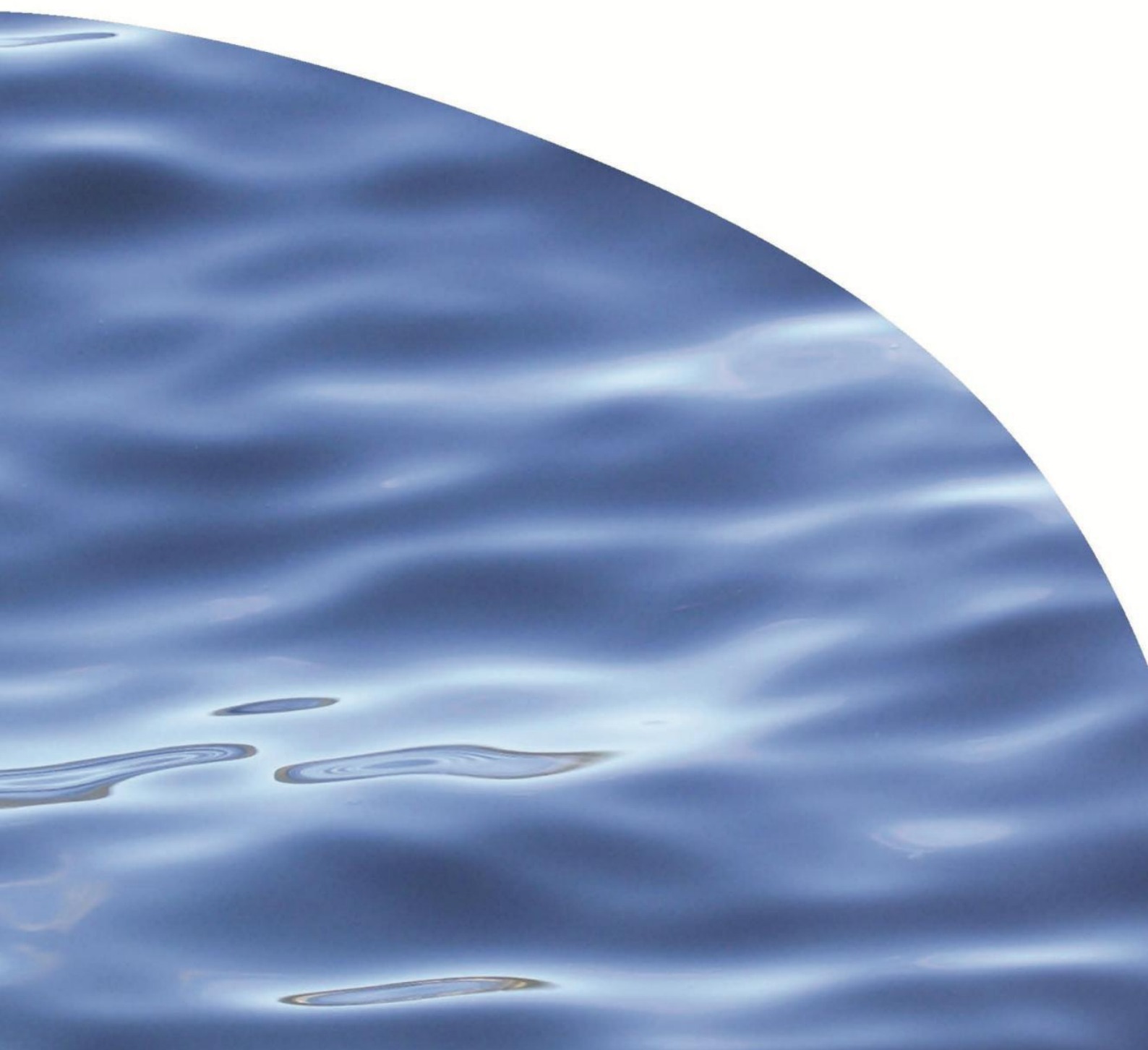


REPORT NO. 3629

**A REVIEW OF OXYGEN NANOBUBBLE
TECHNOLOGY FOR THE RESTORATION OF
DEGRADED LAKES**



A REVIEW OF OXYGEN NANOBUBBLE TECHNOLOGY FOR THE RESTORATION OF DEGRADED LAKES

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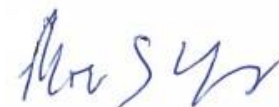
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EXECUTIVE SUMMARY

Nutrient enrichment of lakes because of anthropogenic activities is a significant and increasing issue in New Zealand and around the world. It is resulting in serious declines in ecosystem health as well as impacting on cultural, recreational, economic and aesthetic values. Efforts to stop or reverse these trends generally focus on slowing or stopping the flow of reducing nutrient loads from catchments to lakes. However even once nutrient inflows are reduced, in most lakes the recovery is slow and may be delayed for long periods of time. This is often due to 'internal' nutrient loads stored in lake sediments. These nutrients are released from bottom sediments into the water column, maintaining poor water quality and fuelling algal blooms for some years or even decades.

Attempts to control internal nutrient loads have included using 'geoengineering' products that are added to lakes to keep nutrients bound to sediments or to physically block their release. These have had mixed success and concerns remain about efficacy, toxicity and whether it is culturally acceptable to add 'chemicals' to lakes. For these reasons, the search continues for environmentally benign methods of reducing internal nutrient cycling. Recent research has focused on using modified local soil (MLS) products which aim to flocculate (cause clumping and sinking) and then physically cap lakebed sediments (i.e., 'floc and lock'). Local soils or 'inert' minerals such as zeolites have been mixed with natural flocculants such as chitosan and have shown promising results such as the restoration of aquatic macrophytes. However, such treatments do not deal with sediment hypoxia/anoxia which may result from decomposing organic material on and within the sediment.

