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Lake sediment phosphorus release management—Decision support and risk assessment framework

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Abstract The release of phosphorus (P) from the sediments of eutrophic lakes is often associated with the proliferation of nuisance algal blooms, especially cyanobacteria. The successful implementation of management actions aimed at reducing such algal blooms requires an integrated approach, including both external and internal nutrient loads. The internal load of P can be a significant source of P for primary production, with greatest inputs occurring when lakes stratify and the hypolimnetic waters become anoxic. We reviewed the nature and characteristics of New Zealand lakes in relation to factors which affect the application of technologies to manage internal P loads within individual lakes. New Zealand's windy maritime climate causes lakes to mix more deeply than lakes in continental areas, which are characterised by relatively hot, calm summers. We assessed a range of management options which may be used to control internal P loads, and considered these in a decision-support framework aimed at identifying the key factors which may limit successful application. Methods to reduce P release from sediments include: physical approaches—such as artificial destratification, hypolimnetic aeration, enhanced lake flushing, and dredging/discing; and geochemical approaches—such as the application of alum and iron as flocculation agents, and other products as "capping" materials. The capping materials may be either a passive physical barrier (e.g., sand, gravel, clay) or an active barrier. The active barrier systems are generally pervious chemical or geochemical materials capable of binding contaminants by adsorption or precipitation processes. A decision-support and risk assessment framework is provided to assist managers in the development of appropriate strategies for reducing or controlling internal P loads, and thus cyanobacteria blooms. A review of the sediment characteristics of lakes in the Taupo volcanic zone showed marked variability in sediment P content, and elevated geothermal arsenic concentrations in some lake sediments, which may affect the efficacy of chemical capping agents, indicating that site-specific consideration of capping agent dose is required.

Keywords remediation; capping; alum; allophane; Phoslock™; zeolite

INTRODUCTION

The successful implementation of management actions aimed at reducing algal blooms in lakes requires an integrated approach (United Nations Environment Programme 1999). Generally, the focus of water quality management in eutrophic lakes has been on reducing nitrogen (N) and phosphorus (P) inputs from catchment sources, such as sewage discharges, agricultural wastewater (e.g., dairy lagoons) and diffuse runoff from agricultural land (e.g., Jeppesen et al. 2007). However, these approaches do not consider the roll of internal release of nutrients from the lake sediments. Organic matter in anoxic sediments is continuously being decomposed with the release of dissolved inorganic nitrogen (DIN) and dissolved reactive phosphorus (DRP) into the sediment pore waters (Smolders et al. 2006). When the lake is stratified and the hypolimnion (bottom waters) become anoxic, substantial amounts of nutrients, particularly DRP and ammoniacal-nitrogen (NH_4-N), diffuse into the overlying waters (Burger et al. 2007). The N and P loads from these internal nutrient sources are recycled and do not

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contribute to the external nutrient budget of a lake (Nürnberg 1984). But in summer, they can be considerably greater than the external N and P loads from river inputs (e.g., Burger et al. 2007) and thus may be the main drivers of primary production in a lake. Consequently, the development of an integrated management approach requires an understanding of the relative magnitude of these nutrient sources, when they occur, and the options available to reduce specific nutrient loadings.

Declines in the ecological condition and water quality in New Zealand lakes has been variously linked with deforestation, agricultural intensification, industrial point sources, urbanisation and silviculture practices (Forsyth et al. 1988; Hamill 2006; Ministry for the Environment 2006). Much of the information on environmental degradation of lakes and the linkages with catchment processes was summarised in lake managers' handbooks (Vant 1987; Elliott et al. 2002) and a contemporary review (Viner 1987). However, more recently, tools such as the Trophic Level Index (TLI) and the Lake Submerged Plant Indicators (LakeSPI) have been developed to provide improved characterisation of the degree of nutrient enrichment (Burns et al. 1999, 2000; Clayton & Edwards 2006). A GIS (geographic information system)-based lake classification system that identified 3820 New Zealand lakes larger than 1 ha (0.01 km^2) (Snelder 2006), showed that the majority of lakes are considered "small" (95% or 3615 lakes), and provided the basis for the most recent reviews of lake water quality status (Hamill 2006; Ministry for the Environment 2006). Water quality in New Zealand lakes has been found to be strongly correlated with land-cover classes, with median values of total N (TN), total P (TP) and chlorophyll *a* being four to six times higher in the pasture class than the native class, and 30% of lakes are likely to have "very poor" to "extremely poor" water quality (Ministry for the Environment 2006). Small, shallow, pastoral catchment lakes in a mild climate region constituted 23.6% of the lakes, with 7.3% in the category of larger eutrophic lakes with mixed land-use catchments (Ministry for the Environment 2006). The large proportion of small, medium-temperature lakes (73%) that have non-natural catchment classes (1871 lakes or 50% of total), suggests that small lakes are likely to be under high pressure leading to degraded water quality (Ministry for the Environment 2006). Many of these are likely to have high internal P loads. The predominance of small lakes in pastoral catchments will result in high eutrophication pressure from both external and internal nutrient loads. However, a small lake size increases the potential for successful management intervention measures to minimise nuisance effects.

