Oxygen Nanobubbles for Lake Restoration—Where Are We at? A Review of a New-Generation Approach to Managing Lake Eutrophication

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Review

Oxygen Nanobubbles for Lake Restoration—Where Are We at? A Review of a New-Generation Approach to Managing Lake Eutrophication

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Abstract: Nutrient enrichment of lakes from anthropogenic activities is a significant and increasing issue globally, impairing the health, biodiversity and service provisioning from lakes, with impacts on cultural, recreational, economic and aesthetic values. Internal nutrient loads from lakebed sediment releases are a primary cause of lake eutrophication and have necessitated geoengineering methods to mitigate releases and speed up recovery from eutrophication. Our objective in this review was to evaluate the use of oxygen nanobubbles as a geoengineering technology to remediate low oxygen conditions at the lake sediment/water interface, as a precursor to alleviating eutrophication linked to high internal nutrient loads. Oxygen nanobubbles (NBs) are bubbles < 1000 nm formed at the interface of solid surfaces and aqueous solutions. These bubbles have higher density than water, persist for longer and facilitate greater oxygen solubility than larger bubbles. Methods have been developed to enable NB formation at the surface of carrier materials, which are then used in conjunction with modified local soils (MLSs), to 'floc, lock and oxygenate' to strip nutrients from the water column, locking them in lakebed sediments and oxygenating the sediments to prevent re-release of nutrients. Most studies of NBs for lake restoration have thus far only demonstrated their potential for this purpose, using short-term, small-scale core incubations conducted mainly in laboratory settings. Work is required to (1) address scalability, including procurement and cost, (2) extend laboratory incubation studies to large outdoor enclosures and pond/lake trials, (3) examine longevity of the effects in the natural environment, including potential for MLSs to smother benthos and/or have toxic effects, and (4) extend to a range of lake environments and MLS types. Legal, cultural and social acceptance of the technology is another prerequisite of applications in the natural environment and requires individualised analysis. Until these issues are addressed in a systematic way that addresses scalability and recommends suitable carrier materials and MLSs, NBs may continue to remain largely untried as a geoengineering method to address lake eutrophication.

Keywords: oxygen nanobubbles; lake restoration; internal nutrient loading; eutrophication; geoengineering; sediment capping; flocculation

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1. Introduction

Lake ecosystems around the world have been degraded by anthropogenic eutrophication [1–3]. The increased export of nutrients from lake catchments into lakes (i.e., external loading) has driven excess primary productivity often in the form of harmful cyanobacteria 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 source pollution (e.g., sewerage treatment/diversion) and, more recently, diffuse source nutrients (e.g., erosion control, land use changes, nutrient leaching caps). Such efforts include national scale policy initiatives aimed at restoring surface water quality, such as the Clean Water Act (Federal Water Pollution Control Act 1972. 33 U.S.C. §§1251–1387) in the United States with its total maximum daily loads, the European Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. Off. J. Eur. Communities 2000) and the New Zealand National Policy Statement for Freshwater Management (National Policy Statement for Freshwater Management 2020. New Zealand Government, Wellington, New Zealand). 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 nutrient sources from the lakebed (i.e., internal loading) where nutrients sequestered during times of high external loading are released as conditions in the overlying water change.

Nutrients, in particular phosphorus (P), bound to particulates or taken up by organisms, are generally sedimented to the lakebed. As a result, lake sediments often constitute a large nutrient reservoir from which bioavailable dissolved nutrients (particularly dissolved reactive phosphorus (DRP) and ammoniacal nitrogen (NH_3-N + NH_4^+-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., [4–7]) and the integrated management of both external and internal loading is now considered critical to most lake restoration efforts [8].

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 [8]. 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 prevents the flux of nutrients from the sediments (Figure 1). 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 to 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 directly to surface or bottom waters.