A more recent focus of research has been the use of oxygen nanobubble technology to remediate low oxygen conditions at the sediment/water interface. Oxygen nanobubbles (NB) are tiny bubbles (< 1000 nm) formed at the interface of solid surfaces and aqueous solutions. As well as their use in biomedical and wastewater applications, NB have been touted for lake restoration. Their unique properties of low buoyancy, high gas solubility and long-term stability may offer an effective method of reoxygenating anoxic sediment surfaces. Different methods have been developed to force NB to form at the surface of carrier materials, particularly zeolite minerals, which when used in combination with MLS may provide a 'floc, lock and oxygenate' approach to stripping nutrients from the water column, locking them into the bed sediments and oxygenating those sediments to prevent re-release of nutrients. A number of studies have now successfully demonstrated this concept and shown the ability of these MLS/NB materials to significantly reduce nutrient concentrations in water columns, oxygenate sediment surfaces and to convert the sediment from a source to a sink for nutrients.

While NB show great promise, this research is at a very early stage and the studies so far have been restricted to short-term, small-scale core incubations primarily conducted in laboratory settings. Continuing research is needed to demonstrate the applicability of this technology at lake scales. We recommend that ongoing research focusses in the following areas:

- Scalability. Further research should aim to scale up previous laboratory-incubation studies to larger outdoor enclosure and pond/lake sized trials to demonstrate treatment efficacy at environmentally useful scales.
- Longevity. As larger scale trials are conducted these should also aim to understand how effective the MLS/NB treatments are for aiding long-term restoration.
- System specificity. To date, studies have been conducted in a relatively small number of lakes. Future trials should aim to understand issues regarding site-specificity of the MLS/NB system especially with respect to the use of local materials as carriers for flocculants, and on the interplay of varying water and sediment conditions.
- Ecological/process safety. Research is required to further investigate potential detrimental effects of the MLS/NB system including toxicity and benthic smothering issues, as well as effects on biogeochemical processes. These will need to include site/country specific biota.
- Cultural and social acceptance. The effectiveness of the MLS/NB system in New Zealand will only be of use if the technology is embraced by tangata whenua, local communities and wider society. Research will be required to understand issues pertaining to the social acceptance of these restoration methods in local lakes.
- Practicality and cost. Investigations will be required on the practicality and costs involved with procuring/producing the materials required for the MLS/NB system in New Zealand.

1. INTRODUCTION

1.1. Project scope

Ngā Pae o te Māramatanga, New Zealand's Māori Centre of Research Excellence at the University of Auckland has commissioned Cawthron Institute (Cawthron) to address the following questions:

1. How can local tangata whenua be empowered to make the best decisions for sustainable management of eutrophic lakes in Aotearoa?
2. Do cutting-edge oxygen nanobubble technologies have applicability to satisfy tangata whenua demands for sustainable lake management?

As part of this, a desktop review of oxygen nanobubble technology has been undertaken by Cawthron. The original and ongoing impetus for this work is community, and in particular Māori, alarm about the degraded state of water bodies and concerns about existing geo-engineering technologies. This report summarises the state of knowledge in an emerging field of lake restoration research. The report provides context to this summary by introducing the problem of lake eutrophication and briefly summarising existing technologies. It then discusses modified local soil technology, which is closely aligned to the use of oxygen nanobubbles, before reviewing and summarising current research in oxygen nanobubble technology and its use in lake restoration. Finally, gaps in this research are identified and recommendations for future research are made.

1.2. Background: lake eutrophication and internal nutrient loading

Lake ecosystems in New Zealand and around the world have been degraded by anthropogenic eutrophication (Dodds et al. 2009; Verburg et al. 2010; Abell et al. 2019). The increased export of nutrients from lake catchments into the lakes (i.e., external loading) has driven excess primary productivity often in the form of algal blooms with detrimental effects on the amenity, ecological, cultural and recreational values associated with lakes. Much effort has been expended in decreasing such catchment derived nutrient loads via the control of point sources (e.g., sewerage treatment/diversion) and, more problematically, diffuse source nutrients (e.g., erosion control, land use changes, nutrient leaching caps). However, the success of many of these efforts has not often been reflected in improvements in lake water quality or health. This resistance to restoration often results from internal nutrient sources (i.e., internal loading) whereby nutrients are released from lake-bed sediments where they have been sequestered during times of high external loading. Nutrients, in particular phosphorus (P), bound to particulates or taken up by organisms are generally sedimented to the lakebed. As a result, lake sediments commonly constitute a large nutrient reservoir from which bioavailable dissolved nutrients (particularly dissolved reactive phosphorus (DRP) and ammoniacal nitrogen ($\text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$)) may be

released under certain biogeochemical conditions such as low dissolved oxygen concentrations resulting from the degradation of sedimented organic matter. Such internal nutrient loading, particularly of P, is known to drive algal blooms in many lakes (e.g., Schindler 1977; Søndergaard et al. 2003; Burger et al. 2007; Waters & Webster-Brown 2016) and the integrated management of both external and internal loading is now considered critical to most lake restoration efforts (Hickey & Gibbs 2009).

