to dredge:

- How much sediment needs to be removed? If the lake requires a reduction in nutrient load then the amount of sediment removed will depend on the vertical nutrient profiles of the sediment. However, if the lake requires deepening to facilitate recreational activities, then the desired depth will depend on the requirements for recreation.
- What are the characteristics of the newly exposed sediment? If the sediment exposed by dredging has the same nutrient release characteristics as the old sediment there will be no decrease in nutrient loading (Gulati & van Donk, 2002).
- Are toxic substances present in the sediment? These can be released into the water column during dredging and can contaminate the disposal area.

- Resuspension of sediment during dredging. This can release phosphorus from nutrient rich sediments into the water column, which can stimulate algal blooms or expose the whole water column to any toxic substances present in the sediment.
- Longevity of treatment. High sedimentation rates and external nutrient inputs will decrease the effectiveness and longevity of any benefits arising from sediment removal. Additionally, newly deposited sediment may have the same phosphorus release characteristics as the sediment that is removed (Gulati & van Donk, 2002).
- Increased likelihood of anoxia. If areas of the lake are made substantially deeper than the original lake bed these areas could be sheltered from wind mixing and become prone to anoxia.
- Disposal area. Flooding of trees is likely to kill them and should be prevented. Further contamination of water bodies with disposal runoff is undesirable. Disposal areas are often designed too small; retention times and volume of sediment to be removed should be calculated with a 5 – 10 % oversize safety factor added. Additionally, the disposal site should be capable of withstanding a 25-year flood event (Cooke *et al*. 1993).
- Do the benefits offset the costs? Dredging is an expensive operation and without additional remedial actions (i.e. concurrent catchment nutrient load reductions) would need to be repeated every three to four years to effectively reduce internal nutrient load.

2.1.1 Political issues

One of the political issues that could affect the desirability of dredging is whether there are any historic sites associated with the target lake. For example, there are five pa sites closely associated with Lake Ngaroto, although almost all evidence of these appears to have been removed or destroyed (Amess *et al*. 1978; Pick, 1968). Many other small Waikato lakes appear to have been associated with pa sites and may have special significance to local iwi. Additionally, although all the target lake beds are currently crown-owned, the Waikato-Tainui iwi have a claim over the Waikato River, and these lakes are included as part of the claim (Richard Cox, pers. comm.). Dredging may reduce options for paleolimnological studies on undisturbed lake sediments, such as the study undertaken by Green and Lowe (1985) for Lake Maratoto.

Disturbance and removal of benthic organisms occurs during dredging. However, if areas of the lake bed are left undisturbed there is the potential for migration and reestablishment of these in dredged areas. The location of disposal areas is also important as these may produce offensive smells, or leach into waterways if not designed correctly.

2.1.2 Case studies

Cases studies of sediment removal have been selected from England, the Netherlands, Sweden, South Bohemia and Germany. Unfortunately there are no documented case studies of sediment removal in New Zealand. Both the Alderfen Broad in England and Lake Geerplas in the Netherlands are examples of northern hemisphere peat lakes that have been dredged to decrease internal nutrient loads. Both of these shallow lakes were once located in extensive peat deposits, but differ from the Waikato peat lakes as they were excavated in medieval times, for peat extraction.

In Alderfen Broad (England) (lake area 4.7 ha) phosphorus release from the sediment was determined to be an important nutrient source after the inflow was diverted around the lake to reduce external nutrient loads (Phillips *et al*. 1999). Dredging was undertaken to remove the upper 0.5 m of sediment, to increase lake depth to 1 m. Although the newly exposed sediment was more peaty and had a substantially lower phosphorus content than the sediment that was removed, within a year the total phosphorus content of the sediment had increased to 80 % of its original value. However, phosphorus concentrations in the overlying water were substantially reduced, although they remained higher than concentrations recorded prior to eutrophication. They concluded that sediment removal was not effective in Alderfen Broad as the lake was not adequately flushed due to the small catchment area and lack of inflows. Phillips *et al.* (1999) concluded that sediment removal was more likely to be effective in well flushed systems, but would not provide a long-term restoration solution on its own.

In a similar peaty system the top 25 cm of bottom sediment from Lake Geerplas (28 ha) was removed after external nutrient loads were reduced by 78%. However, dredging did not produce the desired reduction in total phosphorus (TP), as the loose mud layer that formed over the hard sediments after dredging had similar phosphorus release characteristics to the original sediment (Gulati & van Donk, 2002).

An experimental study conducted on sediment cores taken from Lake Muggelsee (Germany) found that the phosphorus release rate from "dredged" cores was 50 % less than the release rate from undisturbed sediment cores (Kleeberg & Kohl, 1999). However, as net phosphorus release is dependent on the P supply via sedimentation, the authors estimated that after one or two years of undisturbed biological production and sedimentation, phosphorus release from the sediments would continue. Subsequently, Kleeberg and Kohl (1999) concluded that a reduction in phosphate deposition rate by reducing the external load would be a better long-term reduction technique than removal of sediments.

On a whole lake scale a similar temporary reduction in nutrients was found in Vajgar fish pond (40 ha) (South Bohemia) following suction dredging in 1992 (Pokorny & Hauser, 2002). A total of 330,000 m^3 of sediment was removed, and in the first year following sediment removal, the pond served as a phosphorus trap. The Vajgar fish pond was dredged in an attempt to reduce internal nutrient loading and to decrease cyanobacteria. In the first year following dredging the phytoplankton community showed more desirable characteristics, with an increase in species diversity and an absence of *Microcystis* sp. However, three years later phytoplankton phenology had returned to the pre-sediment removal state, with the cyanobacterial species *Aphanizomenon flos-aquae*, *Microcystis aeruginosa* and *Microcystis* sp. once more dominant. Pokorny and Hauser (2002) concluded that sediment removal provided a short-term improvement in water quality, and if water quality was to be maintained external nutrient loads should be reduced substantially.

Lake Trummen (100 ha) (Sweden) is one of the best documented cases of successful water quality improvement from sediment removal. High-nutrient wastewater was discharged into the lake from 1895 to 1959. In 1959 wastewater inputs ceased, but the lake remained hypereutrophic, which was found to be due to substantial internal nutrient cycling. From 1970 to 1971 1 m of sediment was removed from the lake bed, increasing the average lake depth from 1.1 m to 1.75 m. The total volume of sediment removed was about 3,000,000 m^3. This treatment reduced the P content in the surface sediment layer from 2.4 mg L^{-1} to 0.1 mg L^{-1} and the phosphate concentration in the water column by 90%. Total nitrogen concentrations were also reduced by approximately 80%. Four years following dredging P increased once more, but this was found to be associated with an influx of planktivorous cyprinid fish. Fish removal followed, with 2 t of fish required to be removed every year to maintain low P levels. This case study demonstrates that reducing the internal nutrient load is possible, but other influences may increase internal nutrient load in a relatively short period (Cooke *et al*. 1993).

2.1.3 Suitability for the Waikato peat lakes

To conclude, dredging is not a solution on its own. It may be beneficial in shallow lakes which need to be deepened, or as a temporary in-lake nutrient reduction measure. Dredging does not appear to be more successful in smaller lakes, although it would certainly be cheaper. Project costs can range widely and will depend on the type of equipment used, the area and depth to be dredged, disposal site proximity, the density of the sediments being removed and whether there is an end use for the removed sediments. Some of the sediment removed from Lake Trummen was sold as potting soil and topsoil dressing, thus considerably reducing the total cost of dredging. However, when Cooke *et al*. (1993) compared alum treatment and dredging costs in 18 lakes, alum application was considerably cheaper (US \$564 ha^{-1}) than dredging (US \$17,894 ha^{-1}).

The case studies listed above all considered reductions in external nutrient load to be essential prior to dredging, and Kleeberg & Kohl, (1999) recommended at least a 50% reduction of the external nutrient load. If drastic external nutrient reductions are not undertaken newly exposed lake sediments will rapidly reabsorb the incoming nutrients. Even when all the aforementioned factors are considered, dredging only provides a temporary reduction in internal nutrient load. However, if the nutrient reduction is managed properly it could provide a window of opportunity for other biomanipulation measures such as fish removal or macrophyte reestablishment (Cooke *et al*. 1993).

Potentially, if peaty soils or lake beds are re-exposed, the humic substances in the peat may bind and prevent the release of phosphorus. In peat lakes where autochthonous (within-lake) primary production is limited, concentrations of phosphorus and nitrogen may be as high as or higher than lakes which are considered eutrophic. This is due to the inactivation of phosphorus by humic acids. Humic substances dissolved in water have the ability to bind nitrogen and phosphorus compounds and metal cations (Górniak *et al*. 1999; Jones *et al*. 1988). The nutrients bound to humic substances cannot be directly utilised by phytoplankton due to their high molecular weights and their imperviousness to enzymatic hydrolysis. Consequently, humic substances accumulate in lakes and generally contain ca. 54% of carbon, 3–6% of nitrogen and a smaller percentage of associated phosphorus, all of which constitute a large unavailable nutrient source for bacterioplankton and phytoplankton (Vähätalo *et al*. 2003).

2.2. Laboratory study

To assess the feasibility of dredging as a nutrient removal technique we examined the 'factors that need to be considered before dredging' (as outlined in section 2.1) for the four target lakes. We condensed these factors into laboratory and field experiments to assess the practical suitability of dredging for these lakes in relation to nutrient concentrations and sediment removal volume, and the potential problems that may be encountered if dredging was carried out (longevity of treatment, toxic substances, disposal area design and sediment resuspension).

2.2.1 Field methods

Duplicate cores were taken with a 0.5 m gravity corer from single or multiple sites within the target lakes (Ngaroto, Kainui, Rotomanuka and Cameron), and sectioned at 10 cm intervals. Duplicate samples from each section were analysed to determine water content, organic content, sediment porewater dissolved nutrient concentrations, and sediment total phosphorus and heavy metal concentrations at each depth to 30 cm.

2.2.2 Porewater dissolved nutrients

Porewaters were extracted by centrifuging sediment samples at 3650 rpm for 40 min. The supernatant was then removed and filtered using a glass microfibre filter (GF/C) (1.0 μm nomimal pore size) and diluted by a factor of six before nutrient analysis using a Flow Injection Autoanalyser system (QuickChem® 8000, Automated Ion Analyser, Zellweger Analytics, Lachat).

Porewaters were used to obtain a vertical profile of the dissolved nutrients (NH_4-N, PO_4-P, NO_3-N, NO_2-N) down to 30 cm within the sediment. As long as the dissolved nutrients are higher in the porewaters than the hypolimnion the potential for nutrients to be released from the sediment remains. Mapping the vertical distribution of both porewater nutrients and total phosphorus within the sediment should enable us to establish the optimal dredging depth, where sediment nutrients are lowest. The amount of porewater nutrients were calculated from the amount of sediment the porewaters were extracted from and scaled to obtain a dry weight (dw) per kilogram measurement.

2.2.3 Total Phosphorus

After sediments had been heated to 550°C for an hour, total phosphorus was extracted using 1.0 M HCl solution and placing Falcon tubes in a 60°C water bath for 2 h (modified method from Johengen, 1996). Samples were then cooled and analysed using the Flow Injection Analyser.

2.2.4 Heavy metals

Lake sediment was analysed at the sediment-water interface and at 30 cm depth, for the presence and concentration of metal cations, including potentially toxic heavy metals. The metals analysed for were iron (Fe), aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). All samples were dried and heated to 550°C for an hour before analysis by ICP-MS by Hill Laboratories (Hamilton).

2.2.5 Sedimentation rate

Sediment traps consisting of four PVC pipes arranged vertically on a weighted wooden frame suspended with a subsurface buoy were deployed for approximately 15 days in each lake. Prior to immersion each pipe was cleaned thoroughly and filled with reverse osmosis-treated water. After removing the pipes only the bottom 0.5 L of settled sediment was retained and dried at 105°C for 24 h to determine sedimentation rates for each lake. For the larger Lake Ngaroto sediment traps were deployed at two sites, in the smaller lakes Kainui, Rotomanuka and Cameron only one sediment trap was required.

2.2.6 Percentage water content

To determine water content, wet sediments were weighed, dried at 108°C for 24 h before cooling in a desiccator and then reweighing:

Percentage water content = [(wet sample (g) – dry sample (g))/ wet sample (g)] * 100

2.2.7 Percentage organic content

To determine the organic content of the sediments, dried sediments were heated to 550°C for 1 hour to produce an inorganic residue, and reweighed:

Percentage organic content = [(dry sample (g) – inorganic residue (g))/ dry sample (g)] * 100

2.2.8 Settling rate

Polycarbonate columns (height = 750 mm, diameter = 138 mm) were deployed in the laboratory to determine settling rate and bulking rate of removed sediment. Settling rate and bulking rate are important parameters required when designing a disposal area for the dredged sediment, as they will determine the size of the disposal area and an overflow rate at which suspended solids are a minimum. Sediment from Lake Cameron was mixed with lake water to obtain three different suspended solids concentrations (70 g L^{-1}, 76 g L^{-1} and 90 g L^{-1}) before pouring into settling columns and measuring the changes in depth from the original sediment surface to the sediment-water interface over time. This test was run over 5 days.

2.2.9 Sediment resuspension

To determine how different lakes were affected by sediment resuspension, the mean lake fetch and mean lake depth of 11 Waikato lakes was plotted on a graph showing sediment shear stresses under different fetch and depth characteristics for a wind speed of 5 m s^{-1}. This graph illustrates the susceptibility of various lakes to sediment resuspension based on their fetch and average depth. Gusts of > 5 m s^{-1} occurred on 59 days of the year in 2003 (Hamilton airport data, Environment Waikato). Sediment resuspension affects the stability of the sediment and clarity of the water, thus the effect of sediment resuspension on the recolonisation of macrophytes can be examined.

2.3 Results and Discussion

2.3.1 Volume of sediment to be removed

Porewater dissolved nutrients

Ammonium concentrations were highest in Lake Ngaroto sediments and increased with depth, reaching a maximum of 960 mg dw kg^{-1}sediment dry weight at 30 cm (Fig 2.3.1). Ammonium concentrations were lowest in Lake Cameron, but also appeared to increase with depth in this lake.

Even the lowest porewater PO_4-P concentration (Rotomanuka at the sediment-water interface, 1.276 mg dw kg^{-1}) was almost 400 times higher than the corresponding lake water PO_4-P concentration (Rotomanuka, 0.0033 mg dw kg^{-1}) (Fig. 2.3.2). Lake water and porewater concentrations for the sediment-water interface showed the smallest difference in Lake Cameron with the porewater concentration only 18.5 times higher than that of the overlying water.

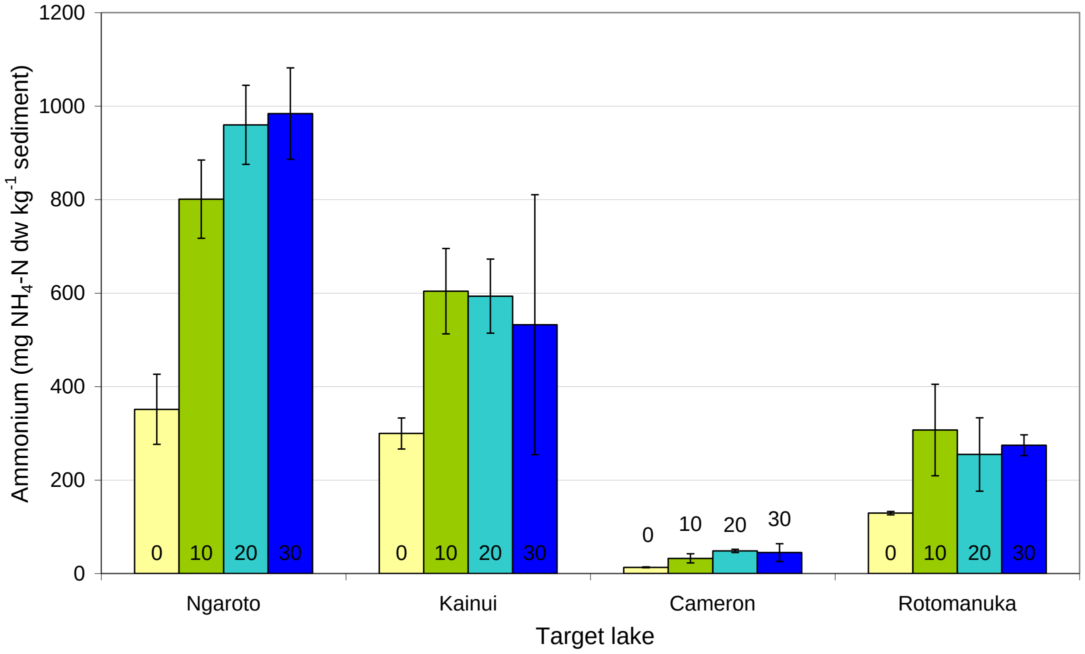

Figure 2. Ammonium (mg NH_4-N dw kg^{-1} sediment) concentrations in porewaters at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means ± 1 S.E.

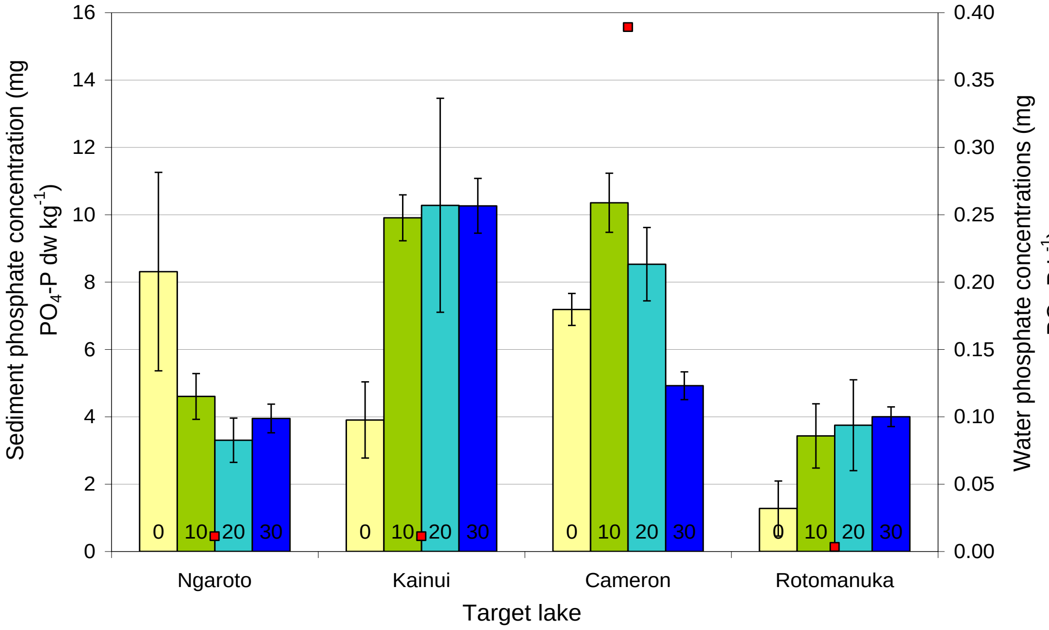

Figure 3. Mean phosphate (PO_4-P, soluble reactive phosphorus; mg dw kg^{-1} sediment) and overlying lake water in each of the four target lakes. Bars are means ± 1 S.E for porewater phosphate concentrations at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes, plotted on the sediment phosphate axis. Overlying lake water DRP concentrations for each lake are represented by squares and are plotted on the water phosphate axis.

Lake Ngaroto had the highest porewater PO_4-P in the top 1 cm of sediment, which appeared to decline with depth down to 20 cm before increasing slightly at 30 cm (Fig 2). In contrast phosphate concentrations in Kainui and Rotomanuka appeared to increase with depth. Lake Cameron's phosphate concentration peaked at 10.4 mg dw kg^1 at 10 cm before declining to 4.9 mg dw kg^{-1} at 30 cm depth.

The amount of sediment that would need to be removed for effective dredging will depend upon the nutrient profiles within the sediments. For example in Ngaroto it would be more cost effective to skim the top 10 cm of sediment as this contains the most available phosphorus for algae growth. If 75% of the lake bed was dredged this would result in approximately 75,000 m^3 of sediment removed. However, sediments below 20 cm still contain between 30–40 times more phosphate than found in the water column, and this phosphate would become available on exposure following dredging.

In both lakes Rotomanuka and Kainui nutrient profiles showed phosphate concentrations were more than two-fold higher at 30 cm than at the surface. This suggests dredging would either be unsuitable, as porewater nutrient concentrations on the newly exposed sediment surface would enhance nutrient release, or dredging would have to be deeper than 30 cm to expose lower porewater nutrients. If for example the amount of sediment to be removed in Kainui was 75 % of the area of the lake bed and exposure was down to 1 m depth, 180,000 m^3 of sediment would need to be removed and a disposal area provided.

Nitrate concentrations in Lake Rotomanuka appeared to increase with depth. Nitrate concentrations were lowest in Lake Cameron across all depths (Fig. 2.3.3). Nitrate concentrations in Ngaroto and Kainui did not appear to vary significantly with depth.

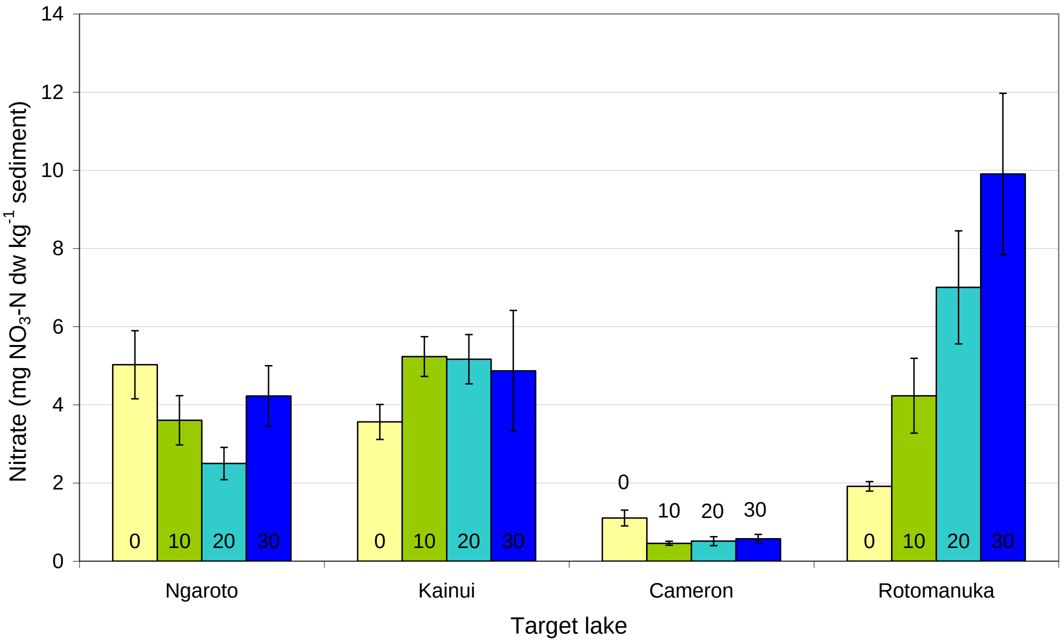

Figure 4 Nitrate concentrations (NO_3-N mg dw kg^{-1} sediment) in porewater at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means ± 1 S.E.