There has been considerable 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®). A full discussion of these products is beyond the scope of this study, but excellent reviews of geoengineering and other restoration technologies are available in a number of publications [9–16]. Hickey and Gibbs [8] outline the general principles of geoengineering approaches and provide a decision support framework, while a special edition of the journal *Hydrobiologia* outlines the use of different flocculants in lake scale trials in Lake Ōkaro in the Bay of Plenty, New Zealand [12]. The most commonly used phosphorus inactivation agent is alum (aluminium sulphate, $Al_2(SO_4)_3 \cdot 14H_2O$) which has been used in the treatment of wastewater for centuries and in lake restoration since at least the 1970s [9]. Despite many successful applications of alum and other phosphorus-binding agents, both internationally [9] and in New Zealand [12], 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 studies of potential ecotoxicological issues [17].

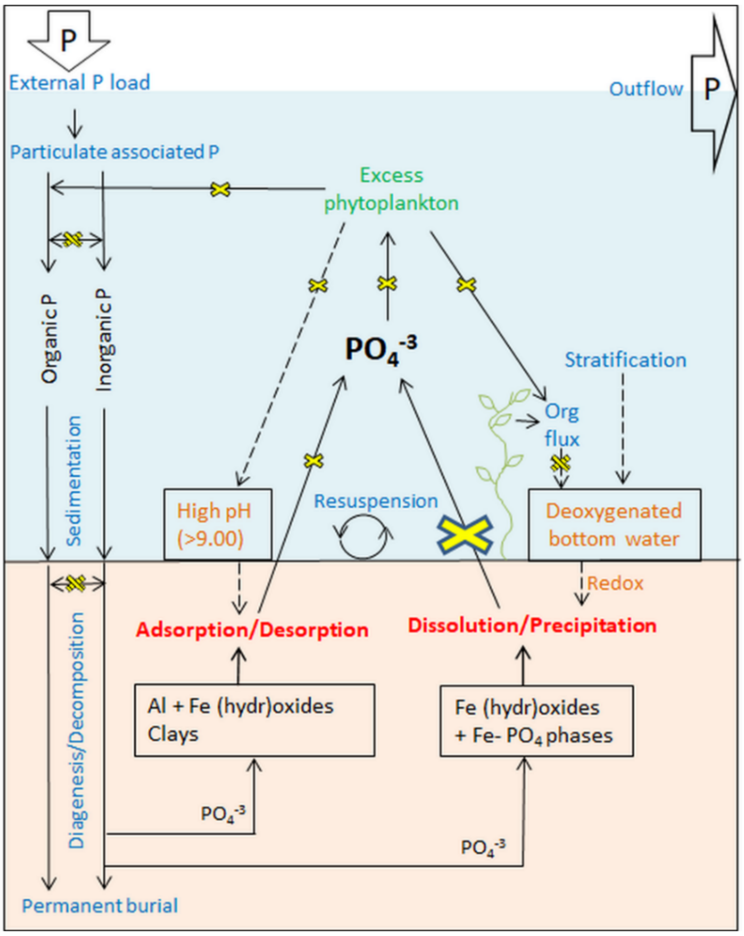

Figure 1. A simplified phosphorus cycle in lake systems showing the dominant processes and pathways of phosphorus cycling between the sediment and water column. The solid lines and blue type refer to physical processes or transport, the dashed line and red type refer to geochemical effect or process, the orange type refers to geochemical state, and the green type refers to a biological effect. The large yellow cross is the point at which most P inactivation agents attempt to block the phosphorus flux from sediment to the water column, while the smaller clear yellow crosses denote the cascading effects of such interventions, and the small hashed yellow crosses denote a decreased magnitude of effect/transport.

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 [9]. However, concerns remain over geoengineering approaches due to the variability of reported results [15,18] as well as potential toxicity issues related to both aluminium- and lanthanum-based products (e.g., [19,20]). 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 [17,20,21]. Cultural concerns have also been raised over the use of chemical additives to restore lake health [22–24]. These issues have led to the ongoing search for more environmentally benign geoengineering products for lake restoration. This search has included early-stage research into the use of oxygen nanobubbles, to remediate poor oxygen status in lakebed sediments and hence to decrease the redox-driven recycling of sediment-bound contaminants. In this paper, we review the status of research into oxygen nanobubbles for lake restoration. Our objectives in this brief review are to:

- collate and summarise research up to this point in time;
- assess emerging information on the likely efficacy of oxygen nanobubbles in lake restoration;
- identify knowledge gaps and use these to frame recommendations on future research.