1.3. The control of internal loading; existing technologies.

The control of internal nutrient loading processes has been the focus of considerable research effort and many approaches and technologies exist. These can be divided into physical and geochemical approaches, both of which generally target the control of phosphorus (Hickey & Gibbs 2009).

Physical approaches include the removal of enriched sediment via dredging, maintenance of hypolimnetic oxygen concentrations by direct oxygenation or artificial mixing, inflow diversion and enhancing lake flushing rates to increase the export of nutrients from the lake.

Geochemical approaches (geoengineering) generally involve the addition of materials to the lake which are intended to flocculate suspended particulates to the lakebed and/or act as either passive or active ‘capping’ material which prevent the flux of nutrients from the sediments. Passive capping agents (e.g., sands, clays and gravels) present a physical barrier on the surface of the sediment that reduces diffusion of nutrients across the sediment-water interface. Active capping agents (phosphorus inactivation agents) consist of materials which bind phosphorus via adsorption or precipitation processes and hence immobilise the nutrient and prevent its release to the water column during periods of anoxia. Many geochemical approaches are designed to both flocculate water column nutrients and then cap the sediments upon settlement. This so-called ‘floc and lock’ approach generally utilises active capping agents which may be applied via slurries to lake inflows or direct to surface or bottom waters.

There has been significant research on an array of solid-phase phosphorus inactivation agents and many have been trialled for lake restoration including iron and aluminium salts, industrial slags, allophane, lanthanum-modified bentonite (Phoslock®) and aluminium modified zeolite (Aqual-P®). Excellent reviews of geoengineering and other restoration technologies are available in Cooke et al. (2005), Spears et al. (2013), Douglas et al. (2016), Hamilton and Landman (2018), Hamilton et al. (2018), Hamilton (2019), Abell et al. (2020) and Steinman and Spears (2020). Hickey and Gibbs (2009) outline the general principles of geoengineering approaches and provide a decision support framework based on various New

Zealand case studies. A special edition of the international journal *Hydrobiologia* outlines the use of different flocculants in lake scale trials in Lake Ōkaro in the Bay of Plenty (Hamilton & Landman 2011).

The most commonly used phosphorus inactivation agent is alum (aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) which has been used in the treatment of wastewater for centuries and in lake restoration since at least the 1970s (Cooke et al. 2005). Despite many successful applications of alum and other phosphorus-binding agents, both internationally (Cooke et al. 2005) and in New Zealand (Hamilton & Landman 2011), applications are not straightforward and require rigorous, lake-specific investigations including external and internal nutrient loading dynamics, water chemistry, sediment phosphorus content and fractionation and potential ecotoxicological issues (e.g., Parkyn et al. 2011).

While ecotoxicity studies conducted during applications of alum and other phosphorus-binding agents, have indicated some short-term negative effects, no large-scale mortalities have been reported (Cooke et al. 2005). However, concerns remain over geoengineering approaches due to the variability of reported results (Spears et al. 2014; Abell et al. 2020) as well as toxicity issues related to both aluminium and lanthanum-based products (e.g., Lurling & Tolman 2010; Clearwater et al. 2014). In particular the chronic effects of long-term exposure on lake biota, as well as smothering effects on benthic organisms are poorly studied, while adverse ecological effects have been reported due to high dose rates (Martin & Hickey 2007; Parkyn et al. 2011; Clearwater et al. 2014). Cultural concerns have also been raised over the use of chemical additives to restore lake health (Tempero 2015; Copetti et al. 2016; Zhang et al. 2020). These issues have led to the ongoing search for more environmentally benign geoengineering products for lake restoration.

1.4. Modified local soils

Much of the recent research in the field of geoengineering for lake restoration has occurred in China. A particular focus has been on the use of local soils modified with natural flocculants, such as the natural polymer chitosan and modified starch, to treat harmful algal blooms (e.g., Pan et al. 2006; Pan et al. 2011; Wang et al. 2016; Shi et al. 2016; Yang et al. 2016; Zhang et al. 2018; Jin et al. 2019). The modified local soils (MLS) methods aim to use a 'floc and lock' approach to flocculate algal material from the water column to the sediment surface where it is physically capped by the added soils, which reduces the flux of nutrients and cyanobacterial toxins from decomposing organic matter to the water column (Xu et al. 2012; Li & Pan 2015; Wang et al. 2016). Pond and lake/bay scale projects with chitosan-amended MLS have resulted in marked improvements in water quality. For example, in a 400 m² pond in Lake Tai (Jiangsu Province, China), Secchi depth (water clarity) increased from < 5 cm to 1.5 m within two days, largely due to chlorophyll-a concentrations decreasing from

85 $\mu\text{g}\cdot\text{L}^{-1}$ to 13 $\mu\text{g}\cdot\text{L}^{-1}$. Concentrations remained low for the 20 days of monitoring while the chlorophyll-a concentration in the control pond increased to 350 $\mu\text{g}\cdot\text{L}^{-1}$. Similar trends were apparent in the total phosphorus (TP), total nitrogen (TN), DRP, nitrate- and nitrite-nitrogen, and chemical oxygen demand (Pan et al. 2019). In the Cetian Reservoir (Shanxi Province), a similar pond-scale trial with modified MLS showed comparable results over a longer monitoring period of 70 days and the capping treatments significantly reduced DRP fluxes from the sediment to the water column (Pan et al. 2019).