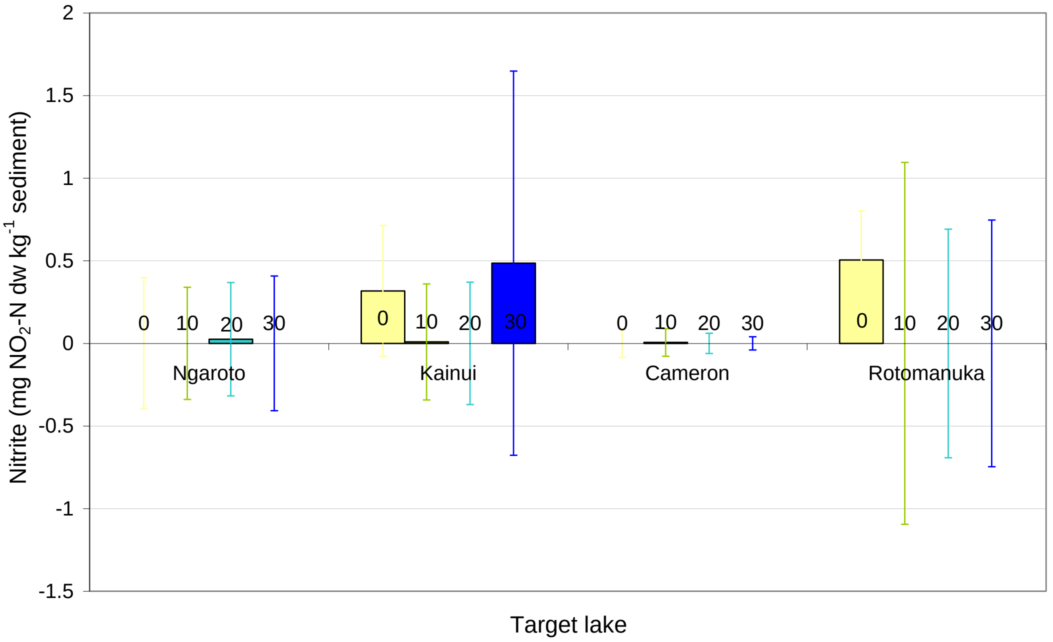

Figure 5 Nitrite (mg NO_2-N dw kg^{-1} sediment) concentrations in porewaters at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means ± 1 S.E.

Nitrite concentrations were highly variable, and concentrations were generally close to detection limits (5 μg L^{-1}). Sediment nitrite concentration at 0 cm in Lake Rotomanuka was the only value for which error bars did not include zero (mean = 0.5 mg dw kg^{-1}, S.E. = 0.3, Fig. 2.3.4).

Total phosphorus

Total phosphorus concentrations were highest in the top sediment layer at Lake Cameron, reaching 2621 mg dw kg^{-1}, although concentrations declined with depth. All lakes exhibited the lowest total phosphorus concentration at 30 cm depth (Fig. 2.3.5).

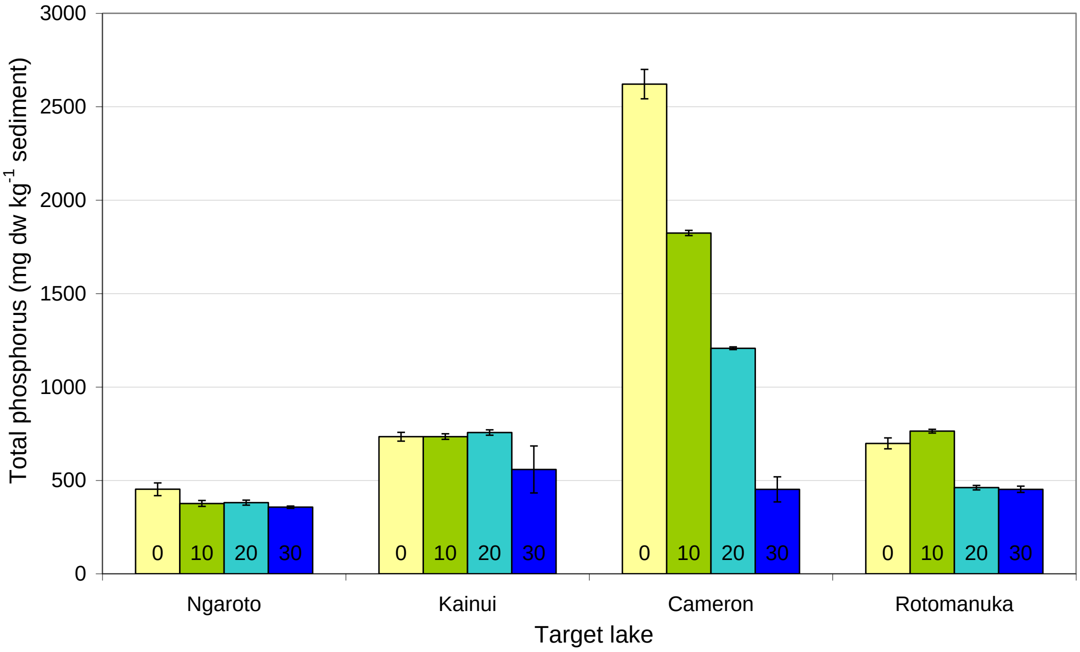

Figure 6 Concentrations of total phosphorus (TP mg dw kg^{-1}) at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means (n = 3) ± 1 S.E.

The high total phosphorus concentrations in Lake Cameron compared to PO_4-P could be due to greater concentrations of organic matter and phosphate binding in these humic sediments. Lake Cameron is the most peaty of the lakes, being adjacent to the Rukuhia peat bog on the south-western side, with a peat depth of 3 m, and the northern margin is bounded by peaty deposits 1.25 m deep (Thompson & Thompson, 1994). As Cameron Lake is very shallow (max. depth, 1.5 m) these peat deposits may have a greater effect on the chemistry of the lake than in Lake Kainui, (max. depth, 6.7 m) which is located on the edge of the Kainui peat bog and surrounded by approximately 1 m of peat (Davoren *et al*. 1978).

2.3.2 Toxic substances

The presence of high concentrations of heavy metals may limit options for disposal or reuse of lake sediments (Copp & Browne, 1984). Water quality guidelines for non-polluted sediment have been established for New Zealand by the Australian and New Zealand Environment and Conservation Council (ANZECC). The New Zealand guidelines (Appendix 1) are based on a statistical probability of effects on invertebrate species, principally amphipods, which are 10% effect-induced for ISQG-Low and 50% for ISQG-High (ANZECC, 2002).

Table 1. Total recoverable heavy metals from sediment depths of 0 and 30 cm in the four target lakes. Values in bold are heavy metal concentrations that exceed the ANZECC (2002) ISQC Low trigger values.

Lake (cm)	**Total recoverable substance mg kg^{-1} dry weight**									
	Fe	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Kainui 0	28300	96000	10	0.8	16	42	< 0.1	11	44.6	**213**
Kainui 30	25000	100000	6	0.4	15	33	< 0.1	9	36.4	119
Rotomanuka 0	52900	38100	7	0.6	11	24	< 0.1	7	**57.7**	**254**
Rotomanuka 30	13900	46900	3	0.2	8	26	< 0.1	5	8.1	76
Ngaroto 0	51400	57500	7	0.6	9	22	< 0.1	7	16.6	197
Ngaroto 30	52400	61000	7	0.7	10	22	< 0.1	7	16.8	**201**
Cameron 0	20800	50300	7	0.7	9	34	< 0.1	6	25.2	188
Cameron 30	13800	56400	5	0.3	10	24	< 0.1	7	19.2	60

All the heavy metal concentrations found in the target lakes are below the ISQG-High values (Table 1). However, the top 1 cm of sediment in Lake Rotomanuka exceeds the ISQG-low trigger values for both lead (50 mg kg^{-1} dry weight) and zinc (200 mg kg^{-1} dry weight) content. Lakes Kainui and Ngaroto also exceed the ISQG-Low trigger values for zinc concentrations.

These high zinc and lead concentrations could have implications for the method of dredging employed and the disposal area design. Dredging would be best done in a manner to avoid sediment contact with the entire water column, such as hydraulic dredging, which removes sediment from the lake bottom directly into a disposal pipe.

Once in the disposal area sediments can either be dried out, to reduce disposal area volume, or left to settle, retaining a layer of surface water. Lee & Skogerboe (1984) examined the presence of heavy metals in run-off water following a storm event to compare dried and wet sediment disposal run-off. Surface run-off water from dried sediments had less suspended solids and total heavy metals, but contained higher amounts of dissolved or soluble heavy metals than wet sediments, especially cadmium, zinc, copper and manganese (Lee & Skogerboe, 1984). Concentrations of soluble chromium, lead, iron, arsenic and mercury were not higher in dried sediment run-off. Consequently any surface run-off from dried sediments of Rotomanuka, Kainui and Ngaroto could have zinc concentrations higher than the ANZECC recommended guidelines.

2.33 Longevity of treatment

Sedimentation rate

Sedimentation rate was measured over approximately two weeks using sediment traps deployed in each lake. Lake Ngaroto has the highest gross sedimentation rate measured as total particulate matter and corrected to per m^2 of lake area. This lake also has the highest catchment: surface area ratio (Table 2). Lake Rotomanuka has a lower sedimentation rate than Kainui, which is inconsistent with its higher catchment area to lake area ratios. Only Lakes Kainui and Cameron meet the requirement of Cooke *et al*. (1993) of a watershed-to-surface area ratio of less than or equal to 10:1 (Table 3).

Table 2. Gross sedimentation rates for each lake calculated in dw kg m^{-2} $year^{-1}$ and in dw kg $lake^{-1}$ $year^{-1}$.

	dw kg m^{-2} $year^{-1}$	***dw kg $lake^{-1}$ $year^{-1}$***
Ngaroto	0.175	190000
Kainui	0.031	9200
Cameron	0.037	1300
Rotomanuka	0.022	3800

Table 3. Lake area and catchment area (ha) data used to calculate the watershed-to-surface area ratio.

	Ngaroto	***Kainui***	***Rotomanuka***	***Cameron***
Lake area (ha)	108.0	24.9	17.1	3.4
Catchment area (ha)	1738.0	107.5	467.0	26.6
Ratio	16: 1	4.3: 1	38: 1	8: 1

External nutrient load

Although some effort has been made to fence all the target lakes and establish a riparian buffer, only Lake Ngaroto has sediment traps in place to reduce sediment and nutrient loads from the inflowing drains. Currently none of the peat lakes meets the >50% reduction in external nutrient load recommended by Kleeberg & Kohl (1999) for dredging to be successful. If drastic external nutrient load reductions are not undertaken, newly exposed lake sediments may rapidly reabsorb the incoming nutrients.

2.3.4 Disposal area design

Water content and organic matter

The proportion of water and organic matter in the sediments needs to be determined in order to decide on the specifications of the dredging machinery, such as type of dredge required, head size and the volume which can be removed over time in order to determine the number of dredging days required (Cooke *et al.*1993). Additionally water content and organic matter content are important considerations for disposal area design.

Percentage water content was higher in the top 1 cm of sediment and generally declined with increasing depth for lakes Rotomanuka, Cameron and Kainui (Fig 7).

Ngaroto exhibited a different trend, with water content increasing marginally with depth from 10 cm to 30 cm.

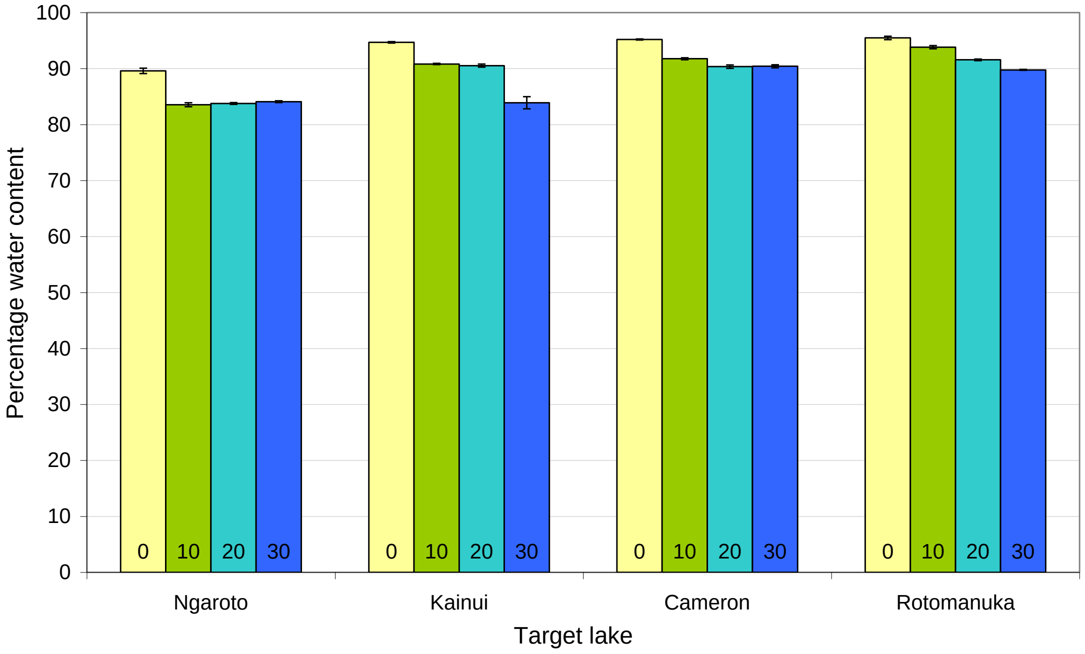

Figure 7. Percentage water content at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means (n = 4) ± 1 S.E.

Organic matter varied substantially between lakes, but Cameron was the only lake where it varied significantly between sediment depths (Fig. 8). Lakes Ngaroto, Kainui and Rotomanuka exhibited stable percentages of organic matter over all depths, with Ngaroto having the lowest value.

Compared with Rotorua lakes, percentage of organic matter in the sediments was high for all lakes examined, with a range of 13.1–60.5% over each depth for each lake), compared with a range of 8.4–22.1% for Rotorua lakes (Blomkvist & Lundstedt, 1995). Percentage water content and organic matter help determine what type of dredge would be most suitable in the lakes. The fine flocculant organic sediments (40–60% autochthonous organics) found in highly productive lakes pose a high risk of sediment resuspension during dredging (Cooke *et al.* 1993). A suction dredge can lessen this risk by reducing the amount of suspended sediment during dredging.

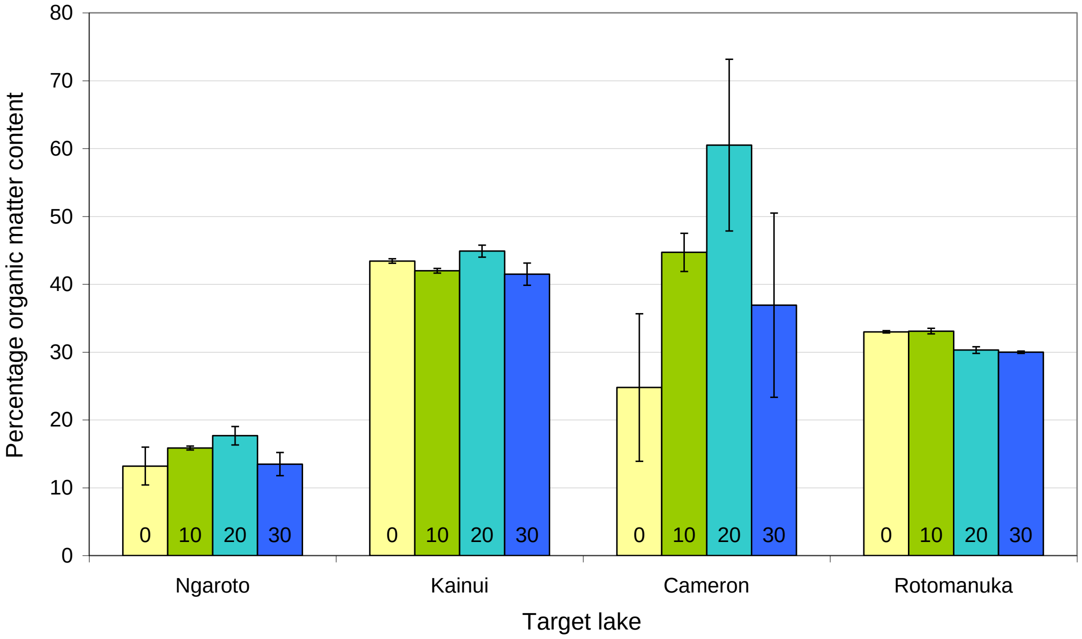

Figure 8 Percentage organic matter at depths of 0, 10, 20 and 30 cm from the sediment-water interface of the four target lakes. Bars are means (n = 4) ± 1 S.E.

The difference in volume between the sediment removed from the lake bed and the volume of sediment deposited in the disposal site is dependent upon the grain size distribution and water content of the sediments (Copp & Browne, 1984). As the water content of the sediment remains above 80%, even at a depth of 30 cm, any sediment that is removed will shrink proportionately on drying.

Settling rate

Polycarbonate columns were used to determine settling rate and bulking rate (Fig. 9). Both bulking and settling rates are required to determine the disposal basin size and overflow rate respectively (Copp & Browne, 1984).

Figure 9 Photo of the top of one of the settling columns used in the experiment. The white arrow indicates the location of the sediment-water interface. This photo was taken after 117 h of settling in the 90 g L^{-1} sediment concentration, showing a depth of approximately 38 mm.

Sedimentation rates were only measured for Lake Cameron, as sediment particle size and water content appeared comparable between lakes, although Lake Cameron did have a higher organic content at 20 cm depth than the other lakes.

The greatest settling velocity in the columns was recorded over the first 50 hours for all settling concentrations. Values were 2.265, 1.010 and 0.425 mm h^{-1} for concentrations of 70, 76 and 90 g L^{-1}, respectively. The overflow rate through the disposal basin must be less than the settling velocity of lake sediments for effective removal of sediments (Copp & Browne, 1984). After 300 h negligible settling occurred for all suspended solids concentrations.

Bulking rates for each sediment concentration were 107% at 90 mg L^{-1}, 116% at 80 g L^{-1} and 128% at 70 g L^{-1}. These values enable estimation of how large the disposal area should be. For example if sediment was removed at a concentration of 90 g L^{-1} (dry weight) from Cameron Lake and 25,500 m^3 was to be removed, the disposal area would have to accommodate a volume of at least (25,500 m^3 * 1.07 =) 27, 285 m^3 of sediment. Cooke *et al*. (1993) recommend 5–10% over-sizing of disposal areas.

Additionally, any water runoff from the disposal basin would be extremely high in nutrients compared to the concentrations found in the lakes, particularly dissolved nutrients, due to the high levels in the porewaters. Therefore, it would be desirable to cap the dredged sediments to prevent porewater nutrient release, or treat the run-off to prevent these nutrients re-entering the lake. Capping could be done with any of the substances reviewed in this report; treating the run-off could be done by filtering through a natural wetland area or by chemical means.

2.3.5 Sediment resuspension

Sediment resuspension may be an important consideration in lake restoration as it has the potential to redistribute sediments across a lake, thereby filling dredged regions, burying and diluting flocculants or capping agents to greatly reduce their effectiveness, and can impede the colonisation of macrophytes – where desirable – by direct physical impact on plants or by adversely altering the nature of the bottom sediments. Counter examples exist, however, where sediment resuspension is not considered to delay recovery of eutrophic systems (Jeppesen *et al*. 2003). Koromatua is the only lake in the Waikato region that has a shear stress above 0.05 N m^{-2} at a wind speed of 5 m s^{-1} (Fig. 10) at the east and west ends of the lake where its depth is less than 0.75 m. Gusts of 5 m s^{-1} and greater occur approximately 13% of the year (based on 2003 data from Hamilton airport), therefore, sediment resuspension due to wind action may not necessarily occur at high enough frequency in the target peat lakes to prevent macrophyte re-establishment. Further analyses that input a range of depths over the lake based on up-to-date bathymetric surveys should be used to provide a more definitive analysis of the frequency, extent and magnitude of sediment resuspension in the peat lakes.

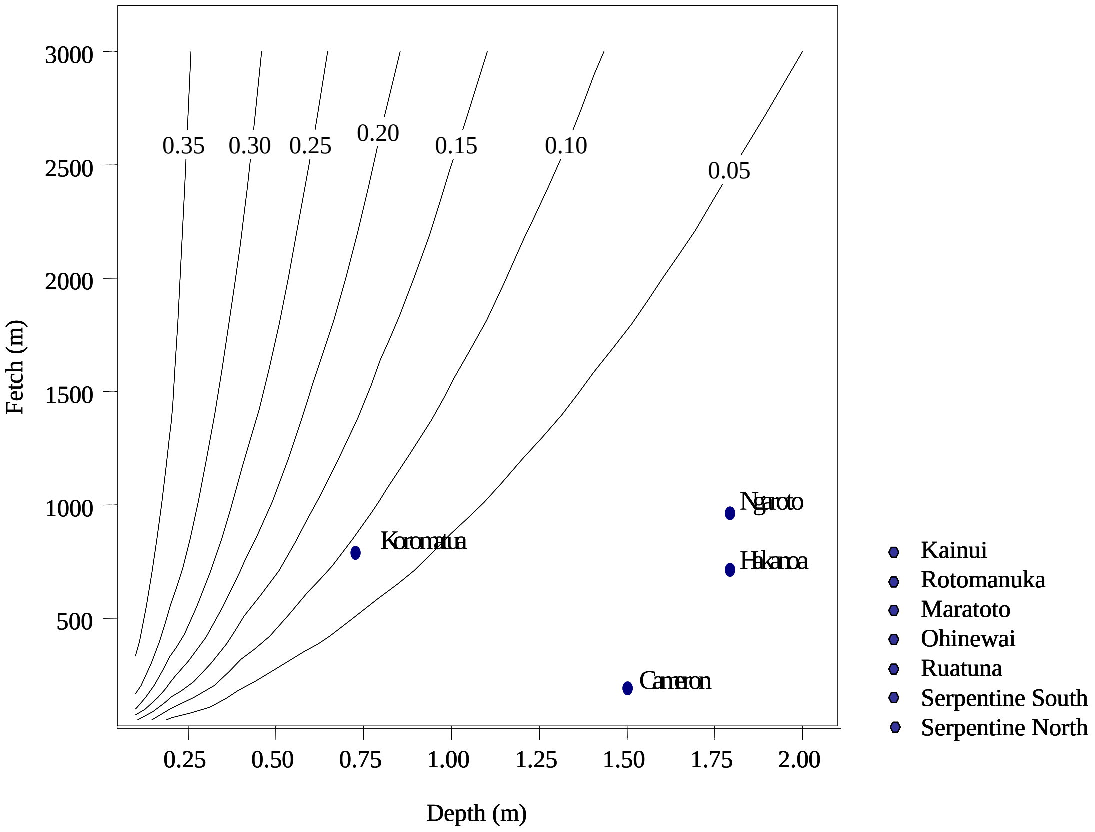

Figure 10. The shear stresses for various Waikato lakes depending on their fetch and mean depth ratios at 5 m s^{-1} wind speed. Lines on the graph represent shear stress values depending on fetch and mean depth. Circles on the graph represent where the Waikato lakes fall in relation to the different shear stresses. The points beside the graph represent lakes that have mean depth values > 2.1 m.

2.4 Do the benefits offset the costs?

Dredging is an expensive operation and outcomes can be highly variable. Costs will depend on the amount of sediment removed and the frequency of dredging that would be required. Additionally, a disposal area will usually need to be purchased and remediation of the sediments would have to occur. Sediment application to agricultural land is a possibility, but would have to be examined further in lab and field trials. Applying sediment directly from the lake would be difficult, as the soil would have to accept a large amount of water during the pumping period. Other considerations would be ground water contamination, soil permeability and nutrient limitation of an agricultural crop (Corey & Peterson, 1984). Dredged sediments have also been used successfully to reclaim land after strip mining (Simmers *et al*. 1984), and to grow forest species (Vandecasteele *et al*. 2005).

2.5 Conclusion

Cooke *et al.* (1993) suggest that lakes suitable for dredging will generally be shallow, have low sedimentation rates, organically rich sediments, be relatively small with watershed-to-surface ratios of nominally 10:1, have long hydraulic residence times and have the potential for extensive use following dredging. An additional requirement is a reduction in external nutrient load of at least 50% (Kleeberg & Kohl, 1999). None of the target lakes meets the external nutrient load reduction requirement of at least 50% and the only target lake that appears to fulfil Cooke *et al.*'s requirements is Cameron. However, dredging Cameron would be undesirable, due to the unique dystrophic state of the lake. Both Kainui and Rotomanuka are already relatively deep lakes and both have high external nutrient loads. Dredging in Ngaroto may be beneficial for recreational activities, but the effects would likely be short-lived due to the high sedimentation rates and high external nutrient load in this lake.