Oxygen nanobubbles are generally used in conjunction with modified local soils (MLS) as flocculants, to create a coherent lake restoration technology. Below, we provide a brief overview of MLS as background information to provide context to the oxygen nanobubbles research.

2. 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., [25–31]). The aim of methods that use MLSs is to 'floc and lock' by flocculating detrital 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 [32–34] as well as stabilising sediments and increasing water clarity (Figure 2). Pond and lake/bay scale projects with chitosan-amended MLS have resulted in marked improvements in water quality, including increases in Secchi depths and decreases in total and dissolved phosphorus and nitrogen, as well as chlorophyll-a concentrations [35].

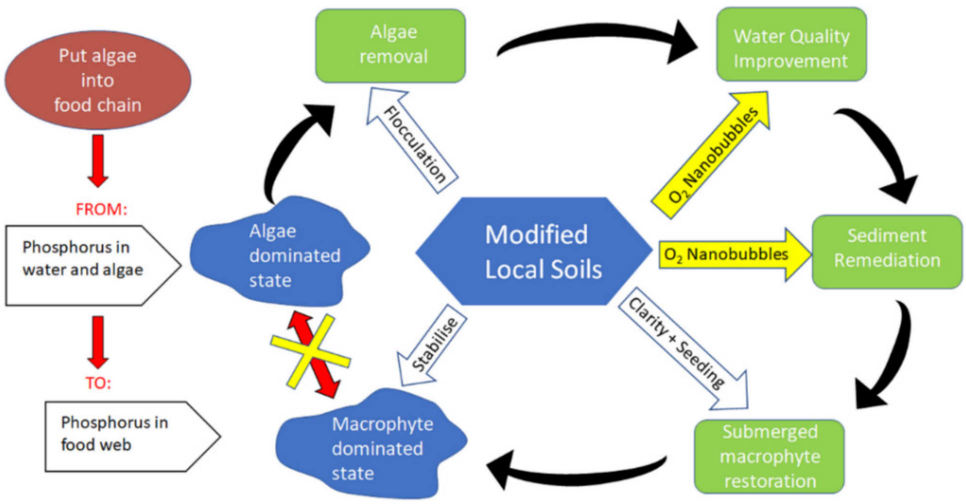

Figure 2. The use of oxygen nanobubbles in conjunction with modified local soils as a multi-disciplinary tool for lake restoration. Modified local soils provide a foundation for lake technologies which can be built on by such additional interventions as oxygen nanobubbles (yellow arrows) and macrophyte seeding. This system is aimed at providing a more holistic and long-term (yellow cross) transition from algae to macrophyte dominated lake-states. Adapted with permission from [35].

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 [26,30,35] (Figure 2). Such an approach applied in a bay-scale trial in Lake Taihu resulted in significant water quality improvements, and within four months of application, macrophytes successfully re-established throughout the bay [26]. In a pond-scale trial, the change in the dominant primary producer from phytoplankton to macrophytes following a 'seeded' MLS treatment was maintained for at least three years [35].

These studies indicate that the use of such MLS flocculants can be effective in the short term by flocculating algae and total nutrients suspended in the water column [36]; however, the sedimentation of 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 application and hence when extended to lake scale, requires the addition of large amounts of MLS. In addition, in shallow lakes, such sediment caps may be susceptible to wind disturbance [15]. Recent research has aimed to enhance the potential of modified local soil technologies and address some of their shortcomings by integrating oxygen nanobubble treatments in order to remediate sediment anoxia.