For shallow lakes, this approach has been developed further by ‘seeding’ the capping soils with macrophyte propagules which then use the decomposing sedimented algae as a nutrient source for enhanced macrophyte restoration (Pan et al. 2011; Zhang et al. 2018; Pan et al. 2019). Such an approach applied in a bay-scale trial in Lake Tai resulted in significant decreases in water column nutrients, chlorophyll-a and cyanotoxins with accompanying increases in water clarity. Within four months of applying the MLS/flocculant mix, macrophytes successfully re-established throughout the bay (Pan et al. 2011). In a pond-scale trial the change from phytoplankton to macrophyte dominance, following a ‘seeded’ MLS treatment, was maintained for at least three years (Pan et al. 2019). These studies indicate that the use of such MLS flocculants can be effective at clearing algae and total nutrients suspended in the water column (Pan et al. 2012); however, the sedimentation of such biomass will increase the oxygen demand within the sediment, potentially exacerbating rather than remediating sediment anoxia. The capping required to prevent the flux of nutrients from these anoxic sediments relies on a thick (centimetre-scale) physical cap and hence, when applied at a lake scale, it requires the addition of very large amounts of MLS. In addition, in shallow lakes such sediment caps may be susceptible to wind disturbance (Abell et al. 2020). Recent research has aimed to remediate sediment anoxia by modifying the MLS approach using oxygen nanobubble treatments.

2. OXYGEN NANOBUBBLES AND THEIR USE IN LAKE RESTORATION

2.1. Oxygen nanobubbles, applications and manufacture

Nanobubbles (NB) are gas-filled bubbles with a diameter of < 1000 nm that can form spontaneously at the interface of solid surfaces and aqueous solutions (Lyu et al. 2019). Until recently they have been considered something of a mystery as their existence cannot be explained by traditional understandings of bubble formation such as Laplace’s law of bubbles (Pan et al. 2016). In the year 2000 the first images and experimental evidence of their existence began to emerge (Wang et al. 2018). Nanobubbles differ from larger bubbles in various ways other than size. Their negative surface charge, low buoyancy, high gas solubility and longevity have seen

NB applied to a range of fields including biomedical research and drug delivery (Lyu et al. 2019), water treatment (Agarwal et al. 2011; Snigdha-Khuntia & Ghosh 2013) and ecological restoration. Ecological applications in lakes include the reduction of methylmercury production (Ji et al. 2020a, 2020b), the decrease in greenhouse gas emissions from lake sediments (Shi et al. 2018; Xiao et al. 2019; Pan et al. 2019) and increasingly, the remediation of degraded lake ecosystems.

One of the main focuses of NB research in lake restoration has been the application of oxygen NB to remediate sediment hypoxia/anoxia, and the associated recycling of nutrients and other redox-sensitive contaminants from the lake sediments to the water column. Lake restoration tools have previously attempted to address this issue through the direct injection of air/oxygen to the sediment or by the oxygenation of the overlying water by hypolimnetic oxygenation or artificial mixing of the water column. Such methods typically have high and ongoing costs (Cooke et al. 2005).

The delivery of oxygen NB to the sediment-water interface is typically by means of loading the NB on the surface of natural mineral carriers such as muscovite (e.g., Yu et al. 2019) and perhaps most commonly, zeolite (e.g., Zhang et al. 2020). Zeolites are microporous aluminosilicate minerals which are commonly used as adsorbents or catalysts. They occur naturally or can be produced on industrial scales. Nanobubbles are loaded onto the mineral surfaces by various methods including the alcohol-water method whereby oxygen is dissolved into ethanol in which the carrier minerals are soaked (e.g., Yu et al. 2019; Wang et al. 2020), and the pressure-swing adsorption method whereby a vacuum is used to remove gas from micropores in the carrier minerals, after which pure oxygen is introduced under pressure (e.g., Zhang et al. 2018; Pan et al. 2019).

2.2. The efficacy of lake nanobubbles for the restoration of eutrophic lakes

Research into the use of oxygen nanobubbles for lake restoration is at an early stage and a limited number of studies are reported in scientific literature. Most studies reviewed for this report have used laboratory-based core-incubations, with only a single *in situ* core incubation study and no pond or lake-scale trials.

The core incubation studies have mostly combined oxygen nanobubbles with an MLS-type approach and they have predominantly been conducted in China where the technology was developed. The combination of MLS and NB provides a 'floc, lock and oxygenate' approach to stripping nutrients from the water column, locking them into the bed sediments and oxygenating those sediments to prevent re-release of nutrients. While there have been some mixed results, this MLS/NB combination has generally resulted in the remediation of anoxia at the sediment water interface (SWI) and reductions in nutrient fluxes to the water column.

Yu et al. (2019) collected six sediment cores from the eutrophic Hongfeng Reservoir in Guizhou Province, China and incubated them over 20 days under anoxic conditions. Three of the cores were dosed with muscovite mineral particles which had been treated with oxygen NB by the alcohol-water method. Dissolved oxygen concentrations around the SWI increased in the treated cores ($6.2\text{--}9\text{ mg}\cdot\text{L}^{-1}$) relative to the untreated cores ($1\text{ mg}\cdot\text{L}^{-1}$); however, the effect was relatively short lived and after three days the oxygen concentrations were $< 2\text{ mg}\cdot\text{L}^{-1}$ in the treated cores. Despite this, TP and DRP concentrations in the water were reduced in the treated cores for the duration of the 20-day incubations, and the release flux of DRP was reduced by 79%. Similar results were obtained by Wang et al. (2020) from four cores also collected from Hongfeng Reservoir and treated with similar methods. Despite bottom waters being artificially maintained at $\text{DO} < 1\text{ mg}\cdot\text{L}^{-1}$, release fluxes from the sediment of TP, TN and $\text{NH}_3\text{-N}$ were decreased by NB treatment by 96, 25 and 51%, respectively, relative to the non-treated cores. Microbial community structure was also studied and the roles of nitrite-oxidising nitrobacteria, denitrifying bacteria and ammonia oxidising bacteria appeared to be strengthened by the NB treatments.