3.0 Phosphorus inactivation using alum

3.1 Literature review

Aluminium sulphate ($Al_2(SO_4)_3$, alum) is commonly used for wastewater and drinking water treatments. Alum is generally applied to lakes to reduce the internal loading of phosphorus in order to improve trophic state and/or reduce algal bloom occurrences in the target lake. When added to water alum forms an aluminium hydroxide complex that sorbs phosphorus:

$$\begin{aligned} Al^{3+} + H_2O &\rightarrow Al(OH)^{2+} + H^+ + 2H_2O \\ &\rightarrow Al(OH)_3 + 3H^+ \end{aligned}$$

Alum works in two ways to reduce available phosphate concentrations. Firstly, alum reacts with soluble P to remove it from the water column, forming an insoluble aluminium hydroxide floc that adsorbs large amounts of inorganic P. Secondly, the floc then settles to the lake bottom where it continues to sorb and retain P even under anoxic conditions (Steinman *et al*. 2004; Cooke *et al*. 1993).

The dose of alum required can be calculated in two ways. The first is based on alkalinity to ensure the alum dose does not exceed the lake water buffering capacity. In lakes with low alkalinity alum addition will not be buffered effectively and the pH of lake water will drop substantially, potentially below the range of 6–8 at which alum is most effective. The second method is based on the amount of phosphorus release from the sediment and alum dose is calculated to give a stoichiometric ratio of 1.0 over five years i.e., the dose is determined as five times the average summer internal phosphorus load (Cooke *et al*. 1993).

Alum is usually applied as a liquid by boat, either by spraying the water surface or applying it to the hypolimnion. If applied to the water surface a larger area of water is treated and consequently greater amounts of phosphate have time to bind to the floc as it sinks. Application to the hypolimnion prevents alum exposure to the whole water column and the possibility of planktivorous grazers being trapped in the floc and settling to the sediment.

The factors that need to be considered before adding alum are:

- pH range: The effectiveness of alum treatment depends on maintaining the pH between 6–8 throughout the entire treatment. At pH values outside this range P will not be bound to $Al(OH)_3$, alum will release any bound P and will form soluble Al^{3+} and other intermediate forms. Al^{3+} is particularly toxic to biota (Cooke *et al*. 1993).
- Alkalinity: Alum treatment will lower pH if the lake has low alkalinity (< 50 mg $CaCO_3$ L^{-1}) (Cooke *et al*. 1993).
- Tannin concentrations: Alum may not be effective if high concentrations of tannins are present in the target lake. Omoike and Vanloon (1999) found that when both tannins and phosphorus were present, high concentrations of tannins inhibited binding of P by alum. However, the toxicity of alum is reduced if alum complexes with humic substances (ANZECC, 2002).
- Longevity of treatment: Buried alum layers in lake sediment have been found to have no effect on the release of P from uppermost fresh sediment layers (Lewandowski *et al*. 2003). Therefore, if the sedimentation rate of the lake is high, alum treatment may have only short term effects.
- Timing: Kleeberg *et al*. (2001) found that 90% elimination of phosphorus following alum treatment is only reached if application occurs when the hypolimnetic P-concentration is at a maximum, or at the end of thermal stratification.
- Mixing regime and wind exposure: High wind exposure can make it difficult to achieve even alum application over the entire lake, and wind mixing could push the alum floc to one area of the lake (Cooke *et al*. 1993). Lakes that are continuously mixed would expose any forms of toxic aluminium species to the entire water column. Alternatively, stratified lakes that have an uneven pH distribution i.e. high surface and low hypolimnion pH values, could lead to the persistence of toxic aluminium species until mixing occurs (Paul & Hamilton, 2004).

- Risk to biota: The precipitation of alum (at pH values below 6 and above 8) in lab trials resulted in 100% mortality of *Daphnia* sp.; important grazers of algae and commonly used bio-indicators. Alum has been found to be most toxic to fish, amphibians, and phytoplankton at pH ranges of 4.4–5.4 at concentrations as low as 0.1 to 0.2 mg Al^{3+} L^{-1} (ANZECC, 2002; Cooke *et al*. 1993).
- External nutrient reductions: aluminium hydroxide has limited binding sites for phosphorus, therefore high inputs of P after application will reduce the effectiveness and longevity of treatment (Lewandowski *et al*. 2003).

3.1.1 Political issues

Political issues that may affect the desirability of alum treatment would be mostly concerned with the potential presence of toxic aluminium species and the resulting effects on biota, including zooplankton grazers, benthic invertebrates and fish species. Additionally, the use of chemicals may affect the mauri of lake waters, therefore cultural considerations will need to be made prior to application.

3.1.2 Case studies

Several case studies have found that alum is an effective long-term method to immobilise P in sediments (Cooke *et al*. 1993). However, there have been mixed results, e.g. in Lake Courtille (France; Van Hullebusch *et al*. 2003) and Lake Okaro in New Zealand (Paul & Hamilton, 2004).

Welch & Schrieve (1994) found alum treatment of six shallow USA lakes successfully reduced the internal phosphate load by 50–80%, and lasted for at least five years. Lakes without macrophytes showed a much greater reduction in total phosphorus concentrations and blue-green algae blooms, as well as greater treatment longevity.

In Lake Courtille (France), one year after application of 1.5 mg L^{-1} of Al^{3+} (as $Al_2(SO_4)_3$, 18 H_2O), Van Hullebusch *et al*. (2003) found P release still occurred from

Fe-bound-P, Al-bound-P and organic-bound-P. They deduced the ineffectiveness of alum treatment was caused by a pH of 10 present at the time of application and/or organic matter mineralization at the end of summer, enhancing sediment P release. Van Hullebusch *et al*. (2003) concluded that a higher dose alum treatment would be required to adsorb porewater phosphate under oxic conditions and to reduce the release into the water column. They suggested that a higher alum dose applied in spring would lower primary production and subsequent organic matter production, and avoid the high pH caused by summer algal blooms.

New Zealand case study: Alum treatment in Lake Okaro.

Alum treatment was applied to Lake Okaro in a low dose (0.6 mg L^{-1} $Al(OH)_3$) during December 2003. Due to the *Anabaena spiroides* bloom occurring at the time, Quinn *et al*. (2004) were unable to determine if the decrease in phosphate concentration from 40 mg m^{-3} to 5 mg m^{-3} was due to algae uptake or alum flocculation. High concentrations of aluminium were found in the surface waters following application, which suggests that binding to phosphorus and settling as a floc did not occur. This could have been due to the high pH in the epilimnion (8.6–9.7) or low levels of phosphorus, both caused by the cyanobacterial bloom (Paul & Hamilton, 2004). Additionally, aluminium concentrations in the water column remained above the 150 mg m^{-3} level recommended for protection of 80% of biota (ANZECC, 2000) for approximately two months following treatment. Associated laboratory trials found 100% mortality of *Daphnia* sp. following alum application (Quinn *et al*. 2004). The timing of the treatment was inappropriate due to high pH values and low phosphate in the epilimnion due to a cyanobacterial bloom. Additionally, the alum dose was very low because of the low alkalinity of the lake water, and it was not possible to identify if this low dose was actually effective.

3.2 Suitability of alum treatment for the Waikato peat lakes

There are several factors that must be considered prior to alum treatment of any target lake (see section 3.1). These factors are examined below, using the existing literature available regarding the four target lakes, and field and laboratory techniques. The variables identified as particularly important include alkalinity and pH, tannin content, sedimentation rates and mixing regimes.

3.2.1 Alkalinity and pH

Whole lake water samples were obtained from each target lake, and pH and alkalinity were measured. Alkalinity was measured using the Gran titration method (Wetzel & Likens, 2000) and converted to mg $CaCO_3$ L^{-1} using the equation:

$$\text{mg } CaCO_3 \text{ } L^{-1} = \text{alkalinity } (\mu\text{eq } L^{-1}) / 20$$

All the lakes were slightly acidic and had low alkalinity (Table 4). A pH of approximately 6 is typical for natural soft water lakes. However, a pH of 5, as recorded in Lake Cameron, is exceptionally low, but consistent with the dystrophic nature of the lake, and is probably caused by the leaching of humic substances.

Table 4. Alkalinity, pH and $CaCO_3$ values for the four target lakes.

	Ngaroto	***Kainui***	***Rotomanuka***	***Cameron***
pH	6.75	6.66	6.70	5.08
Alkalinity (μeq L^{-1})	246	300	525	94.34
$CaCO_3$ (mg L^{-1})	12.3	15	26.25	4.72

Low alkalinity and acidity are products of H^+ release, which occurs when the rate of release of hydrogen ions from the biota is greater than the H^+ consumption caused by weathering (Stumm, 2004). Alkalinity in the target lakes is very low and is comparable to other New Zealand lakes in areas with forests (e.g. Westland lakes, 0–27 mg $CaCO_3$ L^{-1}), intensive crop production and/or peat deposition. Organic acids from the developing soil and vegetation leach into deeper soil layers. As these organic acids travel through the soil profile they condense into humic materials, which contribute to lake acidity.

Waikato lakes all have soft water and low alkalinity, and some are strongly influenced by peat, such as Kainui, Cameron and Rotomanuka (Thompson, 1994; Thompson & Champion, 1993; Newnham *et al*. 1989). Remnants of peat bogs surrounding the lakes have the potential to release humic substances, including humic and fulvic acids and humin, into the water column. These compounds have the potential to reduce pH of the lakes, for example Lake Maratoto has a pH of < 5, which is possibly due to the undisturbed nature of lake and its humic inputs (Green & Lowe, 1985).

The low alkalinity and poor buffering capacity of these lakes make alum treatment undesirable. When aluminium salt (alum) is added to water, hydrogen ions are liberated, causing the pH to fall at a rate dictated by alkalinity (Cooke *et al*. 1993). In lakes with alkalinities less than 50 mg $CaCO_3$ L^{-1} even a low dose of alum can cause a large decline in pH, resulting in increased concentrations of toxic, soluble forms of aluminium. Cooke *et al*. (1993) recommend alum treatment is not used in lakes with low alkalinity, as additional buffering is required, and any miscalculation may result in the presence of soluble toxic forms of aluminium.

3.2.2 Tannins

Colour can be a good indicator of the presence of humic substances, including tannins, as this organic material imparts a yellow hue to lake waters, called ‘yellow substance’ (Davies-Colley, 1987). Not all the target lakes have the same amount of organic material present. Based on Davies-Colley’s (1993) general relationship of dissolved colour to water quality, water quality in Lake Cameron is likely to be strongly influenced by yellow substance, and lakes Ngaroto and Kainui moderately influenced by yellow substance and Lake Rotomanuka least (Fig. 3.2.1).

Alum may bind to humic substances more readily than P in lakes with a high tannin content or ‘yellow substance’, thus rendering the treatment less effective (Omoike &

Vanloon, 1999). Additionally, alum has been shown to decolourise peaty and other coloured waters by coagulating and removing much of the dissolved organic matter (Tucker, 1892).

Figure 11. Water colour of the four target lakes, in order from left to right are: Kainui, Rotomanuka, Cameron and Ngaroto.

3.2.3 Sedimentation rate

Lake Ngaroto has the highest aerial sedimentation rate and Cameron the lowest (Table 4.2.1). Consequently, if Ngaroto has a sediment surface area of 75 ha, every year approximately 3 mm of new sediment would be deposited, suggesting the alum treatment may be spread throughout this top layer of sediment.

3.2.4 Mixing regime

The Waikato peat lakes are all almost continuously mixed, with the exception of Rotomanuka North, which may stratify briefly during summer/autumn. Consequently, if soluble toxic Al^{3+} became available due to pH values outside the 6–8 range, it could be exposed to the entire water column. Alternatively, if alum was applied to Rotomanuka North during stratification, pH values in the metalimnion or hypolimnion could exceed the safe pH range resulting in toxic aluminium exposure to the thermal layer until mixing occurred. Additionally, Lake Ngaroto is highly wind exposed, with regular sediment resuspension in shallower areas of the lake, which could result in an uneven alum application over the entire lake, even if alum is applied on a calm day (Cooke *et al*. 1993).

3.2.5 External nutrient reduction

As previously mentioned in the sediment removal section, although some effort has been made to fence all the target lakes and establish a riparian buffer, only Ngaroto has sediment traps in place to reduce nutrient load from the inflowing drains. Alum is likely to have little impact on nitrogen concentrations within the lake, as previous studies have found alum is ineffective at removing nitrogen from the water column (El-Bestawy *et al*. 2005; Rowan *et al*. 2004). However, alum binds particulate phosphorus readily, which would be the major component of the incoming phosphorus load.

3.3 Conclusion

Application of alum has been a highly effective method to reduce internal nutrient loads through the binding of phosphate from the water column, and the capping of nutrients in the sediment, even under anoxic conditions. However, alum treatment is risky and less effective in soft and low-pH waters with high tannin content, as toxic alum species can be released and binding of P is reduced. Therefore, without careful analysis and remediation of the risk factors, alum treatment is not considered to be a high priority for treatment of the Waikato peat lakes.

4.0 Sediment capping and phosphorus inactivation techniques - Literature Review

The three flocculant and sediment capping techniques, Phoslock, zeolite and iron slag were reviewed and applied in a core incubation study. Although there are many other substances that may be useful to reduce internal nutrient loads, study of these substances is less advanced than the three reviewed in this report, which have shown considerable promise (Miller, 2005). Dissolved organic carbon was reviewed as a method of reducing algae dominance, and carbon was applied as a treatment in the incubation study to examine some of the effects of increasing dissolved organic carbon concentrations in the peat lakes, but primarily as a method to effect more rapid deoxygenation in sediment core incubations.

4.1 Phoslock

Phoslock is a lanthanum modified bentonite clay developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and its research partner, Water and Rivers Commission (Department of Environmental Protection, Western Australia) (Robb *et al.* 2003). Phoslock is designed to bind P and maintain it in complex under most conditions encountered naturally in aquatic systems. The lanthanum ion binds to phosphate to produce a single species of lanthanum phosphate or rabdophane, which is highly insoluble (Martin & Hickey, 2004):

$$La^{3+} + PO_4^{3-} \rightarrow LaPO_4$$

Phoslock was developed to avoid many of the disadvantages of alum application and is effective under a wide range of environmental conditions (Robb *et al.* 2003). Phoslock is usually applied as a slurry, with the intent to cap the sediment surface with a 1 mm thick layer (Douglas *et al.* 1999). Similar to alum, Phoslock can be applied from a boat, either to the surface of the lake, in selected areas or to the hypolimnion.

Phoslock has several advantages over alum treatment:

- Non-toxic under a wide range of environmental conditions (Martin & Hickey, 2004).
- Effective under a wider range of pH values and alkalinities.
- Binding of P to Phoslock is less influenced by humic substances than alum (Omoike & Vanloon, 1999).
- Does not affect pH levels following treatment (Flapper, 2002).

However, there are other factors which must be considered before applying Phoslock:

- Toxicity of Phoslock: Martin & Hickey (2004) used a leachate procedure to test toxicity of Phoslock, which requires the Phoslock slurry to be filtered using a 40 μm nylon mesh filter, and then use of the filtrate to test for toxicity. This method of testing excludes any effects of larger particulate solids, which may be derived from the bentonite component of Phoslock. Normal application of Phoslock, however, does not require the slurry to be filtered prior to application to the lake, although it can be either applied to the hypolimnion or the lake surface. However, laboratory testing alone is not usually sufficient to conclusively state if a substance is toxic or not, given inherent natural environmental variability. For example, field trials conducted by NICNAS (2001) appear to have been interrupted by a large flood event, which caused dramatic changes in the water chemistry that were not associated with the Phoslock application.
- The concentration of lanthanum required to produce acute effects in soft water for *Daphnia carinata* is 33 μg L^{-1} at pH range 7.5–7.8 and 22 mg $CaCO_3$ L^{-1} (ANZECC, 2002). Based on this data and due to lack of available data on toxicity effects, ANZECC (2002) set a trigger value of lanthanum at 0.04 μg L^{-1}, which gives a safety factor of c.1000-fold. This trigger value is set close to the limits of detection of lanthanum in freshwaters and ANZECC (2002) recommends that any detection of lanthanum should be investigated.
- In a study conducted by Arkhurst *et al*. (2004) lanthanum modified bentonite clay was used to bind and prevent phosphate release from sediment cores. Arkhurst *et al*. (2004) modified the bentonite clay in a different manner to the manufacture of Phoslock and applied an 8 mm layer onto the sediments (cf.

0.5 mm application thickness of Robb *et al*. (2003)). The Fe concentration of these cores was 20 times higher than the control cores, and more than eight times higher than the recommended ANZECC (1992) guidelines for the protection of aquatic ecosystems.

- Trials conducted by Robb *et al*. (2003) and Flapper (2002) showed that following significant decrease in phosphate concentrations in both surface and bottom waters in response to Phoslock applications, there was no significant difference in P concentrations from control treatments after 194 days and “two months”, respectively.
- The capping layer deposited over the sediments will change the physical and chemical nature of the bottom sediments, with the potential to alter the survival and behaviour of benthic organisms as well as influencing macrophyte re-establishment. We are unaware of any published information on the effects of Phoslock applications on benthic organisms or macrophyte re-establishment.
- Treatment efficiency: In laboratory trials Phoslock bound less phosphate than aluminium based treatment methods such as *Baraclear* and modified zeolite at equivalent application rates (Yang *et al*. 2004).
- Wind resuspension and settling rate: Phoslock remains suspended in the water column for a substantial amount of time; generally 1–2 days are required for settling (Greenop & Robb. 2001). Phoslock could be expected to be resuspended in shallow, wind-exposed lakes and re-distributed across the lake and within the bottom sediments along with natural lake sediments.

4.1.1 Political/Ethical issues

Large-scale trials in New Zealand may be hindered by several factors. The target lake beds are currently Crown-owned. The Waikato-Tainui iwi has a claim over the Waikato River, including the Waikato peat lakes (Richard Cox, pers. comm.). Tangata whenua consider that the use of chemicals may affect the mauri of lake waters, therefore cultural considerations, in association with Resource Management applications, will need to be made prior to flocculant use in New Zealand. Because of the specific nature of individual lake applications of Phoslock, or any flocculant for that matter, it will be very important to maintain a dialogue based on mutual trust, cooperation and communication amongst environmental managers, iwi, scientists and flocculant proponents. This is a key requirement to maximise the environmental and cultural benefits of costly flocculant applications, and will lead to iterative improvements in application techniques and dosage.

4.1.2 Case studies

In laboratory tests Phoslock removed 87–98% of phosphate present from resuspended core samples, and reduced subsequent P release from sediments (Douglas *et al*. 1999). Two field trials have been completed in Australia, in the Swan-Canning and Vasse-Wonnerup estuaries (Western Australia) and in the Fyshwick lagoons (ACT). Currently SCION is conducting a mesocosm trial in Lake Okaro to examine the effectiveness of Phoslock, modified zeolite, iron making slag and alum in reducing phosphorus concentrations. In addition, Environment Bay of Plenty has applied Phoslock to Lake Okareka, however, results are not yet available from either study.

In the Fyshwick field trials total P in the Phoslock treatment was reduced by 83–96% compared with the control mesocosm. This reduction in P lasted only 67 days before phosphorus concentrations began to increase and became the same as the untreated area. It is possible the Phoslock application prevented a bloom of *Microcystis aeruginosa*, which developed in the control mesocosm soon after the start of the experiment (Flapper, 2003).

Following the first Phoslock treatment in the Vasse River, phosphate concentrations were reduced from 50 μg L^{-1} to 20 μg L^{-1}. After the second treatment was applied, phosphate concentrations at the control site had reached almost 200 μg P L^{-1}, but phosphate at the treatment site remained low, reaching the detection limit of 5 μg P L^{-1}. However, after 194 days phosphate concentrations in both the control and treatment areas were the same (Robb *et al*. 2003).

4.1.3 Suitability for the Waikato peat lakes

Phoslock is stable at a wide range of pH values, alkalinities and phosphorus concentrations. Consequently it would be safer to use in the peat lakes than alum, although the toxicity of Phoslock in whole lake applications requires careful consideration as well as a thorough monitoring regime. However, as internal nutrient release continues in most lakes for at least 10 years following external nutrient reduction (Søndergaard *et al*. 2002), the short-term effects of Phoslock application may not extend to water quality improvements in the medium to long term. Additionally, although Phoslock is non-toxic, the physical effects of a surface layer of clay on top of a flocculant mud layer has not been examined and may have an effect on benthic species. However, in lakes such as Ngaroto where there is considerable sedimentation and resuspension of sediments, the effects of Phoslock on nutrient release may be affected by the continual burial and resuspension of sediments. Studies on lake water and sediments would need to determine what Phoslock dose would be required to be effective, but ultimately an iterative process of trial and response (i.e. adaptive management) will be required for assessment on a case by case basis.

4.1.4 Conclusion

Although Phoslock is effective under a wide range of environmental conditions a single application is unlikely to produce a long-term solution to a long-term problem.

4.2 Zeolite

Zeolite is a hydrated aluminosilicate mineral that has been used extensively for wastewater treatment (NZ Natural Zeolite Ltd). Natural raw zeolite is generally used in wastewater treatment to adsorb and demobilise ammonia and other cationic pollutants such as Pb^{2+} (Jacobs & Förstner, 1999). Both clinoptilolite and mordenite types of zeolite can effectively bind ammonium ions, removing 87–98% of NH_4^+ at concentrations of up to 150 g L^{-1} (Nguyen & Tanner, 1998). Sakadevan and Bavor

(1998) tested the effectiveness of raw zeolite in the removal of P for wetland restoration. They found raw zeolite was an effective adsorbent of P, but had only limited phosphate binding sites available, with a maximum P adsorption capacity of 2.15 g kg^{-1}.

However, modified zeolite can be effective in removing PO_4-P and NO_3-N from lake waters (Yang *et al*. 2004; Jacobs & Förstner, 1999). Natural raw zeolite was used by Yang *et al*. (2004) after modification and treatment with 0.1 M HCl to remove any residual organic salts. The three modified zeolite compounds all exhibited a higher phosphate binding potential compared with unmodified zeolite, with the Z2 treatment binding up to 90% of phosphate ions at the highest concentration of application (30 g L^{-1}). The Z2 modified zeolite bound 98% of the NO_3-N ions in solution even at NO_3-N concentrations of up to 1000 mg L^{-1}.

Factors to be considered before applying zeolite treatment include:

- Results of long-term studies are unavailable at this time, therefore it is unknown how long modified zeolite will effectively bind phosphate.
- Zeolite settles out of solution more rapidly than clay-based Phoslock. This may be an advantage in highly turbid lakes where sediment capping is the main priority (Yang *et al*. 2004), but could be a disadvantage in lakes with high inputs or resuspension of flocculant sediments, as the zeolite layer would rapidly become buried. Additionally, more rapid settling may allow less time for flocculation of particles and binding to phosphate as it sinks through the water column.
- Sediment capping may remain more permeable with zeolite than Phoslock application, due to the larger particle size of zeolite (Yang *et al*. 2004).
- Not all of the dissolved phosphorus in the water column will be in ionic forms that are readily sorbed by zeolite or Phoslock molecules, e.g. organic compounds.
- At this stage no toxicity tests have been conducted using modified zeolite.
- The binding potential of zeolite under anoxic conditions has not been thoroughly examined.

4.2.1 Suitability for the Waikato peat lakes

An advantage of using modified zeolite is that they are physically and chemically stable under normal water column conditions (Jacobs & Förstner, 1999), and even appear to have increased binding efficiency at lower pH values, with zeolite treatments at pH 5 binding phosphate better than pH 7, which was better than pH 9 (Yang *et al*. 2004). There may be similar problems with rapid burial and wind focusing as suggested with both alum and (Phoslock treatments. Currently there is too little information on the toxicity of zeolite, long-term effects or large scale trials to recommend its use in the Waikato peat lakes. This situation will change as more laboratory and field trials are carried out.

4.2.2 Conclusion

Modified zeolite appears to bind phosphate effectively in laboratory situations; however, no field trials, whole lake studies, long-term effects or toxicity tests have been carried out to date. Zeolite is an abundant mineral in New Zealand's central plateau and would probably be a very cost effective method to reduce available nutrients if it proves successful.