3. Oxygen Nanobubbles

3.1. 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 [37]. 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, and experimental evidence of their existence only began to emerge in the early 2000s [38,39]. Nanobubbles differ from larger bubbles in various ways other than size. Their negative surface charge, low buoyancy, and longevity facilitate oxygen solubility, properties which have resulted in NBs being applied in a range of fields, including biomedical research and drug delivery [37], water treatment [40,41] and ecological restoration. Ecological applications in lakes include the reduction of methylmercury production [42,43], the decrease in greenhouse gas emissions from lake sediments [35,44,45] and increasingly, the remediation of degraded, eutrophic 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 [9].

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., [46]) and perhaps most commonly, zeolite (e.g., [24]). 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., [46,47]), 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., [30,35]).

3.2. The Efficacy of Oxygen 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 (Table 1).

Table 1. Studies reviewed here which directly investigate the use of oxygen nanobubbles in the restoration of lake eutrophication. (NB, oxygen nanobubbles).

Year	Laboratory/Lake	Source of Sediment	Country of Study	Method	Notes	Experiment Duration (Days)	Citation in This Review
2017	Laboratory	Lake Millich	New Zealand	Cores	Compared nanobubble treatment with other P inactivation agents.	2 × 4 day anoxia 2 × 4 day oxic	50
2018	Laboratory	Lake Taihu	China	Cores	Oxygen nanobubble amended zeolite.	20	44
2018	Laboratory	Lake Ngaroto	New Zealand	Cores	Compared oxygen nanobubble amended zeolite and local soils.	127	49
2019	Laboratory	Hongfeng Reservoir	China	Cores	Oxygen nanobubble amended muscovite.	20	46
2020	Laboratory	Hongfeng Reservoir	China	Cores	Oxygen nanobubble amended muscovite.	25	47
2020	Laboratory	Lake Taihu	China	Cores	Oxygen nanobubble amended zeolite. Algal bloom material added.	30	24
2021	Lake	SP Lake	China	Cores	Oxygen nanobubble amended zeolite. Cores incubated in-situ in lake.	35	48
2021	Laboratory	unnamed	China	Bulk NB in water column	Investigated effect of water column NB on macrophyte growth.	21 and 40 days	24

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 removal of anoxia at the sediment water interface (SWI) and reductions in nutrient fluxes to the water column.

Yu et al. [46] 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 (6.2–9 $mg \cdot L^{-1}$) relative to the untreated cores (1 $mg \cdot L^{-1}$); however, the effect was relatively short lived, and after three days, the oxygen concentrations were <2 $mg \cdot L^{-1}$ in the treated cores. Possible reasons for this rapid decrease in oxygenation were not discussed in the study but may result from experimental variables such as the materials used or application rates. Results such as these highlight a need to better understand the efficacy of differing carrier materials and methodologies. However, despite the decline in oxygen concentrations near the sediment surface, Yu et al. [46] found that 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. [47] from four cores also collected from the Hongfeng Reservoir and treated with similar methods. Despite bottom waters being artificially maintained at DO < 1 $mg \cdot L^{-1}$, release fluxes from the sediment of TP, TN and NH_3-N 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, 48 sediment cores were collected from Lake Tai (Jiangsu Province) [24], 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 mg·L^{-1}. Capping by unmodified zeolites increased concentrations to 3–4 mg·L^{-1}, but these dropped back to 0.5 mg·L^{-1} within 5 days. In contrast, in the NB zeolite treatment, DO increased to 4–6 mg·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. [48] 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 mg·L^{-1}, −200 mV), unmodified zeolites (2 mg·L^{-1}, −100 mV), modified zeolites (3.3 mg·L^{-1}, −50 mV) and NB-modified zeolites (6.2 mg·L^{-1}, +173 mV). The NB-modified zeolite was the only treatment that eliminated the flux of DRP and NH_4^+-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. [49] 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 (4–7.5 mg·L^{-1}) over the length of the incubation relative to the control (DO = ~1 mg·L^{-1}). The ORP was reversed from −200 to 180–210 mV in the NB zeolite treatment while ORP decreased from −200 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. [50]. 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 with 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 NH_4-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).