In a more extensive study Zhang et al. (2020) collected 48 sediment cores from Lake Tai (Jiangsu Province), which has high nutrient concentrations and annual blooms of the toxic cyanobacteria *Microcystis* sp. Non-treated (control) cores were compared with cores treated with unmodified zeolites and with cores treated with NB modified zeolites. In treated cores, water was dosed with chitosan-modified zeolite to flocculate particulates to the sediment surfaces, which were then 'capped' with 1.5–2 cm of unmodified or NB zeolites. The control cores had consistent DO concentrations in the water column of $0.5\text{ mg}\cdot\text{L}^{-1}$. Capping by unmodified zeolites increased concentrations to $3\text{--}4\text{ mg}\cdot\text{L}^{-1}$ but these dropped back to $0.5\text{ mg}\cdot\text{L}^{-1}$ within 5 days. In contrast, in the NB zeolite treatments DO increased to $4\text{--}6\text{ mg}\cdot\text{L}^{-1}$ and these concentrations were maintained throughout the 30-day incubation. These treatments also increased the penetration of oxygen into the bed sediments from 0 to 3 cm. The NB treatments were highly effective at reducing the TP and DRP concentrations in the water column due to a decrease in redox-related release from the sediment as well as reducing the direct release from decomposing sedimented algae.

In a variation of the laboratory based core-incubation approach Zhang et al. (2021) placed eight core tubes into the sediment of a shallow eutrophic lake in Beijing, China. This *in situ* mesocosm approach also used slightly different materials with a modified zeolite being treated with AlCl_3 to increase its phosphorus adsorption capacity. Control cores (non-treated cores) were compared to unmodified zeolites, modified zeolites and modified zeolites treated further with NB. Following the 35-day incubation, dissolved oxygen concentrations and oxidising-reduction potential (ORP) were analysed for the control ($1.5\text{ mg}\cdot\text{L}^{-1}$, -200mV), unmodified zeolites ($2\text{ mg}\cdot\text{L}^{-1}$, -100mV), modified zeolites ($3.3\text{ mg}\cdot\text{L}^{-1}$, -50mV) and NB-modified zeolites ($6.2\text{ mg}\cdot\text{L}^{-1}$, $+173\text{ mV}$). The NB-modified zeolite was the only treatment that eliminated the flux of DRP and $\text{NH}_4^+\text{-N}$ to the water column and turned the sediment

from a source to a sink for these nutrients. This study also identified an increase in denitrifying bacterial activity as a result of the NB treatment.

Two studies have been conducted in New Zealand. Zhang et al. (2018) conducted laboratory-based core incubation using sediments from Lake Ngaroto, a hypertrophic peat lake in the Waikato region. Nanobubble-treated zeolites as well as NB-treated local soils were used in the incubations, which were conducted for 127 days. The water columns overlying the treated cores maintained significantly higher dissolved oxygen ($4\text{--}7.5\text{ mg}\cdot\text{L}^{-1}$) over the length of the incubation relative to the control ($\text{DO} = \sim 1\text{ mg}\cdot\text{L}^{-1}$). The ORP was reversed from -200 mV to $180\text{--}210\text{ mV}$ in the NB zeolite treatment while ORP decreased from -200 mV to -350 mV in the control. These oxygen and redox potential changes were accompanied by negative fluxes of TP to the water column in both the NB zeolite and NB soil treatments indicating that the sediment had become a phosphorus sink, as opposed to the control core where the sediment remained a phosphorus source throughout the incubation.

Waikato peat lake sediments (Lake Millicich) were also used for a core incubation study by Woodward et al. (2017). This study compared an MLS product (which combined a chitosan modified local soil with an NB-modified zeolite) with various phosphorus inactivation agents (alum, allophane, Aqual-P) and a flocculant (anionic polyacrylamide). Cores were exposed to alternate cycles of aerobic/anoxic conditions. The results were variable with the phosphorus binding efficacy of all products decreasing during subsequent periods of anoxia, and only alum producing a statistically significant decrease in anoxic DRP flux from the sediment throughout the experiment. The NB-modified soil was the only material to provide a sink to $\text{NH}_4\text{-N}$ throughout the incubation. The NB treatment of zeolites for this study was undertaken in China and there is a possibility that product effectiveness was compromised during the period between production and deployment (G. Pan, University of Chinese Academy of Sciences, pers. comm. 2020).