4.3 Iron addition

Inorganic iron exists in lake water and lake sediments in either the oxidised ferric (Fe^{3+}) or the reduced ferrous (Fe^{2+}) forms, depending on solution pH and oxidation-reduction potential:

$$Fe^{2+} + \tfrac{1}{4}\,O_2 + 2\,OH^- + \tfrac{1}{2}\,H_2O \rightarrow Fe(OH)_3$$

Under oxygenated conditions $Fe(OH)_3$ binds phosphate from the water column and sinks to the sediment surface, effectively providing high P retention. However, if the sediment surface becomes anoxic and dissolved oxygen levels drop below c.1 mg O_2 L^{-1}, Fe^{3+} becomes an alternate electron acceptor to oxygen:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

In the reduced state (Fe^{2+}) iron is soluble and iron-bound P is released into the water column. This change can happen so rapidly that in some lakes it occurs diurnally, so that P is bound to ferric iron during the day and released during the night (Carlton & Wetzel, 1988). However, where appreciable sulphide has been formed by the biological reduction of sulphate, ferric iron can be reduced by the formation and precipitation of insoluble iron sulphide (FeS):

$$Fe_2O_3 + 3H_2S \leftrightarrow 2FeS + 3H_2O + S$$

Caraco *et al*. (1989) found the amount of P released from ferric iron was dependent on the amount of sulphate present in the hypolimnion. Lakes with low sulphate concentrations (60 µm) had low P release under both oxic and anoxic conditions and lakes with high sulphate concentrations (> 3000 µm) had high P release under both conditions. Roden & Edmonds (1997) found a direct correlation between the amount of sulphate present and the release of phosphate from ferric iron complexes and the subsequent formation of iron sulphide. These results suggest the amount of sulphur present can determine the ability of iron to bind phosphorus.

A modification of the application of iron is to use steel or iron making slag. Iron making slag has been used as a substrate for constructed wetlands and to remove phosphorus from wastewater as part of a filter system. The elements that comprise iron slag will depend on the process used to produce it and can be highly variable between suppliers.

These studies illustrate that there are many factors to consider before applying iron:

- Does the sediment-water interface become anoxic even for short periods and what are the concentrations of sulphate in the sediment and hypolimnion? As indicated above iron will release bound P under anoxic conditions, when moderate amounts of sulphate are present, and will release P in aerobic conditions when high amounts of sulphate are present.
- Is the hypolimnion iron-limited? Varying optimal ratios of Fe:P have been recommended. Stauffer (1981) stated that natural precipitation of phosphate will occur in the hypolimnion when the Fe:P ratio is higher than 3:1. Gächter & Müller (2003) supported this result, stating that the minimum molar stoichimetric Fe:P ratio of 'ferric phosphate' is 2:1. Jensen *et al.*'s (1992) recommended ratio was higher, suggesting that the total Fe: TP ratio is 8: 1 moles or 15:1 by weight for aerobic Fe retention of phosphate.
- pH: Iron has a maximum sorption of P at pH values between 5–7, but will still sorb P at values outside this range (Cooke *et al.* 1993). The effect of pH on phosphate binding to iron making slag has not been examined extensively, but in one study phosphate was most effectively adsorbed at a pH range of 7–8. Outside this range P adsorption decreased substantially and at pH 5.5 adsorbed phosphate was released (Yamada *et al.* 1984). Additionally, if iron making slag is applied in large quantities it has the potential to reduce pH (Bourke *et al.* 2005).
- Treatment efficiency: Some studies have found that for $FeCl_3$ addition to be successful, high doses (10 mg L^{-1}) may be necessary.
- Sediment capping may be more permeable using iron slag than either zeolite or Phoslock, as iron slag is readily available as a larger particle size (Yang *et al.* 2004), while at the same time reductions in surface area to volume of the material will decrease adsorption capacity.
- Similarly to the previous sediment capping techniques reviewed, iron or steel making slag may be ineffective once buried within the sediment. Consequently treatment may be more effective in lakes with low sedimentation rates.
- What are the elements and their percentages in the specific iron making slag that may be used? The chemical components of iron making slag vary greatly

depending on what they are produced from and where the material was sourced.

- Will the type of slag used be toxic to lake biota in the long- or short-term? Toxicity tests would have to be conducted on the specific type of slag used at the pH of the target lake water, as different slags may have different chemical properties that can vary with pH, and in turn the slag material may influence the pH of the water (Bourke *et al*. 2005).

4.3.1 Political/Ethical issues

The effectiveness of iron making slag has not yet been proven for in-lake applications. Large slag particle sizes may disrupt the naturally soft substrate of the lakes, or alternately, sink into the sediment thus becoming ineffective in reducing nutrient release from the sediment surface. Additionally, the short- and long-term toxicity effects of any leachate from iron slag are unknown and would have to be thoroughly tested before whole lake application. Leachate toxicity tests were conducted in the late 1980s to test for harmful leachates in association with iron making slag applications in road making and drainage aggregates (Bourke *et al*. 2005). As a result of these trials it is recommended that slag material be washed prior to application in wastewater treatment to reduce the likelihood of boron leaching. Additionally, very high leachates of boron, manganese and iron were found when exposed to waters of pH 5–5.5. Therefore treatment of acidic water < 5.5 was not recommended without either specific testing for leachates or buffering of water to a higher pH.

4.3.2 Case studies

Many studies have shown that under conditions of low redox and low pH, dissolved humic matter, ferric iron and orthophosphate form aggregates that render P unavailable to biotic assimilation (Steinberg, 2000). Iron making slag has been examined more extensively as an external nutrient reduction technique than as an ‘in lake’ treatment. Currently in New Zealand iron making slag is being trialled in the form of ‘socks’ to filter nutrients from inflows to Lake Rerewhakaaitu (AgResearch) and in four different inflows to the Rotorua lakes, as part of a MSc. thesis by Lisa Zheng from the University of Waikato. Iron making slag is also being tested in the Okaro mesocosms at present by SCION and the University of Waikato in association with Environment Bay of Plenty regional council (EBOP).

The first case study reviewed of iron application for nutrient removal for a lake water column is from Poland, where $FeCl_3$ was added to two hypereutrophic lakes. The second is a laboratory study conducted by URS for EBOP, who tested $FeCl_3$ addition to Hamurana and Utuhina stream samples in New Zealand. Currently no literature is available regarding the use of iron making slag as an in-lake nutrient removal technique; consequently, the examples given here are situations where iron making slag has been used as a substrate for artificial wetlands to reduce the amount of phosphorus entering aquatic ecosystems.

Wisńiewski (1999) found a high dose of $FeCl_3$ in a laboratory study (20 g L^{-1} in 1.5 L over 50 cm^3 of lake sediment) reduced PO_4-P concentrations of interstitial water by 69%, without significantly altering oxygen saturation, pH or conductivity. However, this was dependant on the presence of oxygen, and a very low initial Fe: P mass ratio (Fe: P ranged from 4.8–0.4). In situ experiments using 33.3 g L^{-1} of $FeCl_3$ in mesocosms showed either negligible or slight reduction of phosphate in surface waters, but 59.5–64% of phosphate from the hypolimnion was removed.
Browne *et al*. (2004) found that a 10 mg L^{-1} dose of $FeCl_3$ removed 79.8% and 73.4% of the phosphate and TP, respectively, from Hamurana stream water. Higher doses of 100 mg L^{-1} $FeCl_3$ removed 91.5% and 95% of phosphate and TP respectively. Laboratory results for Utuhina Stream were similar, with 10 mg L^{-1} $FeCl_3$ removing 80% PO_4-P and 59.3% TP and 100 mg L^{-1} $FeCl_3$ removing 92.2 and 95% PO_4-P and TP respectively. Both of the above studies relied on oxic conditions for Fe to bind P and high doses of $FeCl_3$ were required to remove most of the phosphate.

Blast furnace slag was most effective in removing phosphate of all the wetland substrates tested by Sakadevan & Bavor (1998) (soils obtained from Australian wetlands, steel furnace slag and raw zeolite). Blast furnace slag removed all phosphate from an initial solution concentration of < 100 mg P L^{-1} and had an adsorption maximum of 44 g kg^{-1}. Phosphate adsorption was found to be most closely correlated with a combination of total Al and Fe ($r^2 = 0.901$) ion components of the slag. Additionally, phosphate binding was found to be dependant on the length of exposure to the Fe ions, which could explain why less P was removed from surface waters than the hypolimnion in Wisniewski's (1999) mesocosm experiment.

Mann (1997) found that blast furnace slag, steel furnace slag and granulated blast furnace slag were all better removers of phosphate from wetlands than constructed wetland gravels, with adsorption capacities of 400, 380, and 450 mg kg^{-1} respectively. Additionally, none of the slag types released any phosphate once bound. In contrast to Sakadevan & Bavor's (1998) experiment, Mann (1997) found that adsorption capacity was best correlated with Ca ($r^2 = 0.921$) and Mg ions ($r^2 = 0.868$), and both Al and Fe components of the slag did not effect adsorption capacity. This was probably due to the high pH conditions this experiment was conducted under as Ca-P and Mg-P reactions will dominate over Al-P and Fe-P at high pH.

4.3.3 Suitability for the Waikato peat lakes

These studies illustrate that high concentrations of $FeCl_3$ may have to be added to reduce P significantly, and will not have a large effect if the lake is not iron limited initially. When the concentrations of Fe and total phosphorus from the sediments were compared, only the top 1 cm of surface sediment from Lake Cameron had a Fe: TP ratio of less than 15:1 (Jensen *et al*. 1992) (Table 5). These ratios do not necessarily reflect the ratios of Fe: TP in the hypolimnion, but give an indication of the concurrent sedimentation rates of Fe and TP.

Table 5. Sediment Fe: TP ratios for the top 1 cm and sediment at 30 cm depth. Ratios of less than 15: 1 of Fe: TP by weight represent potential iron limitation.

Lake and sediment depth (cm)	**Fe (mg kg^{-1} sed)**	**TP (mg kg^{-1} sed)**	**Fe: TP ratio**
Kainui 0	28300	734	39
Kainui 30	25000	558	45
Rotomanuka 0	52900	698	76

Rotomanuka 30	13900	452	31
Ngaroto 0	51400	452	114
Ngaroto 30	52400	357	147
Cameron 0	20800	2621	8
Cameron 30	13800	452	31

The concentrations of iron making slag used are not listed in the two studies reviewed (Sakadevan & Bavor, 1998), as the phosphorus absorbing potential of iron making slag was tested by passing phosphorus enriched water through a column packed with iron slag and the P concentration measured on removal. This method appears effective but is dependant on the contact time between the slag and the P enriched water. Different types and sources of slag appear to have different ratios of elemental components, which will affect the optimal pH for phosphate adsorption and the adsorption capacity of the material. High concentrations of manganese, iron and boron leachates from iron making slag were recorded in acidic waters and therefore, iron making slag may not be suitable for use in peat lakes with low pH.

4.4 Organic matter or carbon addition

Dystrophic lakes (peat influenced) are characterised by large inputs of dissolved organic carbon (DOC), which occurs because of the migration of humic substances from surrounding peat bogs and the catchment basin. In peat lakes where autochthonous primary production is limited due to the light attenuation characteristics of humic substances, concentrations of P and N may be as high as, or higher than lakes which are considered eutrophic. This is due to the inactivation of the phosphorus by humic acids. Humic substances dissolved in water have the ability to bind nitrogen and phosphorus compounds and metal cations (Jones *et al*. 1988; Górniak *et al*. 1999). These humic substances cannot be directly utilised by phytoplankton due to their high molecular weights and their imperviousness to enzymatic hydrolysis. Consequently, humic substances accumulate in lakes and generally contain ca. 54% carbon, 3–6% nitrogen and associated phosphorus, all which constitute a large potential, but unavailable, nutrient source for bacterio-plankton and phytoplankton (Vähätalo *et al*. 2003). Although humic substances are better substrates for bacterial growth than phytoplankton growth, generally less than ~

15 % of lake water humus is readily available for bacterial growth (Jansson *et al*. 2000).

Carpenter & Pace (1997) found inputs of dissolved organic carbon (DOC) work synergistically with high biomass of large grazers (a consequence of reduced fish predation due to low pH and low visibility) to suppress responses of algae to P inputs. However, if the light intensity reaching the lakes is increased or is already high, the level of dystrophy in peat lakes may be reduced. Increased UV irradiation may induce a partial degradation of DOC, causing a breakdown of mineral-humus complexes and the release of Fe, Ca and P and N ions, thus making them accessible to phytoplankton in the water column (Vähätalo *et al*. 2003; De Haan, 1992). When Vähätalo *et al*. (2003) irradiated water from humic Lake Vlkea-Kotinen, they recorded a 78 % photochemical mineralization of DOC. Additionally, they noticed an increase of bioavailable phosphorus and nitrogen from P-Fe-humus compounds when exposed to irradiation. Another factor known to influence dissociation of P-Fe-humus substances is pH. Jones *et al*. (1993) found the association of Fe and P with humic substances declined as pH decreased.

Shifts between food chains based on heterotrophic production and food chains based on primary production can take place at moderate increases or decreases in the concentration of dissolved organic carbon from allochthonous sources (Jansson *et al*. 2000). The amount of total organic carbon entering Finnish lakes is determined primarily by the proportion of the catchment area that is covered by peatlands (Kortelainen, 1993). Humic substances are responsible for holding the iron in solution, resulting in iron-organic matter complexes. Iron interacts with dissolved humic substances to bind phosphorus at acidic to near-neutral pH values, irrespective of redox conditions, in the surficial sediments of certain softwater lakes – thus enhancing P retention in lakes with high loading of iron and humic substances (Wetzel, 2001; Jones *et al*. 1988).

Carpenter & Pace (1997) suggested dystrophy and eutrophy may be alternative ecosystem states dependant on the amount of organic carbon reaching the lake. Adding DOC to lake by anthropogenic means may be difficult and costly and has not been examined. Natural sources of carbon and associated dissolved humic substances are from wetlands, ground water or dead organic matter. Organic matter produced by dead algae, which sinks to the sediments, can also bind phosphate. However, this form of organic matter will release the bound P directly via microbial mineralization and indirectly due to the high oxygen demand of the microbes creating an anoxic sediment surface (Van Hullebusch *et al*. 2003). Enhancing wetlands remains as a potential feasible method of increasing lake organic matter content.

Some considerations that must be addressed when considering organic matter inputs as a restoration method are:

- Was the lake ever naturally dystrophic?
- How close is the lake to a dystrophic state? If the current state is highly stable it may be difficult to 'flip' to a dystrophic state (Carpenter & Pace, 1997).
- High concentrations (> 40 mg L^{-1}) of humic substances could be toxic to aquatic life (De Haan, 1992).
- The amount of UV radiation reaching the water surface. Increased irradiation can result in degradation of DOC and release of bound phosphates.
- Can enough DOC or humic substances be added to switch the lake state? Are there potential areas surrounding the lake which could be developed into productive wetlands to provide the necessary DOC input?
- Will the addition of DOC have the desired effect on trophic state? Was dystrophy the natural historical state of the lake and is it the desired future state of the lake?
- External nutrient loads would have to be reduced substantially, as autochthonous carbon stimulates respiration thus could speed up the consumption of allochthonous carbon, although dissolved organic matter is utilised slowly and can persist in lakes for years (Wetzel, 2001).

4.4.1 Case studies

No case studies of added humic substances or DOC to lakes in order to encourage a change in trophic state could be found. However, several lab studies have tested the potential for DOC or organic matter to bind phosphates and other studies have examined the availability of phosphate within dystrophic systems.

Jansson *et al*. (2003) concluded the low phytoplankton production in dystrophic lakes was due to bacterial respiration of allochthonous organic carbon (AOC) enabling community respiration to exceed primary production. Because AOC is not readily available to phytoplankton as an energy source (and often serves to limit the available light), bacterial utilisation of AOC increases bacterial production at the expense of phytoplankton production. Drakare *et al*. (2003) also found that DOC appeared to inhibit phytoplankton dominance over bacteria.

Carpenter & Pace (1997) suggested that dystrophy and eutrophy are alternative stable states that are governed by external inputs of refractory dissolved organic carbon (RDOC). Wetlands are a major source of RDOC to lakes and when they are significantly reduced, RDOC inputs are also reduced, leading to an increased sensitivity of the ecosystem to changes in P input, P recycling or grazing. In this situation if P inputs increase there may be a switch from a dystrophic state to a eutrophic state. Granberg (1985) partially ascribed the eutrophication of Lake Lestifjarvi to the drainage of adjacent peatlands and the associated reductions in DOC.

4.4.2 Suitability for the Waikato peat lakes

Carpenter & Pace (1997) suggest that dystrophy and eutrophy may be alternative ecosystem states and that may be applicable to the Waikato peat lakes. As agricultural activity increased in the Waikato, peatlands were drained to prevent flooding of pasture and fertilisers, including super-phosphate, were applied to increase productivity, causing the amount of RDOC entering the peat lakes to decrease and the amount of phosphate to increase. The amount of RDOC available from peatlands has been found to decrease proportionally with a decrease in discharge from the peatlands (Pastor *et al*. 2003). Decreased discharge of RDOC from the surrounding peat bogs to the Waikato peat lakes may have occurred due to lowered water tables and associated peat shrinkage. However, Moore (1987) found runoff from ditched peatlands (Quebec) contained higher amounts of DOC and phosphate than from undisturbed systems, although they did not measure changes in discharge volumes.

Based on the literature reviewed above there is potential for the internal nutrient load of peat lakes to be reduced naturally, through the conservation or restoration of peat bog remnants on the lake margins, and associated elevation of humic substance and DOC inputs. Restoration of mined peat substrate has been successful at the Torehape peat bog in the Hauraki plains (Clarkson, 2002). Further study is required to assess how carbon addition would affect primary productivity and the availability of phosphate for algae growth.

5.0 Sediment capping and phosphorus inactivation techniques - Core Incubation Experiment

A core incubation experiment was carried out in the laboratory to examine the effects of Phoslock, zeolite, iron making slag and carbon addition on nutrient concentrations under both aerobic and anoxic conditions. This was done to assess the potential of each technique to remove nutrients from the water column and prevent nutrient release under anoxic conditions. Lake Ngaroto was chosen because, of the four target lakes, it is the most important for recreation, and suffers from severe cyanobacterial blooms that limit the recreational use of this lake over the summer months. Consequently, a larger proportion of the community will benefit from the reduction of algae blooms in Lake Ngaroto than in the other target lakes.

5.1 Methods

An incubation test was used to compare the effects of Phoslock, modified zeolite, electric arc furnace steel-making slag (Appendix 3) and carbon addition (molasses) on dissolved and total nutrient concentrations in Lake Ngaroto. Fifteen sediment cores were collected by SCUBA from Lake Ngaroto. The cores (ID = 9.5 cm, area = 71 cm^2, height = 30 cm) were inserted into the sediment to a depth of 12 cm retaining about 1.1 l of water overlying the sediment (3/5 of total volume) and sealed with o-ring fitted lids. The cores were removed form the sediment without disturbing the sediment water interface, placed on ice in the dark and carefully transported to the laboratory. In the laboratory the cores were incubated for 5 days with oxygenated whole lake water sourced from Lake Ngaroto pumped through each core to prevent anoxia and small stirrer bars inside the top of the core prevented stratification (Fig. 5.5.1).

The same concentration of each chemical treatment was used for three replicates each (200 g m^{-2}, as obtained from the recommended Phoslock dose). Following treatment each core was separated and sealed. Oxygen concentrations, total and dissolved nutrients, pH and temperature were measured prior to treatment. At time selected time intervals throughout the experiment dissolved oxygen concentration was measured and dissolved nutrient water samples (15 mL) were removed until every core had achieved 0 mg L^{-1} oxygen concentration. After all cores had reached 0 mg L^{-1} oxygen concentration, total phosphorus and total nitrogen water samples (50 mL) were withdrawn and pH was measured.

Dissolved nutrient samples were filtered using a GF/C (0.1 μm nominal poresize) filter and frozen prior to nutrient analysis using a Flow Injection Autoanalyser system. Total nutrient samples were frozen and analysed using a persulfate digestion, and a Flow Injection Autoanalyser system.

Figure 12. Core incubation set-up with peristaltic pumps visible to the right of the blue basins. The sealed ends of the tubes used to cycle lake water through the cores are clearly visible in the foreground. White taps were used to place the oxygen sensor into the water column and withdraw water samples for nutrient analysis. The cylinders on top of the cores are the magnetic stirrers used to prevent stratification during the experiment.

5.2 Results

Ammonium concentrations increased as oxygen decreased over time in all cores (Fig 13). All treatments exhibited very similar ammonium concentrations as oxygen decreased, although zeolite consistently had the lowest ammonium concentrations throughout the experiment.

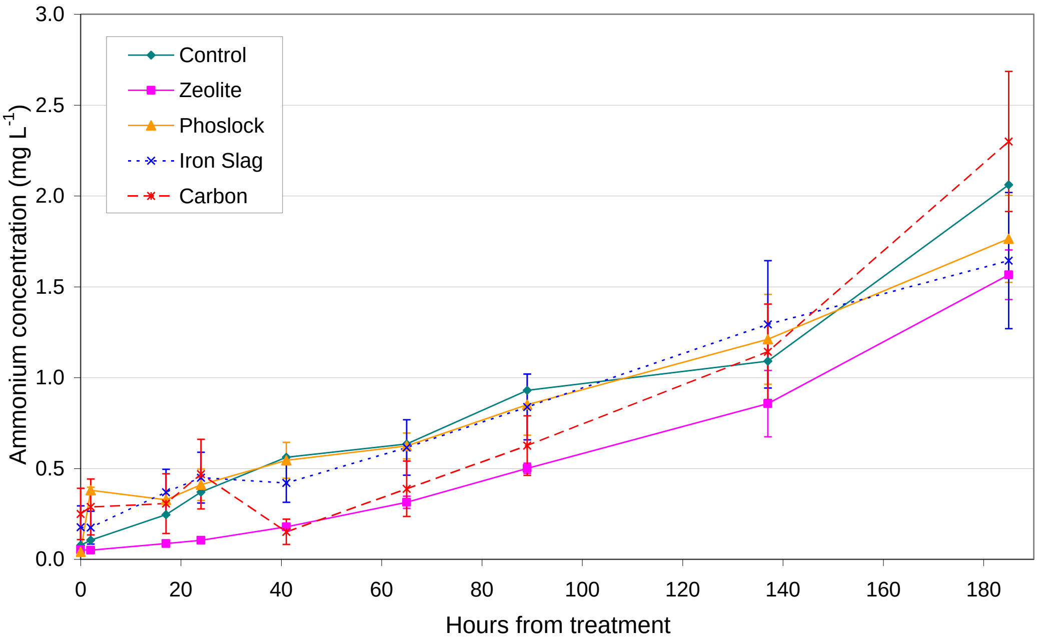

Figure 13. Mean ammonium (NH_4-N mg L^{-1}) concentrations over time in the incubation experiment for the treatments Phoslock, zeolite, iron slag, carbon and a control. Data points are means ± 1 S.E. (n = 3).

Oxygen concentrations declined at different rates in each treatment. Oxygen concentrations declined most rapidly in the carbon treatment, having much lower oxygen concentrations from 17 through to 41 h (Fig. 5.2.2). Consequently, it is difficult to compare treatments without considering the oxygen concentrations in each treatment.

Phosphate concentrations throughout the experiment were very low, ranging from mean = 0.002507 mg L^{-1}, s.e. = 0.000803 (Phoslock, 24 h) up to mean = 0.0373 mg L^{-1}, s.e = 0.0142 (control, 185 h)], with comparably large standard deviations (Fig. 5.2.3). Consequently, it is difficult to ascertain if any of the treatments produced a significant decline in phosphate concentration. Despite this, Phoslock consistently had the lowest phosphate concentration of the four treatments, although the final phosphate concentration in these cores was still higher than the initial concentration (Before treatment: mean = 0.0053 mg L^{-1}, s.e. = 0.0018; 185 h following treatment: mean = 0.0113 mg L^{-1}, s.e. = 0.0034). Phosphate increased in the Phoslock treatment cores from 89 h to the end of the experiment. A spike in phosphate concentration was recorded two hours after treatment addition in the carbon treated cores.