4. Research gaps and Recommendations for Future Research

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., [35]). However, in some systems, dense macrophytes can themselves produce conditions conducive to phosphorus mobilisation [51], in which case, the oxygenation of the SWI by NB addition may be of great benefit. In deeper systems where treatment is below the photic zone and hence where macrophytes will not re-establish, this question of longevity of oxygenation is critical. 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 or varying depths. 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 [52]. Yang et al. [29] reported the non-toxicity of chitosan, the flocculant used in many recent MLS products, while an ecotoxicological study by Wang et al. [34], 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. [38] 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. [48] have estimated costs ranging from EUR 0.5–1.5 M per km^2 for the use of their NB- and $AlCl_3$-treated MLS, compared with EUR 0.3–0.8 M per km^2 for some commercial aluminium- and lanthanum-based P-capping material. They indicate an expectation that costs will come down and that product performance is significantly superior to traditional materials; however, country-specific costs and product performance are yet to be ascertained.

For any new product to be widely utilised, it needs to comply with legal requirements as well as enjoy 'social licence'. Hence, in addition to a good understanding of the appropriate legal frameworks, there also needs to be a good understanding of potential causes of resistance to use due to cultural, social and management factors. These may include cost, concerns about toxicity or cultural issues with using 'additives' to solve our environmental problems (e.g., [22,23]). Research into why geoengineering products meet such resistance may be critical to gaining wider acceptance of new generation tools such as MLS/NB technology.

5. Conclusions

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 physically cap algal material and to oxygenate the sediment water interface. To date, the 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 these studies and the limited ecotoxicological work undertaken, the data suggest that relative to other geo-engineering solutions, MLS/NB may be an effective and environmentally benign method of lake restoration. However, further work is needed to provide a full understanding of the practical, ecological, legal, social and financial applicability of the technology.

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References

1. Dodds, W.K.; Bouska, W.W.; Eitzmann, J.L.; Pilger, T.J.; Pitts, K.L.; Riley, A.J.; Schloesser, J.T.; Thornbrugh, D.J. Eutrophication of U.S. freshwaters: Analysis of potential economic damages. *Environ. Sci. Technol.* **2009**, *43*, 12–19. [CrossRef] [PubMed]
2. Andersen, N.J.; Bennion, H.; Lotter, A.F. Lake eutrophication and its implications for organic carbon sequestration in Europe. *Glob. Chang. Biol.* **2014**, *20*, 2741–2751. [CrossRef] [PubMed]
3. Abell, J.M.; Özkundakci, D.; Hamilton, D.P.; van Dam-Bates, P.; Mcdowell, R.W. Quantifying the extent of anthropogenic eutrophication of lakes at a national scale in New Zealand. *Environ. Sci. Technol.* **2019**, *53*, 9439–9452. [CrossRef] [PubMed]
4. Schindler, D.W. Evolution of phosphorus limitation in lakes. *Science* **1977**, *195*, 260–262. [CrossRef]
5. Søndergaard, M.; Jensen, J.P.; Jeppesen, E. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* **2003**, *506–509*, 135–145. [CrossRef]
6. Burger, D.; Hamilton, D.P.; Pilditch, C.A.; Gibbs, M.M. Benthic nutrient fluxes in a eutrophic, polymictic lake. *Hydrobiologia* **2007**, *584*, 13–25. [CrossRef]
7. Waters, S.; Webster-Brown, J.G. The use of a mass balance phosphorus budget for informing nutrient management in shallow coastal lakes. *J. Hydro-Environ. Res.* **2016**, *10*, 32–49. [CrossRef]
8. Hickey, C.W.; Gibbs, M.M. Lake sediment phosphorus release management- decision support and risk assessment framework. *N. Z. J. Mar. Freshw. Res.* **2009**, *43*, 819–856. [CrossRef]
9. Cooke, G.D.; Welch, E.B.; Peterson, S.A.; Nichols, S.A. *Restoration and Management of Lakes and Reservoirs*; CRC Press: Boca Raton, FL, USA, 2005.
10. Spears, B.M.; Meis, S.; Anderson, A.; Kellou, M. Comparison of phosphorus (P) removal properties of materials proposed for the control of sediment P release in UK lakes. *Sci. Total Environ.* **2013**, *442*, 103–110. [CrossRef]
11. Douglas, G.B.; Hamilton, D.P.; Robb, M.S.; Pan, G.; Spears, B.M.; Lurling, M. Guiding principles for the development and application of solid-phase phosphorus adsorbents for freshwater ecosystems. *Aquat. Ecol.* **2016**, *50*, 385–405. [CrossRef]
12. Hamilton, D.P.; Landman, M.J. Lake restoration: An experimental ecosystem approach for eutrophication control. *Hydrobiologia* **2011**, *661*, 1–3. [CrossRef]
13. Hamilton, D.P.; Collier, K.J.; Quinn, J.M.; Howard-Williams, C. *Lake Restoration Handbook*; A New Zealand Perspective; Springer International: Cham, Switzerland, 2018.
14. Hamilton, D.P. *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, QLD, Australia, 2019.