2.3. Research gaps

The research conducted on oxygen NB-modified products is promising and suggests that they have the potential to help restore degraded lake ecosystems. However, studies to date have largely been conducted in the laboratory and *in situ* and lake-scale studies are needed. There is also considerable uncertainty regarding the longer-term efficacy of the technology, with the longest time frame of the core incubation studies being 127 days. It may be that in lakes where external nutrient loading has been adequately controlled, the combination of the 'floc, lock and oxygenate' approach of the MLS/NB system will break the cycle of sediment-derived nutrients for long enough to tip the system back into a state of better ecological health. This appears to have been the case in some studies of MLS (without NB) which have resulted in the prolonged re-establishment of macrophytes (e.g., Pan et

al. 2019). However, in some systems dense macrophytes can themselves produce conditions conducive to phosphorus mobilisation (Waters et al. 2021) in which case the oxygenation of the SWI by NB addition may be of great benefit. Such research questions will likely require testing at larger experimental scales and the efficacy of the MLS/NB technology will need to be tested by progressively increasing the size of research settings, i.e., scaling up to larger mesocosms and then pond/small lake systems. Working in these larger systems will progressively introduce potentially confounding factors such as wind resuspension, bioturbation and benthic-feeding fish. Further studies will likely also require site-specific testing of potential carrier materials used for the MLS/NB systems, e.g., whether local soils or zeolite materials are best suited to local conditions and algal species.

The ecological effects of the NB treatments will also require further research. A study into the effects of NB treatments on aquatic macrophyte growth demonstrated beneficial effects up to a threshold above which plant growth was inhibited (Wang et al. 2021). Yang et al. (2016) reported the non-toxicity of chitosan, the flocculant used in many recent MLS products, while an ecotoxicological study by Wang et al. (2016) on the effects of various flocculants with potential for use in MLS systems determined chitosan and cationic starch dose rates that can be used with minimal adverse effects. Such studies will need to be expanded to include the complete suite of MLS/NB materials and a range of biota including country-specific species.

The practical applicability of MLS/NB technology to lake restoration also raises questions of logistics and costs. While the addition of flocculants (such as chitosan) to carrier materials (such as local soils or zeolites) may be relatively easily resolved in a local setting, the practicalities of dosing zeolites with oxygen NB at lake-scale quantities remain to be demonstrated. In terms of costs, Pan et al. (2016) presents some cost estimates for flocculation and capping by MLS as well as application of NB-treated materials but the NB costs appear not to include the cost of laboratory preparation. Zhang et al. (2021) has estimated costs ranging from €0.5–1.5 M per km² (NZ\$0.85–2.5 M per km²) for the use of their NB- and AlCl₃-treated MLS, compared with €0.3–0.8 M per km² (NZ\$0.5–1.3 M per km²) for some commercial aluminium and lanthanum based P-capping material. They indicate an expectation that costs will come down and product performance is significantly superior to traditional materials; however, country-specific costs and product performance needs to be ascertained.

3. CONCLUSIONS AND RECOMMENDATIONS

Oxygen nanobubble technologies offer significant promise for the remediation of degraded lake ecosystems. When combined with MLS they may provide an integrated, treatment system which aims to flocculate and sink suspended

particulate material including algae, physically cap the sedimented organic-rich material and oxygenate the sediment water interface. To date research has predominantly been undertaken in small-scale short-term laboratory-based trials. In these studies MLS/NB systems have produced major reductions in nutrient concentrations within the water column and decreased or reversed the flux of nutrients and other contaminants from the sediment to the water column. Based on the limited ecotoxicological work undertaken, the data suggests that relative to other geo-engineering solutions, MLS/NB may be a relatively environmentally benign method of lake restoration. Future studies should focus on:

- Scalability. Further research should aim to scale up previous laboratory-incubation studies to larger outdoor enclosure and pond/lake-sized trials to demonstrate treatment efficacy at environmentally relevant scales.
- Longevity. As larger scale trials are conducted, these should also aim to understand how effective the MLS/NB treatments are for aiding long-term restoration.
- System specificity. To date, studies have been conducted in a relatively small number of lakes. Future trials should aim to understand issues regarding site-specificity of the MLS/NB system especially with respect to the use of local materials as carriers for flocculants, and on the interplay of varying water and sediment conditions (e.g., ionic strength, alkalinity and potential for interference by a range of existing chemicals).
- Ecological/process safety. Research is required to further investigate potential detrimental effects of the MLS/NB system including toxicity and benthic smothering issues, as well as effects on biogeochemical processes. These will need to include site/country specific biota.
- Cultural and social acceptance. The effectiveness of the MLS/NB system in New Zealand will only be of use if the technology is embraced by tangata whenua, local communities and wider society. Research will be required to understand issues pertaining to the social acceptance of these restoration methods in local lakes.
- Practicality and cost. Investigations will be required on the practicality and costs involved with procuring/producing the materials required for the MLS/NB system in New Zealand.

4. REFERENCES

- Abell JM, Özkundakci D, Hamilton DP, van Dam-Bates P, McDowell RW 2019. Quantifying the extent of anthropogenic eutrophication of lakes at a national scale in New Zealand. *Environmental Science and Technology* 53(16): 9439-9452.