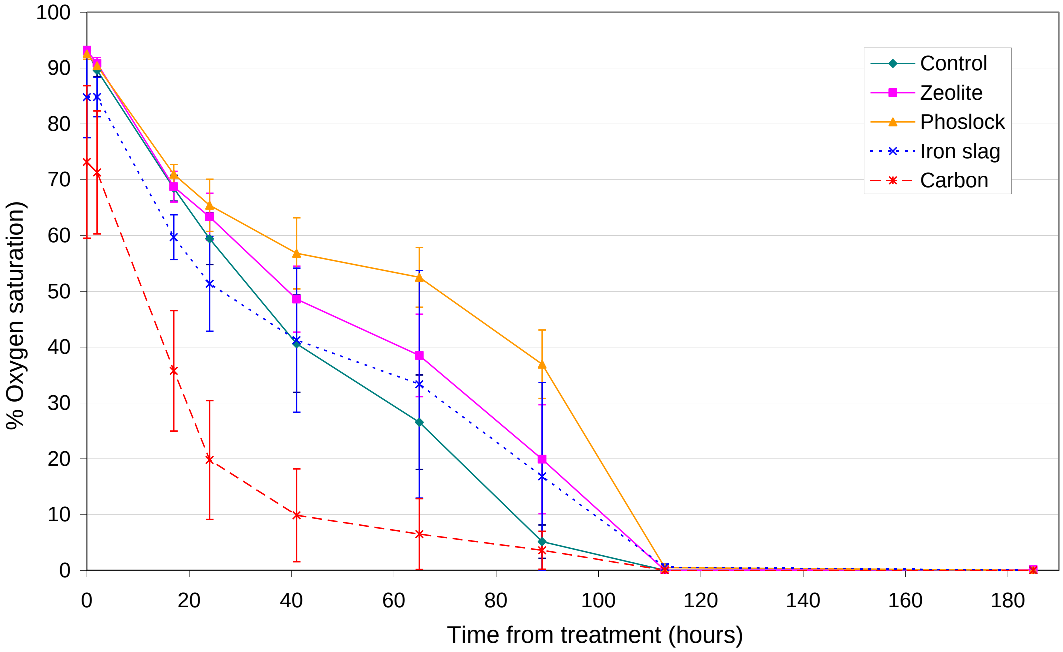

Figure 14. Percentage oxygen saturation over all five treatment levels for the duration of the experiment. Data points are means ± 1 S.E. (n = 3).

Appendix 2 shows how phosphate concentrations varied with oxygen concentration for each treatment. Phosphate concentrations appeared to increase when oxygen concentrations reached zero in all experimental cores except for zeolite. In the zeolite treatment, phosphate appears to increase when oxygen availability was low at 113 h, but then declines again at 183 h when oxygen concentrations were zero. Initial phosphate concentrations in the zeolite treatment are significantly higher than those of the other treatments. Consequently, it is difficult to compare any changes in phosphate across all the treatments. Despite the variability in phosphate concentrations over time within the zeolite treatment cores, the 'before treatment' phosphate concentration is never reached and the final phosphate concentration even after deoxygenation is substantially lower than that recorded prior to treatment.

Oxygen declined exponentially and most rapidly in the carbon treatments (Fig. 14). All cores appeared to release phosphate at zero oxygen concentration (Fig. 15). This release may not necessarily be caused by the release of phosphate from the treatment medium, but release of phosphate ions from the sediment itself.

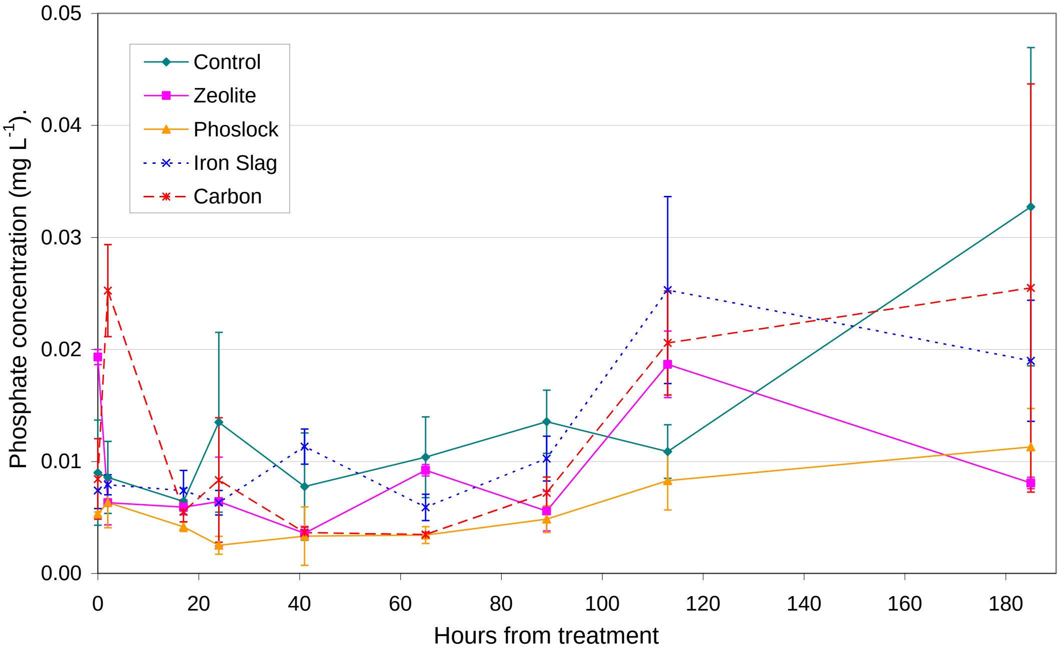

Figure 15. Mean phosphate (PO_4-P mg L^{-1}) concentrations over time in the incubation experiment for the treatments Phoslock, zeolite, iron slag, carbon and a control. Data points are means ± 1 S.E. (n = 3).

Both the control and iron slag treatments exhibited no difference in TP at the conclusion of the experiment (Fig. 16). Zeolite had a significantly lower final TP than initial TP concentration, as did the carbon treatment. Phoslock final TP appeared to be marginally lower than the initial TP measurement. Treatments with lower TP may have bound more particulate phosphorus during settling than treatments where final TP was not different from the initial concentration. Binding of both total phosphorus and phosphate is beneficial to nutrient reduction as mineralization of TP can result in phosphate becoming bioavailable.

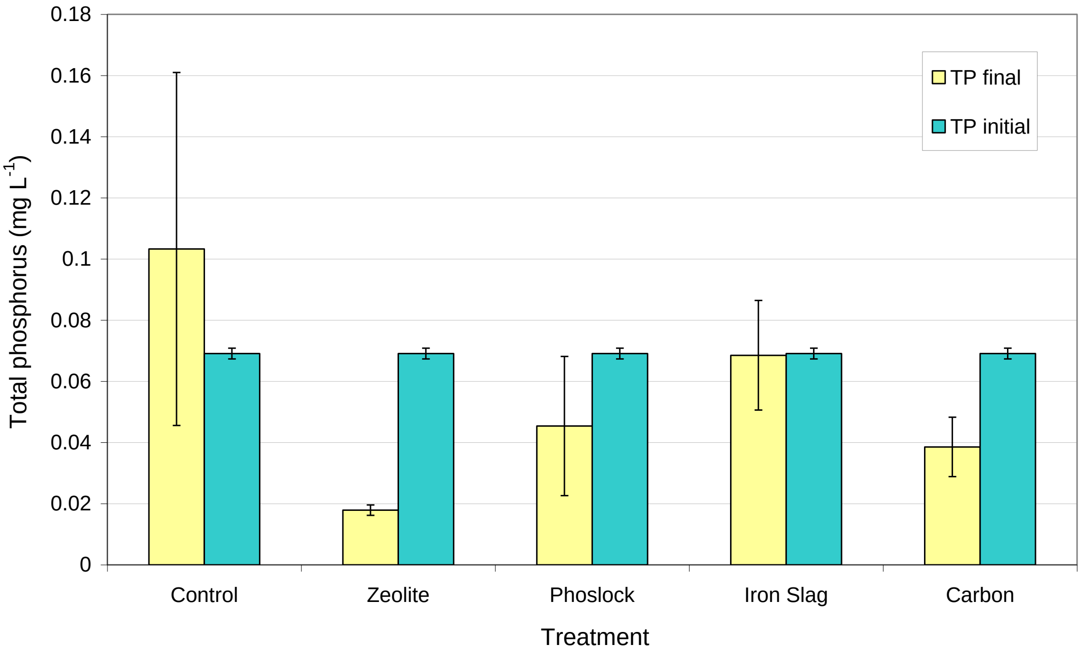

Figure 16. Initial and final total phosphorus concentrations (mg L^{-1}) of the water column for the five treatments. Bars are means ± 1 S.E. (n = 3).

Nitrate concentrations decreased as oxygen content decreased and ammonium increased. The carbon treatment had lower nitrate concentrations at 24 and 41 hours (Fig. 17), which may have been due to the substantially lower oxygen concentrations present in the carbon treatment compared with the other treatments (Fig. 18).

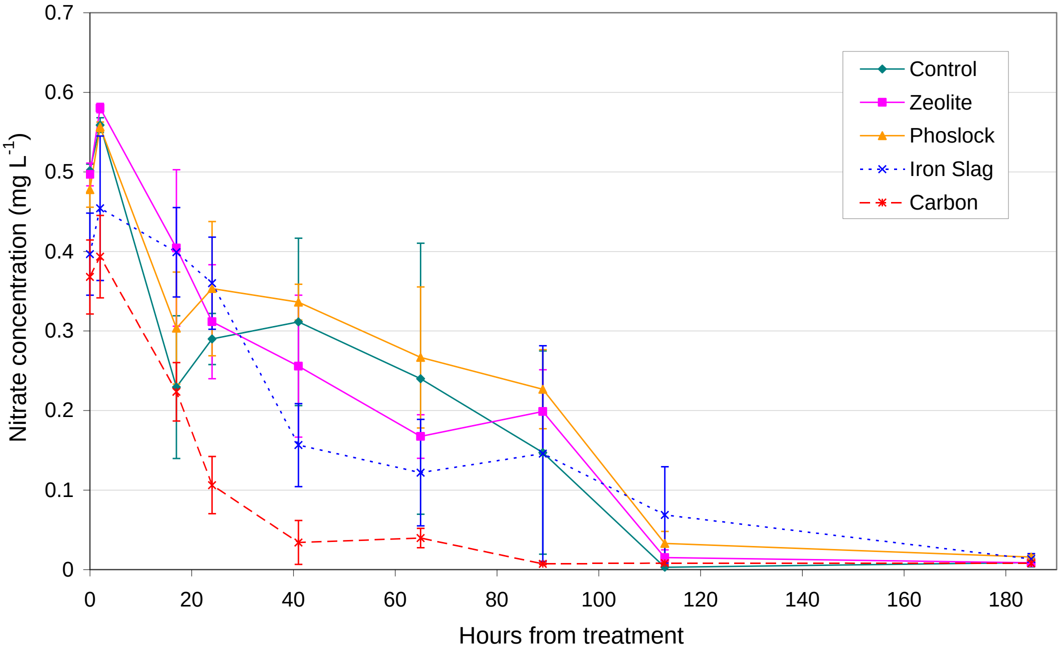

Figure 17. Mean nitrate (NO_3-N mg L^{-1}) concentrations over time in the incubation experiment for the treatments Phoslock, zeolite, iron slag, carbon and a control. Data points are means ± 1 S.E. (n = 3).

Nitrite concentrations were variable across all treatments except the Phoslock treatment, in which nitrite decreased rapidly and stayed low throughout the treatment. The large nitrite value for carbon (mean = 0.5461 mg L^{-1}, s.e. = 0.2737) is two orders of magnitude higher than nitrite concentrations recorded in any other treatment, however this value was included as two of the three replicates were in this range, these high values could be a result of contamination or as a bacterial denitrification intermediary product, which is consistent with the lowest concentrations of nitrate and the highest nitrite concentrations occurring in the carbon treatment (Fig 18).

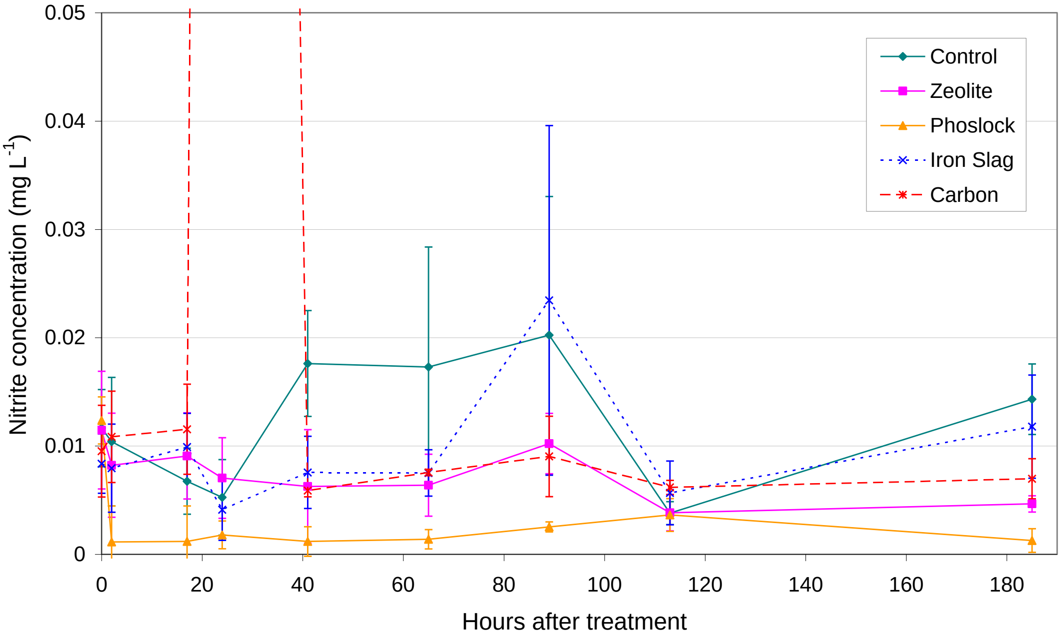

Figure 18. Mean nitrite (NO_2-N mg L^{-1}) concentrations over time in the incubation experiment for the treatments Phoslock, zeolite, iron slag, carbon and a control. Data points are means $\pm$ 1 S.E. (n = 3).

5.3 Discussion

The above experiments were designed to provide quantitative evidence on the effectiveness for nutrient removal of different materials that may potentially be used for whole lake restoration. A decision was made to carry out core incubation in the laboratory in order to have controlled and reproducible conditions that would allow comparative assessment of each material.

5.3.1 Phoslock

Phoslock appears to be the most effective treatment for removing phosphate and nitrate ions from solution in Lake Ngaroto, as long as the sediments remain oxidised. The phosphate concentration in the Phoslock cores increased during the course of the experiment and after 185 h was actually higher than the phosphate concentration recorded before treatment. However, as the core study was only run over 8 days it remains unknown how effective Phoslock would be as a long-term nutrient reduction measure. Additionally, if the bottom waters become anoxic Phoslock may reduce the amount of phosphorus released from the sediments due to the low permeability of the Phoslock treatment owing to its small particle size, although some phosphate may still be released depending on the availability of free lanthanum for binding.

5.3.2 Zeolite

A large reduction in phosphate was recorded following zeolite treatment, although the zeolite cores had much higher initial phosphate concentrations than the other experimental cores. However, phosphate concentrations after this initial decrease were variable in the zeolite treatment, with only the measurement on day 4 and on day 8 being substantially lower than the control treatment. Nevertheless, the phosphate concentrations remained below the initial phosphate concentration prior to zeolite treatment throughout the experiment. Additionally, the final TP concentration was significantly lower than before treatment, which suggests some particulate phosphorus was bound to the zeolite particles. Based on the results from the cores it appears zeolite may be capable of reabsorbing phosphate ions released during initial anoxia. Because the zeolite cores had a significantly higher initial P concentration we were unable to directly compare it with the other treatments. It appears zeolite may have reduced ammonium concentrations, as all ammonium values from the zeolite cores had very small standard errors and were substantially lower than the control ammonium concentrations. This is interesting when compared with Yang *et al.*'s (2004), study, which found both zeolite and Phoslock were capable of binding approximately 50% of NO_3-N ions from Okaro water at a dosage of 4 g L^{-1}.

5.3.3 Carbon

Carbon appeared to remove nitrate most effectively of any of the treatments and although carbon compounds have the ability to bind nitrogen ions, (Górniak *et al.* 1999; Jones *et al.* 1988), the low concentrations of nitrate could be due to the rapid decline of oxygen within the carbon treatment cores and subsequent denitrification. The rapid decline of oxygen recorded in the carbon treatment is probably due to the stimulation of bacterial activity and concomitant oxygen consumption, as carbon is a major energy source for bacteria (Wetzel, 2001). When carbon was added, there was a pulse of phosphorus two hours following treatment. This initial release was followed by a decline in phosphate, with concentrations at 65 h and 89 h being as low as the Phoslock treatment and substantially lower than the control cores. However, when the cores became anoxic, phosphate was released. More particulate phosphorus was either bound or assimilated due to bacterial productivity in the carbon cores than in the control, Phoslock or iron slag treatments, but not zeolite.

5.3.4 Iron making slag

Iron making slag was the least effective of the treatments trialled, and remained within the control range for all nutrients examined. The only substantially different result in the iron making slag cores was a higher phosphate concentration than the control for initial anoxia of the cores. All forms of iron slag should not be discarded based on the results from this study, however, as the type of slag used and its chemical components have a major impact on the chemical binding of phosphate.

5.4 Conclusion

Currently, none of the lakes is suitable for any of the internal nutrient load reduction methods we have reviewed. This is because their external nutrient loads remain too high to expect any internal nutrient reduction technique to be successful in the medium- to long-term. In almost every case study reviewed, the reason for unsuccessful nutrient reductions has been attributed to external nutrient loads remaining too high (Lewandowski *et al*. 2003; Gulati & van Donk, 2002; Pokorny & Hauser, 2002; Søndergaard *et al*. 2002; Kleeberg, *et al*. 2001; Kleeberg & Kohl, 1999; Hanson 1998). Therefore, it would be recommended that every effort is made to reduce external nutrient loads before commencing any in lake nutrient reduction treatment.

Even after the external nutrient load has been reduced many lakes may not show reductions in P and N concentrations, as nutrients accumulated in the sediments will be released into the water column. When the external nutrient load is reduced, and water column nutrient concentrations are reduced, lake sediments which previously had acted as a nutrient sink may now become a nutrient source. The extent to which sediments will act as a nutrient source depends upon the amount of iron contained in the sediments (Wetzel, 2001), the degradability of sedimentary organic matter as an energy source for micro-organisms, and the size of the phosphorus pool (Søndergaard *et al*. 2002). This release of phosphorus can be very persistent, with a conservative estimate of at least ten years after an external load reduction (Welch & Cooke, 1999). Consequently, it may be desirable to employ internal nutrient reduction techniques to speed up lake recovery following a decrease in external loading.

Based on the results of this study, zeolite, and to a lesser extent Phoslock, appear to be the most effective in-lake methods for internal nutrient load reduction. Increasing carbon inputs from the surrounding bog areas, by restoring bog vegetation and natural discharge rates, may be an effective method to enhance control of the internal nutrient load in lakes which are peat influenced (e.g. Kainui, Cameron, Posa, Koromatua, Kaituna, Rotokawau and Komakorau; Champion *et al*. 1993). Additionally, due to the high numbers of coarse fish present in the lakes, reductions in fish numbers may also contribute to reduced internal nutrient loading.

6.0 Hypolimnetic withdrawal (Deep water discharge)

Hypolimnetic withdrawal and/or oxygenation of the hypolimnion are restoration techniques designed for use in lakes that stratify over summer and become anoxic at the sediment-water interface. Redox reactions at the sediment-water interface result in releases of phosphate into porewaters and into the water column, and subsequent breakdown of the thermocline, internal wave diffusion, or wind mixing results in phosphorus becoming available to algae throughout the water column (Cooke *et al*. 1996). Hypolimnetic withdrawal removes not only the anoxic bottom waters but also settling organic particles and products of their degradation, as well as phosphorus and other substances released from the bottom sediments (Dunalska, 2002). Rotomanuka North is the only peat lake known to stratify and become anoxic during the summer (Boswell *et al*. 1985). However, other localised anoxic microzones may become present in lakes that do not stratify at times if there is high bacterial activity and concurrent oxygen demand on the sediment surface.

Subsequently, there a several criteria that must be met and several factors that must be considered before using hypolimnetic withdrawal as a means of nutrient reduction:

- Does the lake have a long period of stratification and anoxia, and a long hypolimnion residency period? (Cooke *et al*. 1993) None of the peat lakes is known to stratify except for Rotomanuka North, which may not stratify for a long enough period for hypolimnetic withdrawal to be effective.
- Water characteristics: Often hypolimnetic water has different characteristics to surface waters, with high levels of phosphorus, ammonia, hydrogen sulphide and metals, and no oxygen. Consequently, the presence of these substances would have to be determined and appropriate treatments of the hypolimnetic water would have to be made before release downstream (Cooke *et al*. 1993; Nürnberg, 1987).
- Temperature: The cold temperature of discharged water may alter downstream environments, or negatively affect flora and fauna.
- Is the natural refilling rate of the lake high enough to reduce lake drawdown resulting from hypolimnion discharge? Smaller lakes, or lakes that rely on

rainwater inputs may refill too slowly for hypolimnetic withdrawal to be effective.

- Hypolimnetic discharge can increase hypolimnion temperature, resulting in oxygen depletion rates 35–55% higher than normal (Grochowska & Gawrońska, 2004; Dunalska, 2003). However, contrasting results have also been found; in Nürnberg's (1987) review of 17 lakes, anoxia tended to be reduced by hypolimnetic discharge.
- Destabilisation of the thermocline: This can result in partial mixing of the lake, enabling nutrients from the hypolimnion to become available for phytoplankton growth in the epilimnion (Grochowska & Gawrońska, 2004; Dunalska, 2003).

6.1 Political issues

Lowering of the lake levels would be the biggest concern in the peat lakes. During summer when stratification occurs (if it does at all), and hypolimnetic withdrawal could take place lake levels are unlikely to refill naturally. Lowering the lake levels even temporarily could result in further peat shrinkage, thus contributing to the permanent lowering of lake levels. Additionally, downstream water may be used for irrigation or stock drinking water and any changes in water quality due to hypolimnetic discharge would have to be mitigated or use of downstream water discouraged. Additionally, as none of the lakes have outflows below the elevation of the lake surface, active pumping and the associated expense would be required to remove hypolimnetic water.

6.2 Case studies

One review and one case study are presented here: Lake Kortowskie (Poland) and a review based on a selection of lakes from around the world.

Of twelve lakes with hypolimnetic withdrawal systems installed, as reviewed by Nürnberg (1987), eleven had reductions in hypolimnetic P concentrations and epilimnetic phosphate concentrations decreased in eight lakes. The shallowest lake reviewed had a mean depth of 3.9 m and a maximum depth of 6.8 m, the other lakes were all greater than 14 m deep. The reduction in P from the hypolimnion is a direct effect of withdrawal, but epilimnetic reduction in P is an indirect effect, demonstrating entrainment of P from the hypolimnion to the epilimnion was reduced. Decreases in epilimnetic P were found to be proportional to withdrawal duration during stratification, although as long as 5 years may be required before a significant decrease in epilimnetic P is recorded.