15. Abell, J.M.; Özkundakci, D.; Hamilton, D.P.; Reeves, P. Restoring shallow lakes impaired by eutrophication: Approaches, outcomes and challenges. *Crit. Rev. Environ. Sci. Technol.* **2022**, *52*, 1199–1246. [CrossRef]
16. Steinman, A.D.; Spears, B.M. *Internal Phosphorus Loading in Lakes: Causes, Case Studies, and Management*; J. Ross Publishing: Plantation, FL, USA, 2020.
17. Parkyn, S.M.; Hickey, C.W.; Clearwater, S.J. Measuring sub-lethal effects on freshwater crayfish (*Parenephrops planifrons*) behaviour and physiology: Laboratory and in situ exposure to modified zeolite. *Hydrobiologia* **2011**, *661*, 37–53. [CrossRef]
18. Spears, B.M.; Maberly, S.C.; Pan, G.; Mackay, E.; Bruere, A.; Corker, N.; Douglas, G.; Egemose, S.; Hamilton, D.; Hatton-Ellis, T.; et al. Geo-engineering in lakes: A crisis of confidence. *Environ. Sci. Technol.* **2014**, *48*, 9977–9979. [CrossRef]
19. Lurling, M.; Tolman, Y. Effects of lanthanum and lanthanum-modified clay on growth, survival and reproduction of *Daphnia magna*. *Water Res.* **2010**, *44*, 309–319. [CrossRef]
20. Clearwater, S.J.; Hickey, C.W.; Thompson, K.J. The effect of chronic exposure to phosphorus-inactivation agents on freshwater biota. *Hydrobiologia* **2014**, *728*, 51–65. [CrossRef]
21. Martin, M.L.; Hickey, C.W. *Scion Zeolite Bioassays*; NIWA Report for Scion, Rotorua. SCI07201; HAM2007-030; NIWA: Hamilton, New Zealand, 2007; 60p.
22. Tempero, G.W. *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, 2015; 37p.
23. Copetti, D.; Finsterle, K.; Marziali, L.; Stefani, F.; Tartari, G.; Douglas, G.; Reitzel, K.; Spears, B.M.; Winfield, I.J.; Crosa, G.; et al. Eutrophication management in surface waters using lanthanum modified bentonite: A review. *Water Res.* **2016**, *97*, 162–174. [CrossRef]
24. Zhang, H.; Chen, J.; Han, M.; An, W.; Yu, J. Anoxia remediation and internal loading modulation in eutrophic lakes using geoengineering method based on oxygen nanobubbles. *Sci. Total Environ.* **2020**, *714*, 136766. [CrossRef]
25. Pan, G.; Zou, H.; Chen, H.; Yuan, X. 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. *Environ. Pollut.* **2006**, *141*, 206–212. [CrossRef]
26. Pan, G.; Yang, B.; Wang, D.; Chen, H.; Tian, B.; Zhang, M.; Yuan, X.; Chen, J. In-lake algal bloom removal and submerged vegetation restoration using modified soils. *Ecol. Eng.* **2011**, *37*, 302–308. [CrossRef]
27. Wang, L.; Pan, G.; Shi, W.; Wang, Z.; Zhang, H. Manipulating nutrient limitation using modified local soils: A case study at Lake Taihu (China). *Water Res.* **2016**, *101*, 25–35. [CrossRef] [PubMed]
28. Shi, W.; Tan, W.; Wang, L.; Pan, G. Removal of *Microcystis aeruginosa* using cationic starch modified soils. *Water Res.* **2016**, *97*, 19–25. [CrossRef] [PubMed]