- Abell JM, Özkundakci D, Hamilton DP, Reeves P 2020. Restoring shallow lakes impaired by eutrophication: Approaches, outcomes and challenges. *Critical Reviews in Environmental Science and Technology*: 1-48. in press.
DOI: 10.1080/10643389.2020.185464
- Agarwal A, Ng WJ, Liu Y 2011. Principle and applications of microbubble and nanobubble technology for water treatment. *Chemosphere* 84: 1175-1180.
- Burger D, Hamilton DP, Pilditch CA, Gibbs MM 2007. Benthic nutrient fluxes in a eutrophic, polymictic lake. *Hydrobiologia* 584(1): 13-25.
- Clearwater SJ, Hickey CW, Thompson KJ 2014. The effect of chronic exposure to phosphorus-inactivation agents on freshwater biota. *Hydrobiologia* 728(1): 51-65.
- Cooke GD, Welch EB, Peterson SA, Nichols SA 2005. Restoration and management of lakes and reservoirs. CRC Press. Boca Raton, Florida USA.
- Copetti D, Finsterle K, Marziali L, Stefani F, Tartari G, Douglas G, Reitzel K, Spears BM, Winfield IJ, Crosa G, D'Haese P, Yasseri S, Lurling M 2016. Eutrophication management in surface waters using lanthanum modified bentonite: a review. *Water Research* 97: 162–174.
- Dodds WK, Bouska WW, Eitzmann JL, Pilger TJ, Pitts KL, Riley AJ, Schloesser JT, Thornbrugh DJ 2009. Eutrophication of U.S. freshwaters: Analysis of potential economic damages. *Environmental Science and Technology* 43(1): 12-19.
- Douglas GB, Hamilton DP, Robb MS, Pan G, Spears BM, Lurling M 2016. Guiding principles for the development and application of solid-phase phosphorus adsorbents for freshwater ecosystems. *Aquatic Ecology* 50(3): 385-405.
- Hickey CW, Gibbs MM 2009. Lake sediment phosphorus release management-decision support and risk assessment framework. *New Zealand Journal of Marine and Freshwater Research* 43: 819-856.
- Hamilton DP 2019. Review of relevant New Zealand and international lake water quality remediation science. ARI Report No. 1802 to Bay of Plenty Regional Council. Australian Rivers Institute, Griffith University, Brisbane.
- Hamilton DP, Landman MJ 2018. Lake restoration: an experimental ecosystem approach for eutrophication control. *Hydrobiologia* 661(1): 1-3.
- Hamilton DP, Collier KJ, Quinn JM, Howard-Williams C 2018. Lake restoration handbook. A New Zealand perspective. Springer International, Switzerland.
- Ji X, Liu C, Pan G 2020a. Interfacial oxygen nanobubbles reduce methylmercury production ability of sediments in eutrophic waters. *Ecotoxicology and Environmental Safety* 188: 1-9.
- Ji X, Liu C, Zhang M, Yin Y, Pan G 2020b. Mitigation of methylmercury production in eutrophic waters by interfacial oxygen nanobubbles. *Water Research* 173: 1-10.

- Jin X, Bi L, Lyu T, Chen J, Zhang H, Pan G 2019. Amphoteric starch-based bicomponent modified soil for mitigation of harmful algal blooms (HABs) with broad salinity tolerance: Flocculation, algal regrowth, and ecological safety, *Water Research* 165: 1-8.
- Li H, Pan G 2015. Simultaneous removal of harmful algal blooms and microcystins using microorganism- and chitosan-modified local soil, *Environmental Science and Technology* 49(10): 6249-6256
- Lurling M, Tolman Y 2010. Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction of *Daphnia magna*. *Water Research* 44 (1): 309-319.
- Lyu T, Wu S, Mortimer RJG, Pan G 2019. Nanobubble technology in environmental engineering: revolutionization potential and challenges. *Environmental Science and Technology* 53: 7175-7176.
- Martin ML, Hickey CW 2007. Scion zeolite bioassays. NIWA Report for Scion, Rotorua. SCI07201; HAM2007-030: 60 p.
- Pan G, Zou H, Chen H, Yuan X 2006. Removal of harmful cyanobacterial blooms in Taihu Lake using local soils. III. Factors affecting the removal efficiency and an in-situ field experiment using chitosan-modified local soils. *Environmental Pollution* 141: 206-212.
- Pan G, Yang B, Wang D, Chen H, Tian B, Zhang M, Yuan X, Chen J 2011. In-lake algal bloom removal and submerged vegetation restoration using modified soils. *Ecological Engineering* 37: 302-308.
- Pan G, Dai L, Li L, He L, Li H, Bi L, Gulati RD 2012. Reducing the recruitment of sedimented algae and nutrient release into the overlying water using modified soil/sand flocculation-capping in eutrophic lakes. *Environmental Science and Technology* 46(9): 5077-5084.
- Pan G, He G, Zhang M, Zhou Q, Tyliczszak T, Tai R, Guo J, Bi L, Wang L, Zhang H 2016. Nanobubbles at hydrophilic particle-water interfaces. *Langmuir* 13: 11133-11137.
- Pan G, Miao X, Zhang H, Wang L, Wang Z, Chen J, Ali J, Pan M, Zhang J, Yue B Lyu T 2019. Modified local soil (MLS) technology for harmful algal bloom control, sediment remediation and ecological restoration. *Water* 11(6): 1123.
- Parkyn SM, Hickey CW, Clearwater SJ 2011. Measuring sub-lethal effects on freshwater crayfish (*Parenephrops planifrons*) behaviour and physiology: laboratory and in situ exposure to modified zeolite. *Hydrobiologia* 661: 37-53.
- Schindler DW 1977. Evolution of phosphorus limitation in lakes. *Science* 195: 260-262.
- Shi W, Tan W, Wang L, Pan G 2016. Removal of *Microcystis aeruginosa* using cationic starch modified soils, *Water Research* 97: 19-25.