Lake Kortowo (Poland) (area 89.7 ha, mean depth 5.9 m, max depth 17.2 m) has been restored since 1956 by withdrawing nutrient-rich hypolimnetic water directly by means of a pipeline. This withdrawal system must operate for the whole period of summer stagnation, and especially the second half when the amount of nutrients accumulating near the bottom is maximal (Dunalska, 2002). Lake Kortowo had very high nutrient inputs from the catchment that were not reduced before hypolimnetic withdrawal commenced. Subsequently, a significant amount of nutrients were reserved within the lake. Between 1990-1994, 56% of nitrogen entering the lake was retained and 26% of phosphorus was retained. Without the hypolimnetic withdrawal system Dunalska (2002) estimated the lake would retain 49.6% of nitrogen and 57.8% of phosphorus. Kleeberg *et al*. (2001) suggested the external phosphorus load would need to be reduced by 75% in Lake Jabel before the removal of P via hypolimnetic discharge would be effective.

Hypolimnetic withdrawal is not a process that is effective on its own, but if combined with external nutrient reductions it does have the potential to reduce internal nutrient load. However, this is likely to take at least five years of withdrawal and constant lake levels would have to be maintained during this time to prevent drawdown, erosion of the littoral area and peat shrinkage. Hypolimnetic withdrawal involves a large initial investment, but has low annual maintenance costs (Cooke *et al*. 1993). However, it would become more expensive if the water removed had to be treated to reduce nutrient concentrations.

6.3 Suitability for the Waikato peat lakes

Lake attributes will determine if hypolimnetic withdrawal will be a successful nutrient removal technique. Suitable lakes will stratify for a reasonable amount of time to allow the nutrient enriched hypolimnetic water to be removed, and the lakes should be large enough to cope with the volume of water drawn off. Using the above case studies as a guideline for the minimum size for hypolimnetic withdrawal, lakes Rotomanuka and Kainui would be the only suitable candidates, although they probably both only stratify for a very short period of time. Historically the Waikato peat lakes had no inlet or outlet drains and water levels fluctuated according to precipitation and associated groundwater levels. Subsequently, none of the lakes is equipped to cope with the amount of water removal required for hypolimnetic withdrawal. Therefore hypolimnetic withdrawal would not be a suitable method to remove internal nutrient load from the Waikato peat lakes.

7.0 Hypolimnetic aeration

The aim of hypolimnetic aeration is to increase the oxygen content of the hypolimnion in order to decrease concentrations of phosphate, ammonium, Mn and Fe, which can all increase under anoxic conditions (Cooke *et al*. 1993). This is done by injecting the hypolimnion with air or directly at a greater cost with pure oxygen. The initial estimate of oxygen demand is calculated by measuring the decline in hypolimnetic oxygen content following the onset of spring stratification. However, oxygen demand generally increases with operation of an aerator; therefore, the hypolimnion must be supplied with more oxygen than predicted on the basis of present oxygen demand (Moore *et al*. 1996). Hypolimnetic aeration can be undertaken to maintain oxygen levels in the hypolimnion, thus reducing P transport to the epilimnion, or can be used to destabilise the thermocline, resulting in a relatively even oxygen concentration throughout the water column.

However, Gächter and Müller (2003) concluded that anoxia does not necessarily result in benthic P release in lakes with high iron, but low sulphate concentration and increased sulphide production could induce increased P release. Consequently, they concluded that hypolimnetic oxygenation will only have a positive effect on P retention if the sulphate concentration of the hypolimnion is low.

Factors that must be considered when choosing hypolimnetic aeration:

- Does the hypolimnion of the target lake become anoxic, and how long is the duration of this anoxia? Some lakes may be continuously mixed and never experience hypolimnetic anoxia, and other lakes may have a diurnal cycle of anoxia and oxygenation (Calton & Wetzel, 1988). Aeration will have greater benefits for lakes with longer periods of anoxia, as a larger amount of phosphate would remain bound in the sediments.
- How large is the hypolimnion? Hypolimnetic aerators tend to be more efficient and less likely to disrupt stratification if the hypolimnion is large.
- Is there sufficient iron in the sediment to bind the available phosphorus under oxygenated conditions? Different studies have found differing optimal ratios

of iron to phosphorus (Gächter & Müller, 2003; Jensen *et al*. 1992; Stauffer, 1981).

- What are the sulphide concentrations at the sediment-water interface? High sediment sulphide concentrations can result in phosphate release from iron even in oxic conditions (Gächter & Müller, 2003; Caraco *et al*. 1989).
- The effects of hypolimnetic aeration may not be as large or as permanent as other techniques such as hypolimnetic withdrawal or P inactivation with alum (Cooke *et al*. 1993).
- If external loading exceeds the retention capacity of the sediment, aeration will not affect the amount of P released. Therefore external nutrient loads should be reduced substantially prior to commencement of hypolimnetic aeration.
- Are blue-green algae a nuisance species? In some cases where hypolimnetic aeration mixes the whole water column it may produce enough turbulence to reduce the buoyancy and dominance of blue-green algae (Westwood & Ganf, 2004; Visser *et al*. 1995).

7.1 Political issues

The initial cost of purchasing and installing aerators would be expensive, however, once purchased the aerators could potentially be moved between lakes. Operating costs would depend on electricity prices.

7.2 Case studies

The case studies reviewed below are from Switzerland, Poland and the Netherlands.

Ten years of data from lakes Sempach and Baldegg (Switzerland) led Gächter & Wehrli (1998) to conclude that hypolimnetic aeration had no effect on the P content of the hypolimnion. They attributed any reduction in P to the decrease in external loading of nutrients.

In contrast, Lake Dlugie (Poland) has shown improvements in trophic state and reductions of phosphate after being subjected to more than 10 years of artificial circulation (Grochwska & Gawrońska, 2004). Reduced P concentrations were attributed to severe reductions in the release of phosphorus from the bottom sediment. However, this may have also been due to a reduction in external loading. Although hypolimnetic oxygenation reduced nutrient concentrations, Lake Dlugie is still considered eutrophic and no decrease in chlorophyll *a*, cyanobacterial blooms, Secchi transparency or biochemical oxygen demand was noted during the study. Grochwska & Gawrońska (2004) concluded that the high phosphorus concentrations were due to a lack of iron present to bind P within the sediments.

In the Bautzen Reservoir (Netherlands) aeration of the hypolimnion was combined with simultaneous addition of Fe, which decreased the forecast internal P-loading by 68.4% in 1996 and 52.1% in 1997. Where the Fe:P ratio is above 15 by weight it should be possible to control internal P loading by keeping the sediments oxidised (Jenson *et al*. 1992). Additionally, *Microcystis* bloom formation was suppressed in 1996 and delayed in 1997, which was found to be a function of aeration, as opposed to environmental factors (Deppe *et al*. 1999). However, the bloom suppression was not necessarily due solely to nutrient reductions within the lake, but due to turbulence increases.

7.3 Suitability for the Waikato peat lakes

As the peat lakes are all relatively shallow and well mixed it is unlikely hypolimnetic oxygenation would be effective. The sediment-water interface of Rotomanuka has been recorded as anoxic during the summer months, but it is probably the only lake with a significant anoxic water volume. As previously mentioned it is unlikely that the hypolimnion of the other lakes becomes anoxic, but there may be localised anoxic microzones that would be difficult to target with a large aerator. Although hypolimnetic aeration may not effectively aerate the hypolimnion, it may produce enough turbulence to reduce the buoyancy and thus dominance of blue-green algae (Westwood & Ganf, 2004; Visser *et al*. 1995).

8.0 Fish Removal (Biomanipulation)

One of the functions of fish removal is to reduce predation on zooplankton, which is intended to result in higher zooplankton consumption of phytoplankton and reduced biomass. Generally this is true during the first year following biomanipulation, but often zooplankton abundances decline and return to pre-fish removal numbers (Jeppesen *et al*. 1990a). Despite this, chlorophyll *a* concentrations, Secchi depth and TP concentrations were at low levels for at least 5 years in most of the lakes reviewed by Hansson *et al*. (1998), which were subjected to fish removal. A planktivorous fish density of 20–30 kg ha^{-1} is known to reduce zooplankton grazers (Jeppesen *et al*. 1990a). However, reducing fish density may not reduce cyanobacterial populations, as cyanobacteria may not be effectively grazed by large filter feeders due to the presence of toxins and possible large colonial forms (Jeppesen *et al*. 1990a).

A second function of fish removal is to reduce phosphate release from lake sediments. The rate of phosphorus release from lake sediments approximately doubles if the sediments are disturbed by agitation from turbulence (Wetzel, 2001). Herbivorous fish reduce the erosion resistance of the sediment by reducing the abundance of macrophytes, thus indirectly contributing to sediment resuspension. Bottom feeding fish may directly contribute to sediment agitation and resuspension during feeding activities. The reestablishment of macrophytes can result in a reduction of P release from lake sediments, as macrophytes assimilate phosphorus from both the water column and the sediment for plant growth. Thus the reestablishment of macrophytes can work in two ways to reduce internal P loading, by reducing the resuspension of sediment and by assimilating P into the plant tissue. However, it must be noted that a change from macrophyte dominance back to a turbid state can still occur, as the total amount of nutrients entering the lake has not decreased and neither has the total amount of nutrients within the lake ecosystem.

Fish removal is more effective in shallow than deep lakes if phosphate concentrations are < 200 μg P L^{-1}. This is because the competitiveness of cyanobacteria decreases with decreasing mean depth (Jeppesen *et al*. 1990a) and the production of zooplankton per unit of volume is higher in shallow lakes due to higher primary production (Jeppesen *et al*. 1990b). Fish removal may also be more successful in eutrophic lakes, as the potential predation pressure on cladocerans is continuously high in eutrophic productive shallow lakes, as planktivorous fish may sustain high densities by feeding on the sediment or benthic dwelling organisms when cladoceran numbers are low (Jeppesen *et al*. 1990b).

Factors to consider when examining fish removal are:

- What species of fish are in the lake? Both functions outlined above aim to reduce the internal phosphorus load in the lake, but will depend on the species of fish present and their ecological niche. Obviously if any native or rare fish species are present non-selective fish removal may not be desirable.
- External phosphorous loading: Hanson (1998) recommends that phosphorus concentrations within the lake should be lower than approximately 100 μg L^{-1}.
- Is macrophyte reestablishment or increasing the number of zooplankton more important? If macrophyte reestablishment is the goal of fish removal it may be more successful to build fish exclusion enclosures to establish founder communities of charophytes. Dugdale *et al*. (in press) found when catfish, rudd, perch, tench and goldfish were present, charophytes that had established in fish-free enclosures survived and expanded after re-exposure to the fish population. This method increased charophyte abundance more successfully than intensive fish removal.

8.1 Political issues

The Waikato region is the only region in New Zealand where coarse fish, including rudd are classified as sports fish. Consequently, there may be some opposition to removal of these coarse fish species. The smelt found in Rotomanuka are considered a genetically separate group to the diadromous smelt commonly found throughout the Waikato River (Michell *et al*. 1993). Therefore, non-selective fish removal in Rotomanuka may be undesirable.

8.2 Case studies

In Lake Wolderwijd coarse fish removal allowed sediments to consolidate during periods of low wind speed, which enabled the erosion resistance of the sediments to increase. Consequently, the suspended solids concentration within the lake was heavily reduced during the following period of high wave action (Scheffer *et al*. 2003).

Hansson *et al*. (1998) reviewed the long term effects of piscivore fish reduction and non-selective fish reduction over 10 (6 and 4 respectively) lakes. Piscivore and non-selective fish reduction both produced declines in chl *a* concentrations over all lakes examined. After 5 years non-selective fish removal had reduced total phosphorous concentrations, but only 2 lakes had reduced total phosphorus 5 years after piscivores were removed. Based on a review of 14 lakes which had undergone fish manipulation, Hansson *et al*. (1998) established a list of guidelines for successful biomanipulation:

- The planktivorous fish stock should be reduced by at least 75% over a short period of time (1–2 years). Planktivorous fish include the juvenile stages of all fish species found in the Waikato peat lakes, most native fish species and goldfish.
- Benthic fish numbers should be strongly reduced e.g. koi carp, catfish, goldfish.
- Recruitment of young fish should be reduced.
- Establishment of macrophytes should be encouraged e.g. removal of rudd and goldfish.

8.3 Suitability for the Waikato peat lakes

Many of the peat lakes contain introduced fish species, often coarse fish such as rudd (*Scardinius erythrophthalmus*), carp (*Cyprinus* sp.) or catfish (*Ameriurus nebulosus*). Lake Rotomanuka contains native short finned eels (*Anguilla australis*), smelt

(*Retropinna retropinna*) and common bullies (*Gobiomorphus cotidianus*). The smelt are considered a genetically separate group to the diadromous smelt commonly found throughout the Waikato River (Mitchell *et al*. 1993). Introduced fish found in Lake Rotomanuka were catfish and rudd (Speirs & Barnes, 2002). Rudd have a dietary preference for native macrophytes (Lake, 1998). Kainui contains catfish, rudd and gambusia (*Gambusia affinis*). Ngaroto contains catfish, eels, common bully and carp, and koi carp may also be present (R. Kelleher, pers comm.). All of these introduced fish possess the ability to reduce water quality by disturbing bottom sediments and preying on native macrophytes, fish or zooplankton (Department of Conservation).

8.4 Conclusions

Coarse fish removal from the peat lakes would probably successfully reduce phosphorus loading within the lake, as resuspension of bottom sediments would be reduced, and may, when coupled with macrophyte enclosures encourage the reestablishment of some native charophyte species. Non-selective removal of fish would result in a reduction of total planktivores, thus potentially increasing zooplankton grazers and decreasing algal biomass within the lake. However, re-invasion of pest fish would be difficult to prevent in some lakes, (e.g. Ngaroto, and Kainui, which all have several inlet/outlet drains) and fish removal would have to occur on a regular basis, depending on the rates of fish reproduction and reinvasion. Additionally, all native fish in New Zealand will eat zooplankton, but it may be undesirable to remove these species.

9.0 Conclusions and recommendations

Every lake is different, and the peat lakes are unique ecosystems in that they all exhibit some characteristics of dystrophy, for example low alkalinities, comparatively high concentrations of humic substances from surrounding peat bogs, low pH and/or brown stained waters. Consequently, not all the techniques reviewed in this report will be suitable or effective in reducing the internal nutrient load of the peat lakes (Table 9.0.1), and some techniques would need to be tailored specifically for the peat lake under consideration:

- Alum treatment is not recommended as the risk of toxic insoluble aluminium forms occurring is high, due to low pH and buffering capacity in all the target lakes.
- Sediment removal would be most suitable for use in Lake Ngaroto, however, the potential for rapid return to the pre-removal state, particularly given the relatively high sedimentation rate, as well as high costs of sediment removal, make this option less attractive.
- Phoslock and zeolite both effectively reduced phosphate concentrations in the incubation cores. Zeolite was more effective than Phoslock in preventing nutrient release from the sediments following anoxia. However, Phoslock was more effective than zeolite at removing nutrients from the water column. The usefulness of flocculants such as Phoslock may be limited to producing a short term clear-water state that allows macrophyte growth to occur; however, new products such as modified zeolite may have longer-term effects that become apparent with further research.
- The use of iron making slag to reduce internal nutrient load is not recommended, as nutrient concentrations were not reduced in the iron treated cores in the incubation study where progressive anoxia occurred.
- Dissolved organic carbon may be useful in the naturally dystrophic peat lakes, and may be added naturally if measures are taken to conserve the surrounding peat substrate (e.g. riparian vegetation, maintenance of lake levels). However,

there is still uncertainty about whether 1) such an addition would be successful and 2) whether it would be possible to add sufficient of this natural (or similar) humic material to be fully effective.

- Hypolimnetic withdrawal and hypolimnetic aeration are methods well suited to large deep lakes that stratify for long periods, but would be relatively ineffective in all of the target lakes. However, hypolimnetic aeration may have some benefits in Lake Rotomanuka, as this the only peat lake known to regularly stratify and become anoxic during the summer. Additionally, hypolimnetic aeration can reduce cyanobacterial abundance by disrupting their buoyancy, and may be effective in a lake of the depth of Rotomanuka.

Importantly, any technique available to reduce the internal nutrient load will be less effective if the external nutrient load of the target lake is not significantly reduced prior to treatment. Consequently, it is recommended that a thorough analysis of the feasibility, methods and costs of reducing external nutrient load are examined and applied to the target lake before utilizing internal nutrient load controls. In addition, methods intended to reduce external nutrient loads, i.e. re-vegetation and re-creation of surrounding wetland areas, could also result in increased carbon and humic substance addition to the lakes if designed correctly, potentially causing a shift from a eutrophic to dystrophic state (Carpenter & Pace, 1997).

Nevertheless, reducing the internal nutrient load of these lakes remains a priority. Even after the external nutrient load has been reduced, lakes may not show an improvement in P and N concentrations, as lake sediments that had previously acted as a nutrient sink may now become a nutrient source. This release of phosphorus can be very persistent, with a conservative estimate of at least ten years after an external load reduction for internal loads to be reduced significantly (Welch & Cooke, 1999). Consequently, it may be desirable to employ internal nutrient reduction techniques to speed up lake recovery after a decrease in external loading. Greater cost efficiency, higher rates of success and long-term effectiveness may be the benefits of reducing the external nutrient load substantially prior to an internal nutrient load reduction (Lewandowski *et al*. 2003; Gulati & van Donk, 2002; Pokorny & Hauser, 2002;

Søndergaard *et al*. 2002; Kleeberg, *et al*. 2001; Kleeberg & Kohl, 1999; Hanson, 1998).

Consequently, it is recommended that before a pilot study is undertaken the external nutrient loads of the target lake are reduced as much as possible. As risks will always exist when undertaking a pilot project, the recommended project design should employ several different methods used in concert to decrease internal nutrient loads.

On this basis we recommend that a holistic whole-lake or, by barriers or partitions, pilot lake restoration project be implemented on one or two focus lakes that combines:

- Restoration in a lake or lakes where the catchment has already been substantially re-vegetated and wetland areas have been enhanced or re-created, so the lake will tend to conform to the criteria for external nutrient reduction that are critical for successful internal load reductions;
- Pest fish removal or control. This report was not designed to specifically address the issue of pest fish effects on water quality.
- Consideration of macrophyte re-establishment and the need to potentially control exotic and undesirable species of macrophytes as water clarity is improved.
- Use of Phoslock or zeolite, following detailed consideration of application rate and longevity of treatment effects.

It is important that there is careful scientific documentation of the outcomes of the restoration project. Here we emphasise again that close liaison is required between scientists, iwi, environmental managers and flocculant proponents so that trust is developed to allow progressive confidence to be developed in restoration techniques and the desired outcomes to be attained. In addition, our report was not required to explicitly address issues of pest fish or weed management, but it is clear in many instances that successful restoration will not be achieved without an integrated approach involving these factors together with internal and external nutrient controls. On this basis, we recommend that Environment Waikato conducts a small scoping exercise on the feasibility of combined pest fish and macrophyte control in selected target lakes that are suitable for a restoration strategy. Table 9.0.1 presents a review of the suitability of the four focus lakes for different restoration techniques. It is suggested that this be extended as part of the scoping exercise to include other lakes where restoration involving internal nutrient load controls might be applied.

Table 6. Review of the major requirements for each method and the suitability of the four target lakes. A 'Y' indicates an agreement with the conditions required in all instances. Y = yes, N = no, S = somewhat and U = unknown.

Method	**Requirements**	**Ngaroto**	**Kainui**	**Rotomanuka**	**Cameron**
Sediment removal	Deepening beneficial for recreation	Y	N	N	N
	External nutrient load reduced by at least 50%	N	N	N	N
	Sediment removal will result in substantial nutrient removal	Y	Y	Y	Y
	Low concentrations of heavy metals	S	S	S	Y
	Low sedimentation rate	N	Y	Y	Y
	Disposal site nearby	Y	S	S	N
	Lake values unharmed	Y	S	S	N
All flocculants	Slow sedimentation on top of treatment	N	Y	Y	Y
	Low wind exposure to prevent resuspension and uneven application	N	Y	Y	Y
	External nutrient load reduced	S	N	N	S
Alum	Alkalinity higher than 50 mg $CaCO_3$ L^{-1}	N	N	N	N
	pH range 6 – 8	Y	Y	S	N
	Low concentrations of tannins present?	U	U	U	N
Phoslock	No specific requirements known				S
Zeolite	No specific requirements known				

Iron making slag	Hypolimnion remains oxidised year round	S	S	N	S
	Fe: TP ratio less than 15: 1 by weight	N	N	N	Y
Carbon addition	Unmodified state is dystrophic	N	Y	Y	Y
	Low-moderate water column UV exposure	N	N	N	Y
Hypolimnetic withdrawal	Long period of thermal stratification and anoxia	N	N	N	N
	High natural lake inflows	N	N	N	N
Hypolimnetic aeration	Long period of anoxia and associated P release	N	N	N	N
	Sufficient iron available to bind P under aerobic conditions	U	U	U	U
	Large hypolimnion to prevent destratification	N	N	N	N
Fish removal	Contain planktivorous fish	Y	Y	Y	U
	Over 75% of fish can be removed without rapid recolonisation	N	U	N	Y
	Rare or endangered fish species are not present	Y	Y	N	Y

10.0 Pilot study

Different techniques for reducing internal nutrient loads will work best in different lakes. For example in 1993 when Rotomanuka was surveyed by Thompson & Champion (1993), the Secchi depth was 3.5 m and both native submerged species (*Potamogeton cheesemanii*, *Nitella hookeri*, *Utricularia australis*) and exotic species, e.g. *Egeria densa* were present. In the late 1990s the macrophyte beds collapsed and the lake entered a turbid, phytoplankton dominated state. Therefore, reductions in external nutrient load followed by fish removal (to reduce internal nutrient recycling, resuspension and macrophyte grazing), application of a flocculant to reduce nutrients available for phytoplankton growth, and the use of enclosures to establish native charophytes (Dugdale, *et al*. 2005; Jeppesen & Sammalkorpi, 2002) may be used in combination to restore macrophytes and a clear-water state in Rotomanuka. This method could also be effective in Lake Ngaroto, although macrophytes have previously been a problem for recreation in the lake. However, fish biomass may require ongoing control in both lakes due to the presence of established populations of rudd and other coarse fish (Speirs & Barnes, 2002) and potential for re-introduction through human activity or geographically connected streams.

This pilot study presents a detailed methodology to test if additions of modified zeolite and/or Phoslock would decrease internal nutrient load and may allow the re-establishment of native macrophyte populations within the peat lakes. This pilot study has been designed for use in lakes such as Rotomanuka, Ngaroto, Serpentine Lake complex, Rotokauri, Rotomanuka South and Ngarotoiti, which have all previously supported macrophyte populations and a clear-water state, and are among the less peat influenced lakes (Champion *et al*. 1993). This method would not be suitable for lakes such as Kainui, Cameron, Koromatua, Kaituna, Rotokawau and Komakorau, which are all highly peat influenced. High peat influence has reduced the ability of these lakes to support substantial macrophyte populations, due to low pH levels and high light attenuation (Champion *et al*. 1993).

10.1 Candidate lakes

Suitable lakes to conduct the field trial would be Rotomanuka North and South, Serpentine South, Rotokauri and Horseshoe Lake. These are all relatively small lakes where areas could be partitioned off without too great a cost or disturbance to recreational activities, or where a whole lake restoration could be undertaken, and where relatively easy access is available. Smaller bays of larger lakes, e.g. Waikare, may also be suitable if barriers are effective, and where there is a strong community pressure for implementation of restoration actions. Prior to commencement of the full scale field trial, external nutrient loads would have to be reduced substantially, ideally to an amount that would allow the long-term success of the trials. Some effort has already been made to reduce the external nutrient load of Serpentine South and Horseshoe Lake, and the pilot study would complement the restoration activities occurring at these lakes. Ideally two lakes would be treated at the same time, one whole lake treatment and the other a partial or half-lake treatment.

10.2 Consent requirements

Permission from the Department of Conservation would be required before commencement of an in-lake chemical application on lakes Rotomanuka North and South, and Serpentine South, as these lakes are managed as wildlife reserves. Lake Rotokauri is vested in the Department of Conservation but currently is “controlled and managed” by the Waikato District Council. Additionally, the Waikato-Tainui claim to the Waikato River may have to be considered before any chemical substances are added to the pilot lakes. Consents may have to be obtained from the Auckland/Waikato Fish and Game Council before fish removal.