29. Yang, R.; Li, H.; Huang, M.; Yang, H.; Li, A. A review on chitosan-based flocculants and their applications in water treatment. *Water Res.* **2016**, *95*, 59–89. [CrossRef]
30. Zhang, H.; Shang, Y.; Lyu, T.; Chen, J.; Pan, G. Switching harmful algal blooms to submerged macrophytes in shallow waters using geo-engineering methods: Evidence from a 15N tracing study. *Environ. Sci. Technol.* **2018**, *52*, 11778–11785. [CrossRef] [PubMed]
31. Jin, X.; Bi, L.; Lyu, T.; Chen, J.; Zhang, H.; Pan, G. Amphoteric starch-based bicomponent modified soil for mitigation of harmful algal blooms (HABs) with broad salinity tolerance: Flocculation, algal regrowth, and ecological safety. *Water Res.* **2019**, *165*, 115005. [CrossRef] [PubMed]
32. Xu, D.; Ding, S.; Sun, Q.; Zhong, J.; Wu, W.; Jia, F. Evaluation of in situ capping with clean soils to control phosphate release from sediments. *Sci. Total Environ.* **2012**, *438*, 334–341. [CrossRef] [PubMed]
33. Li, H.; Pan, G. Simultaneous removal of harmful algal blooms and microcystins using microorganism- and chitosan-modified local soil. *Environ. Sci. Technol.* **2015**, *49*, 6249–6256. [CrossRef]
34. Wang, Z.; Zhang, H.; Pan, G. Ecotoxicological assessment of flocculant modified soil for lake restoration using an integrated biotic index. *Water Res.* **2016**, *97*, 133–141. [CrossRef]
35. Pan, G.; Miao, X.; Zhang, H.; Wang, L.; Wang, Z.; Chen, J.; Ali, J.; Pan, M.; Zhang, J.; Yue, B.; et al. Modified local soil (MLS) technology for harmful algal bloom control, sediment remediation and ecological restoration. *Water* **2019**, *11*, 1123. [CrossRef]
36. Pan, G.; Dai, L.; Li, L.; He, L.; Li, H.; Bi, L.; Gulati, R.D. Reducing the recruitment of sedimented algae and nutrient release into the overlying water using modified soil/sand flocculation-capping in eutrophic lakes. *Environ. Sci. Technol.* **2012**, *46*, 5077–5084. [CrossRef]
37. Lyu, T.; Wu, S.; Mortimer, R.J.G.; Pan, G. Nanobubble technology in environmental engineering: Revolutionization potential and challenges. *Environ. Sci. Technol.* **2019**, *53*, 7175–7176. [CrossRef] [PubMed]
38. Pan, G.; He, G.; Zhang, M.; Zhou, Q.; Tyliszczak, T.; Tai, R.; Guo, J.; Bi, L.; Wang, L.; Zhang, H. Nanobubbles at hydrophilic particle-water interfaces. *Langmuir* **2016**, *13*, 11133–11137. [CrossRef] [PubMed]
39. Wang, L.; Miao, X.; Ali, J.; Lyu, T.; Pan, G. Quantification of oxygen nanobubbles in particulate matters and potential applications in remediation of anaerobic environment. *ACS Omega* **2018**, *3*, 10624–10630. [CrossRef] [PubMed]
40. Agarwal, A.; Ng, W.J.; Liu, Y. Principle and applications of microbubble and nanobubble technology for water treatment. *Chemosphere* **2011**, *84*, 1175–1180. [CrossRef]