- Shi W, Pan G, Chen Q, Song L, Zhu L, Ji X 2018. Hypoxia remediation and methane emission manipulation using surface oxygen nanobubbles. *Environmental Science and Technology* 5(15): 8712-8717.
- Snigdha Khuntia SKM, Ghosh P 2013. Removal of ammonia from water by ozone microbubbles, *Industrial & Engineering Chemistry Research* 52: 318-326.
- Spears BM, Meis S, Anderson A, Kellou M 2013. Comparison of phosphorus (P) removal properties of materials proposed for the control of sediment P release in UK lakes. *Science of the Total Environment* 442: 103-110.
- Spears BM, Maberly SC, Pan G, Mackay E, Bruere A, Corker N, Douglas G, Egemose S, Hamilton D, Hatton-Ellis T, Huser B, Li W, Meis S, Moss B, Lurling M, Phillips G, Yasserli S, Reitzel K 2014. Geo-engineering in lakes: A crisis of confidence. *Environmental Science and Technology* 48: 9977-9979.
- Søndergaard M, Jensen JP, Jeppesen E 2003. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 506-509: 135-145.
- Steinman AD, Spears BM 2020. Internal phosphorus loading in lakes. Causes, case studies, and management. J Ross Publishing. Florida, USA.
- Tempero GW, 2015. Ecotoxicological review of alum applications to the Rotorua Lakes. ERI Report No 52. Client report prepared for the Bay of Plenty Regional Council. Environmental Research Institute, Faculty of Science and Engineering, University of Waikato, Hamilton, New Zealand. 37 p.
- Verburg P, Hamill K, Unwin M, Abell J 2010. Lake water quality in New Zealand 2010: Status and trends. NIWA Client report HAM2010-107. Prepared for Ministry for the Environment.
- Wang L, Pan G, Shi W, Wang Z, Zhang H 2016. Manipulating nutrient limitation using modified local soils: a case study at Lake Taihu (China). *Water Research* 101: 25-35.
- Wang Z, Zhang H, Pan G 2016. Ecotoxicological assessment of flocculant modified soil for lake restoration using an integrated biotic index. *Water Research* 97: 133-141.
- Wang L, Miao X, Ali J, Lyu T, Pan G 2018. Quantification of oxygen nanobubbles in particulate matters and potential applications in remediation of anaerobic environment. *ACS Omega* 3:10624-10630.
- Wang J, Chen J, Yu P, Yang X, Zhang L, Geng Z, He K 2020. Oxygenation and synchronous control of nitrogen and phosphorus release at the sediment-water interface using oxygen nano-bubble modified material. *Science of the Total Environment* 725: 138258.
- Wang S, Liu Y, Pan G, Li P 2021. Aquatic macrophytes in morphological and physiological responses to the nanobubble technology application for water restoration. *Environmental Science and Technology* 1(2): 376-387.

- Waters S, Webster-Brown JG 2016. The use of a mass balance phosphorus budget for informing nutrient management in shallow coastal lakes. *Journal of Hydro-environment Research* 10: 32-49.
- Waters S, Webster-Brown JG, Hawes I 2021. The release of legacy phosphorus from deforestation derived sediments in shallow, coastal lake Forsyth/Te Roto o Wairewa. *New Zealand Journal of Marine and Freshwater Research*: 55(3): 446-465.
- Woodward B, Hofstra D, Gibbs M 2017. Waikato shallow lake rehabilitation. Phase one. NIWA Client report 2017205HN. Prepared for Waikato River Authority.
- Xiao, Z, Li D, Zhang R, Wang F, Pan F, Sun Z 2019. An experimental study on the simultaneous removal of NO and SO₂ with a new wet recycling process based on the micro-nano bubble water system. *Environmental Science and Pollution Research* 27(4): 4197-4205.
- Xu D, Ding S, Sun Q, Zhong J, Wu W, Jia F 2012. Evaluation of in situ capping with clean soils to control phosphate release from sediments. *Science of the Total Environment* 438: 334-341.
- Yang R, Li H, Huang M, Yang H, Li A 2016. A review on chitosan-based flocculants and their applications in water treatment. *Water Research* 95: 59-89.
- Yu P, Wang J, Chen J, Guo J, Yang H, Chen Q 2019. Successful control of phosphorus release from sediments using oxygen nano-bubble-modified minerals. *Science of the Total Environment* 663: 654-661.
- Zhang H, Lyu T, Bi L, Tempero G, Hamilton D, Pan G 2018. Combating hypoxia/anoxia at sediment-water interfaces: A preliminary study of oxygen nanobubble modified clay materials. *Science of the Total Environment* 637-638: 550-560.
- Zhang H, Shang Y, Lyu T, Chen J, Pan G 2018. Switching harmful algal blooms to submerged macrophytes in shallow waters using geo-engineering methods: Evidence from a 15N tracing study. *Environmental Science and Technology* 52(20): 11778-11758.
- Zhang H, Chen J, Han M, An W, Yu J 2020. Anoxia remediation and internal loading modulation in eutrophic lakes using geoengineering method based on oxygen nanobubbles. *Science of the Total Environment* 714: 136766.
- Zhang H, Lyu T, Liu L, Hu Z, Chen J, Su B, Yu J, Pan G 2021. Exploring a multifunctional geoengineering material for eutrophication remediation: Simultaneously control internal nutrient load and tackle hypoxia. *Chemical Engineering Journal* 406: 1-10.