A whole or partial lake experiment should not be commenced without thorough toxicity tests being carried out on the flocculant of choice (modified zeolite or Phoslock), including laboratory studies that consider the effects of the particulate nature of the substance, the effects of its resuspension on biota, and any effects on the seed bank size, germination, growth or re-establishment of native macrophytes. This testing may be considered as part of the scoping exercise for restoration effects on pest fish and macrophyte establishment.

10.3 Equipment requirements

Equipment would be required for the deployment of a barrier within a lake, e.g., tough plastic or semi-permeable sheeting and suitable tools to enable an area of the lake(s) to be sectioned off for at least a year without threat of collapse or fish invasion. Treatment and control areas will need to be large enough to include an area of the lake bed representative of the lake itself and to allow natural mixing processes to occur, preferably half of the lake if feasible. Efforts should be made to ensure the areas of treatment and control are as similar as possible (e.g. consider inlet and outlets, existing macrophyte cover, substrate and peripheral vegetation). Sufficient amounts of the chosen flocculant will be required; modified zeolite is available from SCION (Rotorua) and Phoslock is available from Primaxa Ltd (Auckland). We suggest that careful consideration is made before choosing a supplier as different suppliers may have different levels of engagement and expertise to address individual lake management cases. Suitable equipment would be required to remove a high percentage of the introduced fish stocks. Additionally, sufficient equipment to carry out the monitoring regime would also be required, e.g. sediment gravity corer, nutrient analyser, CTD, pH meter, etc.

10.4 Monitoring

Before sectioning the lake, the lake bed should be cored to establish the amount and species of macrophyte seed banks present, and to determine if charophyte planting would be necessary in the presence of depauperate seed banks. Following the successful deployment of a barrier within the lake(s), monitoring of the treatment and control areas would be required weekly for at least a month to establish that the selected areas are similar in nutrient concentrations, temperature and oxygen profiles, pH and conductivity measurements etc. It is difficult to monitor the success of any restoration activity if a nutrient budget has not been established prior to applying any nutrient reduction measure. Therefore, we recommend that the data collected is used to establish a nutrient budget for the target lake, prior to and throughout the experiment. Sediment traps could be deployed to measure the amount of sedimentation and resuspension in the control and treatment areas. At each stage of the experiment, and after each phase of the treatment, monitoring of chlorophyll *a*, Secchi depth, profiles of nutrients (NH_4-N, DRP, NO_3-N, NO_2-N, TP, TN), dissolved oxygen, photosynthetically active radiation, pH, specific conductance, florescence, cyanobacteria and phytoplankton cell counts, rainfall, and percentage sediment surface with macrophyte cover should take place. Additionally, any inlet drains should be monitored for nutrients so that representative external loads are obtained. Monitoring should take place weekly if possible to ensure any sudden changes in nutrients or sediment load or reinvasion of fish species are documented. It would be recommended that the data collected should be integrated with a modelling programme in order to predict how the treatment lake and future lake restoration measures would affect physical and chemical lake processes.

10.5 Treatments

Treatment of the chemical application area would consist firstly of the removal of fish, targeting rudd and other non-native fish, where possible. These fish would need to be killed, and certainly not released into the control area of the lake. The number and species of fish removed should be recorded, and an estimate of the percentage of each made. Secondly, the flocculant should be added in a dose determined by laboratory studies as the most effective dose that has been proven to be non-toxic. Thirdly, fish exclosures should be established for the treatment area and macrophytes either transplanted or allowed to germinate from natural seed banks within these exclosures. The time between flocculant addition and attempting to re-establish macrophytes will depend on the results of laboratory trials on the effects of the flocculant on macrophyte establishment and on the depth of photosynthetically active radiation. The field trial should be run over a relatively long period of time (e.g. one year) to determine if the treatment regime will produce a change in the stable state of the lake treatment area and the nutrient budget of the lake.

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12.0 Appendices

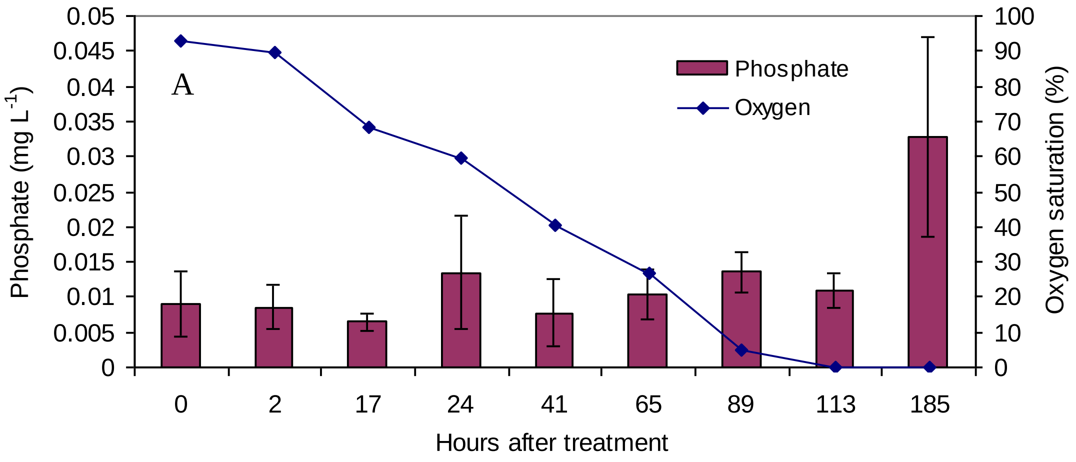
Appendix One

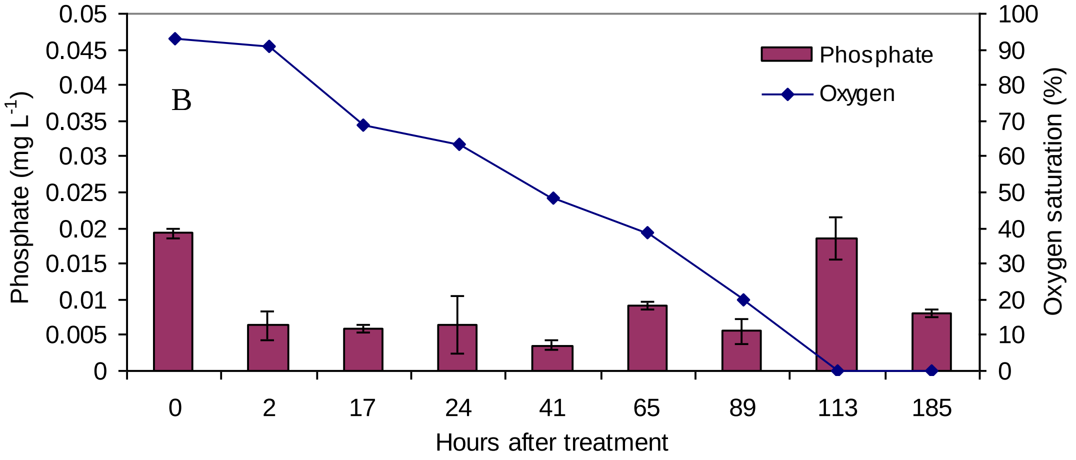
Table 7. ANZECC Recommended sediment quality guidelines for heavy metals (ANZECC, 2002). Adapted from Long *et al*. (1995).

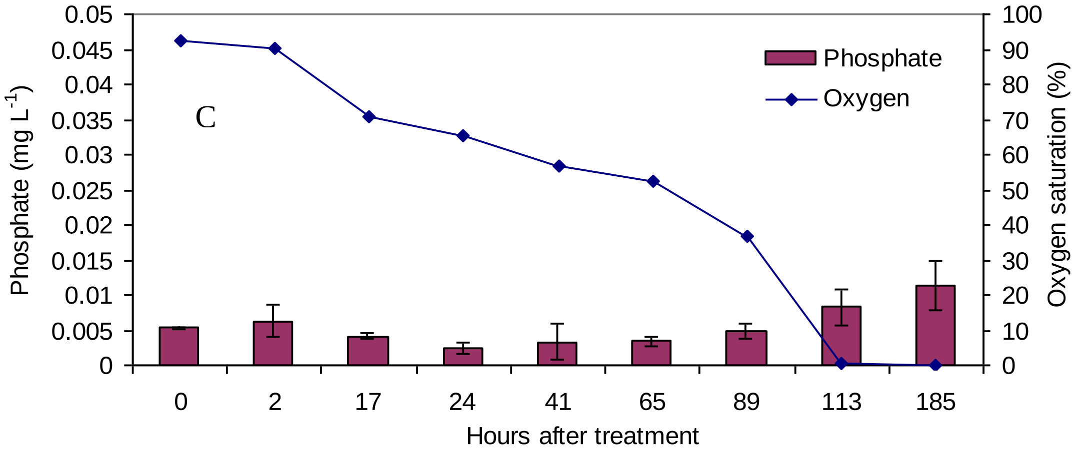
METALS (mg/kg dry wt)	***Contaminant ISQG-Low (Trigger value)***	***ISQG-High***
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Zinc	200	410
METALLOIDS (mg/kg dry wt)		
Arsenic	20	70

Appendix Two

Incubation experiment data.







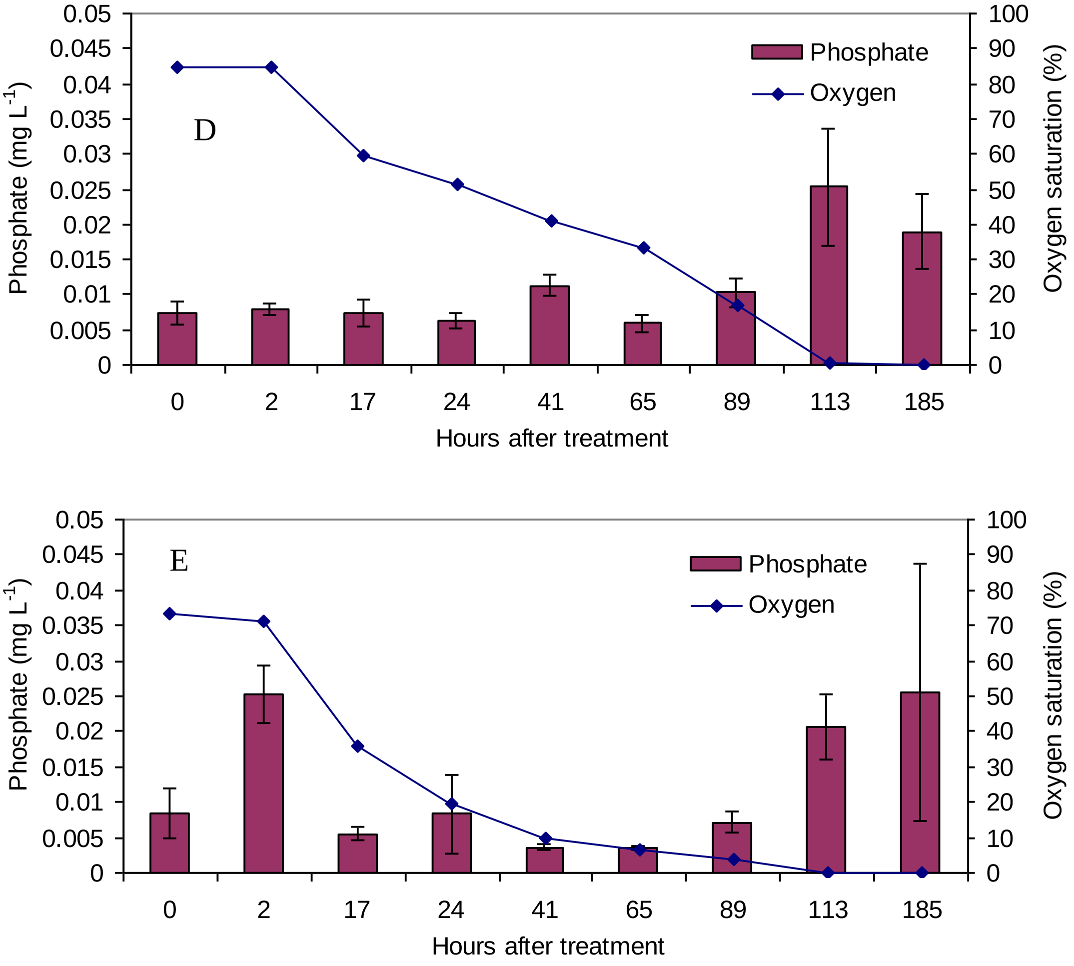


Figure 19. Oxygen concentration and phosphate concentrations for the five treatments: A) control, B) zeolite, C) Phoslock, D) iron slag, E) carbon.

Table 8. Dissolved nutrient concentrations for the four treatments (n = 3) of the core incubation experiment. Values in italics were considered to be outliers and were excluded from the data analysis.

	Core No.	Treatment	Ammonium (NH4+-N)	Phosphate (PO4-P)	Nitrate (NO3-N)	Nitrite (NO2)	Oxygen (%)
Pre-treatment	1	Control	0.12818	0.01838	0.490489	0.004538	92.5
	2	Control	0.080784	0.004357	0.497054	0.01562	93
	3	Control	0.022188	0.00423	0.517233	0.014792	93.8
	4	Zeolite	0.059878	0.018376	0.468076	0.000918	94.3
	5	Zeolite	0.056623	0.020623	0.511015	0.018989	91.8
	6	Zeolite	0.039381	0.01896	0.511054	0.014482	93.3
	7	Phoslock	0.061465	0.005449	0.510714	0.00802	90.7
	8	Phoslock	0.025692	0.005512	0.485847	0.014831	94.2
	9	Phoslock	0.037966	0.004948	0.436072	0.014218	92.7
	10	Iron slag	0.07736	0.010486	0.345547	0.00357	90.4
	11	Iron slag	0.039987	0.005016	0.499854	0.008481	93.5
	12	Iron slag	0.411787	0.006731	0.344379	0.013071	70.4
	13	Carbon	0.0396	0.015608	0.406904	0.00136	93.7
	14	Carbon	0.518766	0.004589	0.275285	0.011631	47.3
	15	Carbon	0.190437	0.005091	0.421334	0.01556	78.5
2 h following treatment	1	Control	0.161363	0.014946	0.545088	-0.001295	88.1
	2	Control	0.127308	0.004728	0.554734	0.014449	88.9
	3	Control	0.027498	0.006037	0.576413	0.018035	91.8
	4	Zeolite	0.076855	0.010137	0.576914	-0.001262	92.7
	5	Zeolite	0.044723	0.003517	0.591412	0.011617	89.1
	6	Zeolite	0.029803	0.005299	0.572159	0.014308	90.7
	7	Phoslock	0.354643	0.01067	0.54577	-0.002808	90.7
	8	Phoslock	0.374392	0.003075	0.566619	0.007744	91.4
	9	Phoslock	0.411592	0.005241	0.557305	-0.00149	89.1
	10	Iron slag	0.111813	0.009421	0.538501	0.002493	87.9
	11	Iron slag	0.058258	0.007994	0.551247	0.015907	88.7
	12	Iron slag	0.35304	0.006336	0.272747	0.005472	77.8
	13	Carbon	0.04566	0.017089	0.38333	0.002654	88
	14	Carbon	0.57348	0.028437	0.308974	0.0132	50.5
	15	Carbon	0.245648	0.030228	0.487816	0.016681	75.4
17 h	1	Control	0.293093	0.008561	0.158999	0.003946	64
	2	Control	0.399901	0.00447	0.407523	0.012863	69.6
	3	Control	0.045273	0.006239	0.121486	0.003453	71.8
	4	Zeolite	0.096327	0.007254	0.208105	0.001644	74.1
	5	Zeolite	0.089755	0.005214	0.513152	0.015238	67.1
	6	Zeolite	0.075051	0.005281	0.491603	0.010363	65
	7	Phoslock	0.324622	0.004756	0.230848	-0.003332	73.1
	8	Phoslock	0.327609	0.004364	0.444314	0.007557	72.3
	9	Phoslock	0.330662	0.003347	0.235489	-0.000653	67.5
	10	Iron slag	0.222854	0.010886	0.471007	0.004018	67.3
	11	Iron slag	0.263439	0.006476	0.437561	0.014549	53.7
	12	Iron slag	0.620775	0.004782	0.288169	0.011168	58.1
	13	Carbon	0.01711	0.007212	0.247803	0.003349	54.3
	14	Carbon	0.585939	0.004215	0.151406	0.016876	16.9

	15	Carbon	0.317305	0.005058	0.271551	0.014413	36
24 h	1	Control	0.545128	0.029315	0.28437	*-0.001663*	51.4
	2	Control	0.49064	0.007991	0.348016	0.007905	59.4
	3	Control	0.073587	0.003179	0.237277	0.009519	67.4
	4	Zeolite	0.100338	0.014333	0.171977	0.001056	70.8
	5	Zeolite	0.11375	0.002609	0.409505	0.009156	56.2
	6	Zeolite	0.101166	0.00229	0.353003	0.010932	63
	7	Phoslock	0.493359	0.004095	0.434224	*-0.000056*	74.4
	8	Phoslock	0.236377	0.001927	0.184523	0.000219	63.1
	9	Phoslock	0.501625	0.0015	0.44073	0.003358	58.7
	10	Iron slag	0.25212	0.007753	0.457995	0.002329	67.8
	11	Iron slag	0.376182	0.007026	0.364606	0.000353	46.7
	12	Iron slag	0.720075	0.004148	0.257388	0.009672	39.5
	13	Carbon	0.817565	0.019442	0.177673	0.0003	36.5
	14	Carbon	0.433033	0.002569	0.078362	*0.783647*	22.8
	15	Carbon	0.15622	0.002983	0.062597	*0.854334*	0
41 h	1	Control	0.820662	0.017193	0.178323	*0.8074*	24.4
	2	Control	0.710466	0.004459	0.236495	0.012736	43.1
	3	Control	0.152639	0.001601	0.519078	0.022496	54.3
	4	Zeolite	0.179768	0.003477	0.185568	-0.001964	59.5
	5	Zeolite	0.147677	0.002608	0.148864	0.004769	39.2
	6	Zeolite	0.209339	0.00467	0.432728	0.015999	47.1
	7	Phoslock	0.651808	-0.001139	0.369392	0.000365	67.9
	8	Phoslock	0.346807	0.007887	0.293165	-0.000653	56.7
	9	Phoslock	0.635891	0.003225	0.345866	0.003841	45.8
	10	Iron slag	0.208575	0.009532	0.216587	0.002118	66.4
	11	Iron slag	0.518139	0.014442	0.200474	0.013617	33.7
	12	Iron slag	0.533895	0.009981	0.05263	0.006949	23.6
	13	Carbon	0.030509	0.004591	0.089403	0.004962	26.4
	14	Carbon	0.273028	0.003248	0.007341	0.00698	3.2
	15	Carbon	0.150849	0.00311	0.005518	0.005736	0
65 h	1	Control	0.68363	0.006374	0.030454	0.000713	12.1
	2	Control	0.92781	0.017573	0.111878	0.012896	26.1
	3	Control	0.292308	0.007171	0.577367	0.038291	41.4
	4	Zeolite	0.36066	0.00973	0.219207	0.000958	52.1
	5	Zeolite	0.333345	0.008199	0.15645	0.007507	26.7
	6	Zeolite	0.2488	0.0097	0.126335	0.010679	36.7
	7	Phoslock	0.753621	0.004031	0.263168	-0.000171	61.9
	8	Phoslock	0.50873	0.00192	0.422002	0.00291	52.2
	9	Phoslock	0.6086	0.004298	0.114984	0.001426	43.4
	10	Iron slag	0.313987	0.004095	0.250759	0.003474	74.1
	11	Iron slag	0.80841	0.0055	0.089167	0.010769	14.6
	12	Iron slag	0.723905	0.008088	0.026049	0.008299	11.3
	13	Carbon	0.083657	0.00381	0.018215	0.007005	19.2
	14	Carbon	0.5350352	0.00352087	0.0602396	0.00761453	0
	15	Carbon	0.54606496	0.00308155	0.0405316	0.00803798	0.3
89 h	1	Control	1.298298	0.017797	0.017294	*0.821297*	0.1
	2	Control	1.073165	0.008204	0.021489	0.007429	4.9
	3	Control	0.419566	0.014623	0.402593	0.033041	10.4
	4	Zeolite	0.495958	0.025287	0.30243	0.00518	38.7
	5	Zeolite	0.551609	0.007345	0.132788	0.014794	5.9
	6	Zeolite	0.454316	0.003793	0.160941	0.010686	15.1

	7	Phoslock	1.048118	0.006942	0.202722	0.002071	49.2
	8	Phoslock	0.51616	0.002823	0.32213	0.003455	30.7
	9	Phoslock	0.988606	0.004763	0.155214	0.00205	30.9
	10	Iron slag	0.588968	0.006476	0.416743	0.055713	50.5
	11	Iron slag	0.735199	0.01327	0.014682	0.007973	0
	12	Iron slag	1.191494	0.011008	0.006011	0.006648	0
	13	Carbon	0.298324	0.008153	0.006676	0.00506	10.4
	14	Carbon	0.784707	0.008998	0.006061	0.016454	0.2
	15	Carbon	0.7938	0.004418	0.008923	0.005607	0.2
137 h	1	Control	1.187731	0.006249	0.001698	0.002743	0
	2	Control	1.213969	0.012151	0.003275	*0.443542*	0
	3	Control	0.870131	0.014238	0.003544	0.004854	0
	4	Zeolite	0.860267	0.021632	0.034136	0.002241	0
	5	Zeolite	0.538394	*-0.014094*	0.00271	0.002095	0
	6	Zeolite	1.171741	0.015704	0.008555	0.007192	0
	7	Phoslock	1.372323	0.013493	0.034287	0.000654	1.4
	8	Phoslock	0.725103	0.005078	0.058173	0.005625	0
	9	Phoslock	1.535406	0.006297	0.006338	0.004611	0
	10	Iron slag	0.795115	0.041841	0.189801	0.001564	1.7
	11	Iron slag	1.115264	0.015152	0.010726	0.004065	0
	12	Iron slag	1.968942	0.018886	0.005322	0.011367	0
	13	Carbon	0.7441	0.016473	0.011553	0.005558	0
	14	Carbon	1.045374	0.015412	0.005163	0.007471	0
	15	Carbon	1.637226	0.029841	0.007464	0.005498	0
185 h	1	Control	2.420761	0.060039	0.01979	0.019179	0
	2	Control	2.328755	0.025881	0.004087	0.015628	0
	3	Control	1.435473	0.012283	0.002529	0.008151	0
	4	Zeolite	1.492854	0.008522	0.01376	0.003619	0.4
	5	Zeolite	1.374409	0.007041	0.005961	0.004235	0
	6	Zeolite	1.830953	0.008663	0.006277	0.006121	0
	7	Phoslock	2.067888	0.012229	0.018111	0.001759	0
	8	Phoslock	1.292277	0.004922	0.009269	-0.000804	0
	9	Phoslock	1.93073	0.016728	0.019683	0.002865	0
	10	Iron slag	1.131215	0.013385	0.026554	0.005522	0
	11	Iron slag	2.373268	0.013775	0.007721	0.008719	0
	12	Iron slag	1.427009	0.029782	0.005812	0.021142	0
	13	Carbon	1.699246	0.002384	0.012529	0.003353	0
	14	Carbon	2.180807	0.012633	0.006844	0.008144	0
	15	Carbon	3.017968	0.061444	0.004509	0.009439	0

Table 9. Total phosphorus and total nitrogen for each of the five treatments at the completion of the core incubation experiment.

Core No.	Treatment	Total Phosphorus	Total Nitrogen
1	Control	0.215553	1.083688
2	Control	0.019046	0.907417
3	Control	0.070318	0.975984
4	Zeolite	0.014583	0.956321
5	Zeolite	0.023967	1.041554
6	Zeolite	0.020059	0.971627
7	Phoslock	0.040475	1.056481
8	Phoslock	0.008676	0.829023
9	Phoslock	0.087033	1.069407
10	Iron slag	0.049281	0.832069
11	Iron slag	0.104309	1.111613
12	Iron slag	0.051982	1.105566
13	Carbon	0.021073	1.051358
14	Carbon	0.039994	1.086488
15	Carbon	0.054607	1.125881

Appendix Three

Table 10. Composition of electric arc furnace steel-making slag (Bourke *et al*. 2005).