41. Snigdha Khuntia, S.K.M.; Ghosh, P. Removal of ammonia from water by ozone microbubbles. *Ind. Eng. Chem. Res.* **2013**, *52*, 318–326. [CrossRef]
42. Ji, X.; Liu, C.; Pan, G. Interfacial oxygen nanobubbles reduce methylmercury production ability of sediments in eutrophic waters. *Ecotoxicol. Environ. Saf.* **2020**, *188*, 109888. [CrossRef]
43. Ji, X.; Liu, C.; Zhang, M.; Yin, Y.; Pan, G. Mitigation of methylmercury production in eutrophic waters by interfacial oxygen nanobubbles. *Water Res.* **2020**, *173*, 115563. [CrossRef]
44. Shi, W.; Pan, G.; Chen, Q.; Song, L.; Zhu, L.; Ji, X. Hypoxia remediation and methane emission manipulation using surface oxygen nanobubbles. *Environ. Sci. Technol.* **2018**, *5*, 8712–8717. [CrossRef]
45. Xiao, Z.; Li, D.; Zhang, R.; Wang, F.; Pan, F.; Sun, Z. An experimental study on the simultaneous removal of NO and SO_2 with a new wet recycling process based on the micro-nano bubble water system. *Environ. Sci. Pollut. Res.* **2019**, *27*, 4197–4205. [CrossRef]
46. Yu, P.; Wang, J.; Chen, J.; Guo, J.; Yang, H.; Chen, Q. Successful control of phosphorus release from sediments using oxygen nano-bubble-modified minerals. *Sci. Total Environ.* **2019**, *663*, 654–661. [CrossRef]
47. Wang, J.; Chen, J.; Yu, P.; Yang, X.; Zhang, L.; Geng, Z.; He, K. Oxygenation and synchronous control of nitrogen and phosphorus release at the sediment- water interface using oxygen nano-bubble modified material. *Sci. Total Environ.* **2020**, *725*, 138258. [CrossRef] [PubMed]
48. Zhang, H.; Lyu, T.; Liu, L.; Hu, Z.; Chen, J.; Su, B.; Yu, J.; Pan, G. Exploring a multifunctional geoengineering material for eutrophication remediation: Simultaneously control internal nutrient load and tackle hypoxia. *Chem. Eng. J.* **2021**, *406*, 127206. [CrossRef]
49. Zhang, H.; Lyu, T.; Bi, L.; Tempero, G.; Hamilton, D.; Pan, G. Combating hypoxia/anoxia at sediment-water interfaces: A preliminary study of oxygen nanobubble modified clay materials. *Sci. Total Environ.* **2018**, *637–638*, 550–560. [CrossRef] [PubMed]
50. Woodward, B.; Hofstra, D.; Gibbs, M. *Waikato Shallow Lake Rehabilitation*; Phase One. NIWA Client Report 2017205HN; Prepared for Waikato River Authority; NIWA: Hamilton, New Zealand, 2017.
51. Waters, S.; Webster-Brown, J.G.; Hawes, I. The release of legacy phosphorus from deforestation derived sediments in shallow, coastal lake Forsyth/Te Roto o Wairewa. *N. Z. J. Mar. Freshw. Res.* **2021**, *55*, 446–465. [CrossRef]
52. Wang, S.; Liu, Y.; Pan, G.; Li, P. Aquatic macrophytes in morphological and physiological responses to the nanobubble technology application for water restoration. *Environ. Sci. Technol.* **2021**, *1*, 376–387. [CrossRef]