Constituent	*Chemical Formula*	*Percentage composition*
Calcium Oxide	CaO	24.8
Silicon Dioxide	SiO_2	9.95
Iron Oxide	Fe_2O_3	29.0
Aluminium Oxide	Al_2O_3	6.29
Magnesium Oxide	MgO	7.39
Manganese Oxide	MnO	4.59
Titanium Oxide	TiO_2	1.16
Potassium Oxide	K_2O	0.007
Vanadium Oxide	V_2O_5	0.32
Sulphur	S	0.073

Appendix Four

Table 11. Summary of chemical and physical statistics for the four target lakes used in this study. Physical statistics were obtained from the most recent literature available for each of the lakes and chemical statistics were measured in this study.

	Ngaroto	**Kainui**	**Rotomanuka**	**Cameron**
Lake area (ha)	108	24.9	17.1	3.4
Catchment area (ha)	1738	107.5	467	26.6
Max depth (m)	4	6.7	8.7	1.5
Average depth (m)	<2	4	5	1.5
pH	6.75	6.66	6.7	5.08
Alkalinity (μeq L^{-1})	246	300	525	94.34
mg $CaCO_3$ L^{-1}	12.3	15	26.25	4.72
TP	0.0724	0.0877	0.0177	0.5120
TN	0.7258	0.9496	0.5326	0.8649
Ratio TP: TN	1: 10	1: 11	1: 30	1: 2
DRP (Phosphate mg/L)	0.0171	0.0113	0.0033	0.3892
Ammonium (NH^+_4-N)	-0.0137	0.0231	-0.0153	-0.0076
Nitrate (mg/L NO_3-N	0.4593	0.2760	0.1330	0.0181
Nitrite (mg/L NO_2-N)	0.0100	0.0099	0.0032	0.0091

Appendix Five

Table 12. Raw data of sediment settling times for three different suspended sediment concentrations in the settling column experiment.

Column One Time (h)	90 g/L Depth of sed (mm)	Column Two Time (h)	75 g/L Depth of sed (mm)	Column Three Time (h)	70 g/L Depth of sed (mm)
0	700	0	704	0	700
0.5	700	0.5	703.5	0.5	698
1	700	2	703.25	1	697.8
2	700	3	703.25	2	697.4
3	699	4	703	3	694.2
4	698	5	702	4	693
5	697.5	7	701.5	5	692
21	689	23	682	21	666
23	688.5	25	680	23	662
26	688	27	677	26	658
45	682	31	672.25	45	599
48	681	47	658	48	590
52	677	49	656	52	578
117	662	51	654	117	514
122	661	55.17	651	122	512
141	658	56	650	141	508
145	657	71	641	145	507
165	655	74.33	636	165	507
167	654.5	76	635	167	506
170	654	78.33	632	170	506
189	654	95	620.5	189	505
285	652	97	618		
		99	616		
		101	614.5		

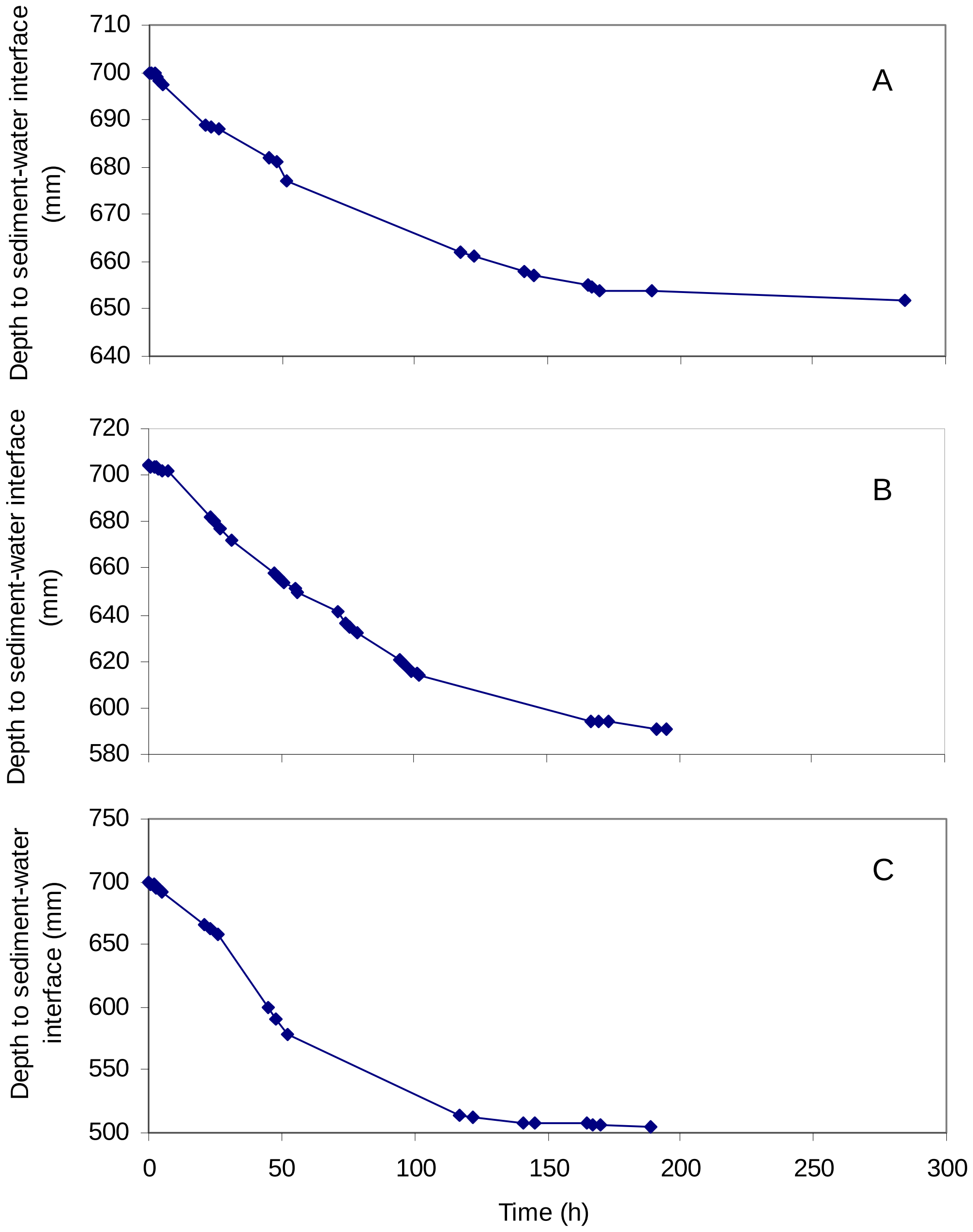


Figure 20. Settling rate for three different suspended solids concentrations of Lake Cameron sediment, A) 90 mg L^{-1}, B) 75 mg L^{-1}, C) 70 mg L^{-1}.

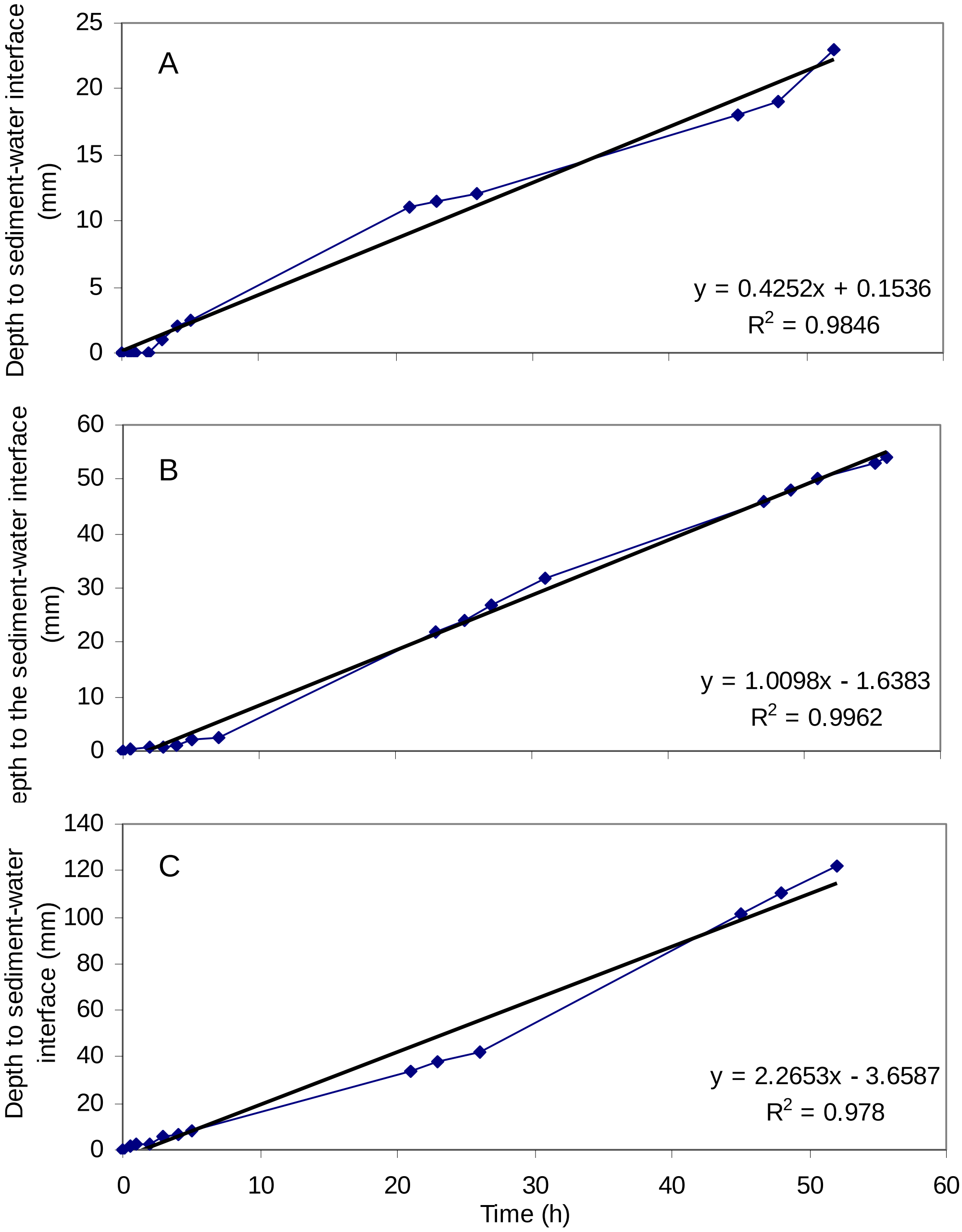


Figure 21. Settling velocities of Lake Cameron sediment over the first 50 hours of settling time, to calculate maximum settling velocity from the slope of the line. A) 90 mg L^{-1}, B) 75 mg L^{-1}, C) 70 mg L^{-1}.

Appendix Six

Table 13. Raw data for the sediment traps deployed in each lake to determine the weight of sediment that enters each lake each year. S1 = Site 1, R1 = Replicate 1.

Lake	**Rep**	**g sed./ tube**	**g m^{-2}**	**g m^{-2} day^{-1}**	**kg m^{-2} year^{-1}**	**g lake^{-1} day^{-1}**	**kg lake^{-1} year^{-1}**
Kainui	R1	0.2554	0.7695	0.0592	0.0216	17404	6352
	R2	0.2565	0.7729	0.0595	0.0217	17480	6380
	R3	0.5230	1.5762	0.1212	0.0443	35647	13011
	R4	0.4446	1.3400	0.1031	0.0376	30304	11061
Rotomanuka	R1	0.3326	1.0024	0.0771	0.0281	13186	4813
	R2	0.3114	0.9383	0.0722	0.0263	12342	4505
	R3	0.2274	0.6852	0.0527	0.0192	9013	3290
	R4	0.1904	0.5738	0.0441	0.0161	7547	2755
Ngaroto	S1R1	2.6163	7.8845	0.5256	0.1919	567683	207204
	S1R2	1.4549	4.3844	0.2923	0.1067	315676	115222
	S1R3	2.5054	7.5503	0.5034	0.1837	543624	198423
	S1R4	2.2736	6.8517	0.4568	0.1667	493320	180062
	S2R1	3.8203	11.5128	0.7675	0.2801	828924	302557
	S2R2	1.4213	4.2831	0.2855	0.1042	308386	112561
	S2R3	1.5602	4.7017	0.3134	0.1144	338520	123560
	S2R4	2.7418	8.2625	0.5508	0.2011	594900	217139
Cameron	R1	0.4962	1.4952	0.1068	0.0390	3631	1325
	R2	0.5499	1.6572	0.1184	0.0432	4025	1469
	R3	0.5578	1.6809	0.1201	0.0438	4082	1490
	R4	0.2789	0.8404	0.0600	0.0219	2041	745

Appendix Seven

Table 14. Data obtained from sediment cores taken from Lakes Cameron, Kainui. Data includes percentage water content and inorganics, porewater dissolved nutrients and total phosphorous (kg $^{-1}$ of dry sediment) for each 1 cm section of sediment removed from the indicated depths. S1 = Site 1, R1 = Replicate 1. Missing results indicated with a * are a result of no porewaters separating during the centrifuging process, due to the low sediment water concentrations at certain sediment depths. Values in italics were designated as outliers and were excluded from the data analysis.

Cameron	Rep.	Water content (%)	Inorganics (%)	Ammonium (NH4-N)	Phosphate (PO4-P)	Nitrate (NO3-N)	Nitrite (NO2-N)	TP
S1R1	a	94.98	94.22	85.2837	53.4915	5.9538	0.0545	2542.459
S1R1	b	95.04	91.43	94.3390	44.2044	10.2307	-0.8771	
S1R1	a	91.52	58.76	277.0618	27.1617	2.2892	0.3359	1809.92
S1R1	b	91.40	50.50	259.8581	33.4359	3.5550	0.9943	
S1R1	a	90.83	58.41	317.7213	68.0468	1.5457	-1.3197	1199.848
S1R1	b	90.92	*2.75*	324.1061	40.4631	2.9296	0.4017	
S1R1	a	90.90	47.16	*124720822.120*	46.8519	*99.7117*	*12646808.7101*	384.9014
S1R1	b	90.87	33.60	41.8782	16.6911	4.6799	0.2905	
S1R2	a	95.35	66.98	70.6730	39.8071	4.9321	-1.5753	2700.077
S1R2	b	95.42	48.26	66.6575	34.9699	5.4112	0.7305	
S1R2	a	92.04	61.42	22.8334	81.9604	2.8412	-1.3732	1837.753
S1R2	b	92.07	50.56	217.5041	105.9476	2.2869	0.1771	
S1R2	a	89.87	53.72	234.8129	41.1677	4.9115	-0.4748	1214.782
S1R2	b	89.79	43.12	281.2270	55.0376	2.8918	-0.0225	
S1R2	a	89.98	91.08	408.1233	27.4055	2.3112	0.0390	518.8846
S1R2	b	89.89	80.51	355.1446	44.4769	3.2861	-0.5125	

Kainui	**Depth**	**Rep.**	**Water content (%)**	**Inorganics (%)**	**Ammonium (NH4-N)**	**Phosphate (PO4-P)**	**Nitrate (NO3-N)**	**Nitrite (NO2-N)**	**TP**
S1R1	0	a	94.62	57.85	317.36698	4.05590	3.91588	-1.56021	737.862
S1R1	0	b	94.78	57.17	439.32276	4.11509	2.36375	-0.01741	
S1R1	10	a	91.26	59.84	*2537.13881*	*1432.88844*	*875.07442*	*476.31939*	728.299
S1R1	10	b	91.15	59.89	703.67220	6.33955	3.35698	-0.54994	
S1R1	20	a	90.19	58.53	190.43816	10.01586	5.64808	-2.72886	761.478
S1R1	20	b	90.31	59.03	*	*	*	*	
S1R1	28	a	89.85	56.40	810.42678	9.30742	3.32554	-0.67685	842.673
S1R1	28	b	89.55	55.16	254.03197	11.21785	6.41382	1.64844	
S1R2	0	a	94.19	57.73	258.42501	4.47390	4.29326	0.45841	797.963
S1R2	0	b	94.21	57.85	*-9.64457*	4.58208	6.01447	-0.15240	
S1R2	10	a	90.73	58.60	843.69750	10.87822	5.52756	-0.74199	775.814
S1R2	10	b	90.65	58.65	865.95457	9.40189	3.65661	-0.50172	
S1R2	20	a	91.38	56.47	755.93787	13.24086	7.57270	-0.27092	792.272
S1R2	20	b	91.39	56.08	845.28980	11.60528	3.98973	-0.89435	
S1R2	24.5	a	90.11	57.00	729.77006	13.72575	7.90745	0.55375	840.583
S1R2	24.5	b	89.62	56.37	359.10618	18.19892	6.87653	-0.65465	
S2R1	0	a	94.88	55.60	229.76515	1.08049	3.82338	0.38759	692.221
S2R1	0	b	94.71	56.02	254.93543	1.87087	1.96202	0.29484	
S2R1	10	a	90.59	57.60	624.59117	9.78501	5.83066	0.71300	707.642
S2R1	10	b	90.64	57.54	96.31681	9.88210	7.16167	-0.94158	
S2R1	20	a	89.36	54.87	652.70918	9.91286	6.53943	-0.44379	724.560
S2R1	20	b	89.72	54.58	630.32636	12.21245	4.18713	0.18524	
S2R1	30	a	85.83	52.01	*	*	*	*	639.608
S2R1	30	b	85.72	52.35	*	*	*	*	
S2R1	32	a	82.17	63.65	*	*	*	*	243.160
S2R1	32	b	81.82	64.28	*	*	*	*	
S2R2	0	a	95.23	56.42	0.637861	0.005775	0.004737	0.004071	0.271713
S2R2	0	b	94.92	55.89	0.422876	0.015531	0.006647	0.00127	

S2R2	10	a	90.54	57.63	0.701382	0.015525	0.006552	0.000695	0.279181
S2R2	10	b	91.05	58.08	0.82642	0.016555	0.009014	0.002302	
S2R2	20	a	91.01	52.35	0.849084	0.012912	0.008414	-0.00017	0.286196
S2R2	20	b	90.94	53.88	0.949967	0.01178	0.004882	-0.00038	
S2R2	28.5	a	83.17	65.94	*	*	*	*	0.194817
S2R2	28.5	b	84.15	62.86	*	*	*	*	

Ngaroto	Depth	Rep.	Water content (%)	Inorganics (%)	Ammonium (NH4-N)	Phosphate (PO4-P)	Nitrate (NO3-N)	Nitrite (NO2-N)	TP
S1R1	0	a	90.77	82.20	192.77260	4.10883	6.01104	0.36075	497.0914
S1R1	0	b	90.84	81.04	189.00919	2.10400	1.37829	-1.70532	
S1R1	10	a	83.42	85.49	712.11830	3.77015	3.88365	-0.44250	415.0822
S1R1	10	b	83.77	84.07	793.40381	3.62344	1.20251	1.27082	
S1R1	20	a	83.56	79.59	1047.06411	2.39708	3.59679	-1.12948	396.6378
S1R1	20	b	84.11	83.54	1241.82755	2.72897	1.78845	1.30073	
S1R1	28	a	84.67	80.94	1082.10323	4.53220	6.40473	0.59536	370.5
S1R1	28	b	84.71	83.15	993.50955	1.91705	3.24384	-0.13747	
S1R2	0	a	90.81	96.95	307.02297	4.33864	5.52758	0.72154	496.1658
S1R2	0	b	90.87	92.17	339.83032	6.14539	6.19214	-2.22490	
S1R2	10	a	83.08	85.09	794.07385	4.63428	6.43211	0.82621	389.2226
S1R2	10	b	82.87	84.09	1266.07344	4.52236	2.03129	-0.28100	
S1R2	20	a	83.03	74.20	965.19670	2.88973	3.72146	0.15118	409.7106
S1R2	20	b	83.99	83.80	1302.13524	5.54804	4.10130	-1.01866	
S1R2	26	a	84.48	93.86	1175.74883	2.42806	2.67220	0.25411	390.6318
S1R2	26	b	84.17	*	1121.99715	2.73465	0.91411	-0.36890	
S2R1	0	a	88.74	97.25	236.09731	27.31824	8.55806	-1.64689	461.6794
S2R1	0	b	88.57	75.91	190.60705	1.99536	1.34719	-0.94826	

S2R1	10	a	82.47	83.35	708.23594	2.03332	3.91606	-1.05000	350.2876
S2R1	10	b	82.66	84.21	1010.41913	3.23464	2.25302	-0.26173	
S2R1	20	a	84.29	82.73	648.85378	2.63754	2.20830	-0.04866	350.7764
S2R1	20	b	84.17	83.07	986.88042	5.12560	1.50666	1.08785	
S2R1	30	a	83.94	85.95	1153.19521	5.79060	3.02996	-1.34658	342.953
S2R1	30	b	84.26	90.29	706.99167	3.54666	4.22868	-0.61091	
S2R2	0	a	88.22	86.42	749.69555	10.63302	5.70724	-1.56838	354.5828
S2R2	0	b	87.89	82.49	604.36442	9.83530	5.48122	-1.36370	
S2R2	10	a	85.02	83.99	551.35618	12.23395	5.58715	0.87411	350.5008
S2R2	10	b	85.01	82.93	572.33852	2.77640	3.51533	-1.39845	
S2R2	20	a	83.26	86.74	691.87342	3.35159	0.89229	-0.89708	365.963
S2R2	20	b	83.68	85.03	794.35510	1.73807	2.17339	0.75373	
S2R2	26	a	80.10	86.76	817.79923	5.86549	15.30105	1.34187	377.8736
S2R2	26	b	80.79	92.03	713.81682	3.52183	4.10471	0.07832	

Rotomanuka	**Depth**	**Rep.**	**Water content (%)**	**Inorganics (%)**	**Ammonium (NH4-N)**	**Phosphate (PO4-P)**	**Nitrate (NO3-N)**	**Nitrite (NO2-N)**	**TP**
S1R1	40	a	89.73	67.32	*1917.40507*	*1680.14888*	*949.15621*	*532.51661*	850.873
S1R1	40	b	89.94	67.77	391.29535	2.47722	6.31474	-1.33746	
S1R1	30	a	89.55	69.98	300.38526	4.26200	11.40222	0.32659	468.928
S1R1	30	b	89.80	69.63	243.36351	3.26574	14.87237	1.42998	
S1R1	20	a	91.80	69.98	170.81970	4.97289	11.05454	-4.33469	473.301
S1R1	20	b	91.79	68.42	396.38763	3.22919	4.41572	0.29014	
S1R1	10	a	94.47	66.25	408.02571	5.83192	6.45106	-1.48662	753.501
S1R1	10	b	94.18	67.15	363.29101	3.02071	5.14042	-3.78260	
S1R1	0	a	94.99	66.64	118.08855	2.48708	1.68364	-0.76568	726.942
S1R1	0	b	94.92	66.85	133.82448	1.22744	1.84733	-0.96574	
S1R2	0	a	95.97	67.19	132.31855	0.81371	2.26299	0.85075	668.647
S1R2	0	b	96.00	67.42	132.36722	0.57751	1.86569	1.16544	
S1R2	10	a	93.37	66.27	439.70176	2.49462	3.08432	0.08331	773.071

S1R2	10	b	93.30	67.99	16.81318	2.37173	2.24803	1.28998	
S1R2	20	a	91.28	69.63	75.64146	3.25360	5.59661	-2.14296	448.734
S1R2	20	b	91.39	70.78	375.78036	3.53526	6.95577	1.09821	
S1R2	30	a	89.74	70.46	323.66156	4.62812	7.94887	-0.64229	435.469
S1R2	30	b	89.98	69.99	230.17710	3.85238	5.38985	-2.08652	
S1R2	39	a	89.31	70.77	299.20968	3.72863	4.66389	0.25394	769.049
S1R2	39	b	88.98	70.18	221.12029	5.86898	6.18484	0.54556	