The issue of high internal P loads in shallow lakes is world wide (Søndergaard et al. 2003). There is evidence of recent increases in the TLI (i.e., declining trophic state) of several of the 12 major Rotorua lakes (Central Volcanic Plateau of North Island, New Zealand) (Burns et al. 2005), including lakes Rotorua and Rotoiti. These lakes are characterised by high internal nutrient loads comparable to their catchment loads on an annual basis (Hamilton et al. 2004; Burger et al. 2007). A recent study of over 14 000 lakes >1 ha (0.01 km^2) in size in Great Britain found that 51% are likely to require P-reduction measures to meet the Water Framework Directive to achieve "good status" by the year 2015 (Carvalho et al. 2005). Results from the same study also showed strong regional patterns with Scotland having the least and England having the highest number of lakes at risk at 18% and 88%, respectively (Carvalho et al. 2005). In New Zealand, similar regional patterns are apparent (Ministry for the Environment 2006). Because of the high P content of their catchment soils and thus their inflow streams (Timperley 1983), lakes in the Taupo volcanic zone of the North Island are more likely to require internal P load management than elsewhere in New Zealand (Parliamentary Commissioner for the Environment 2006).

Although microbial denitrification can permanently remove N from a lake (McCarthy et al. 2007), there is no equivalent process that can remove P. Consequently, phosphorus tends to accumulate in lake sediments leading to an excess of DRP in the water column during summer and the concomitant proliferation of planktonic algae, including cyanobacteria, which often grow to nuisance bloom proportions. Lake Okaro is a Rotorua lake that was regularly experiencing cyanobacterial blooms by 1963 (Forsyth et al. 1988), and in 1979–80 *Microcystis aeruginosa* and *Anabaena* spp. dominated the plankton assemblage (Dryden & Vincent 1986). Lakes Rotoiti and Rotoehu have intermittently experienced cyanobacterial blooms since the 1970s (Cassie 1978). In the past decade, the severity and extent of these blooms has increased and microcystins have been detected, raising environmental and human health concerns (Wilding 2000; Wood 2005).

Cyanotoxins are a diverse assemblage of natural toxins, with a broad range of toxicity mechanisms including hepatotoxicity, neurotoxicity, dermatotoxicity, and inhibition of protein synthesis inhibition (Chorus 2001). A recent survey of cyanotoxins in New Zealand water bodies has found microcystin and saxitoxin concentrations above 1 µg/litre in 75 samples representing 27 lakes, with the highest microcystin concentration (36 500 µg/litre) occurring in scum samples from Lake Horowhenua (North Island) (Wood et al. 2006a). An intensive weekly sampling of phytoplankton and microcystins was undertaken at six locations in lakes Rotoiti and Rotoehu between November 2003 and May 2004, and included a 3-week enclosure experiment measuring tissue bioaccumulation of microcystins in rainbow trout (*Oncorhynchus mykiss*) muscle and liver, and freshwater mussel (kakahi; *Hyridella menziesi*) tissue (Wood et al. 2006b). The highest microcystin concentration in the phytoplankton samples was 760 µg/litre. The microcystins reached higher concentrations in the tissue of the freshwater mussel than rainbow trout, and were rapidly accumulated and removed from freshwater mussel tissue as the concentrations varied in the surrounding water. Rainbow trout in lakes Rotoiti and Rotoehu accumulated microcystins to concentrations which exceeded the daily tolerable intake (TDI) limit for human consumption recommended by the World Health Organisation (TDI 0.04 µg/kg/day), though it was concluded that consumption as part of a regular diet would not have any adverse health effects (Wood et al. 2006b). These studies demonstrate cyanobacterial bloom toxin production in New Zealand lakes, with food-chain accumulation which may potentially be harmful for human consumers. One of the recognised control measures for cyanobacteria is the control of phosphorus concentrations in lake waters (Chorus & Bartram 1999).

A range of methods have been developed to reduce P release from sediments (Søndergaard et al. 2003). These include: physical approaches, such as artificial destratification, hypolimnetic aeration, enhanced lake flushing, and dredging/discing, and geochemical approaches, such as the application of alum and iron as flocculation agents, and other products as "capping" materials. The capping materials may be either a passive physical barrier (e.g., sand, gravel, clay) or an active barrier (Jacobs & Förstner 1999). The active barrier systems are generally pervious chemical or geochemical materials capable of binding contaminants by adsorption or precipitation processes. Their reactive nature allows these materials to be applied as relatively thin layers (2–5 mm) compared with physical capping approaches (>0.1 m). However, large quantities of capping material are still required to cover large areas involved with lake-bed sediments, with an additional requirement for precise application to achieve an even layer. The requirements for potential active barriers include: availability at low cost; active retention of P; physical and chemical stability; low environmental impact; and sufficient hydraulic conductivity to allow the ecosystem to function without disrupting the layer of capping material (Jacobs & Förstner 1999).

The choice of P remediation approaches to achieve the management objectives for a specific lake is influenced by the suitability of the remediation method and the nature of the lake environment. Key lake factors include the depth, morphometry, hydraulic flushing, stratification depth and period, wind fetch, water quality (e.g., alkalinity, pH, clarity), sediment characteristics and aquatic organisms. A combination of these lake factors and the treatment characteristics (e.g., thickness, area treated, application techniques, formulation) are likely to strongly influence the efficacy and outcome of the remediation. There is the potential to cause undesirable environmental effects, both to water quality and to aquatic biota, if used inappropriately. Consequently, it is important to understand both the uncertainty in risk assessment and the limitations and constraints of the relevant legislation to make effective risk management decisions. Management decisions concerning the use of chemicals for the remediation of excessive P in a lake can have high implementation and monitoring costs which warrant a critical assessment process.

This paper presents a decision-support process with an assessment framework that includes a range of approaches in relation to characteristics of the lake concerned. Additionally, we have provided an ecological risk assessment (ERA) relevant to site-specific application of P remediation management using physical and chemical approaches relevant to New Zealand lakes. We also provide information required for an integrated assessment of management options for lake nutrient loadings.

METHODOLOGY

We reviewed the nature and characteristics of New Zealand lakes in relation to factors which affect the application of technologies to manage internal P loads within individual lakes. We have also reviewed the range of management options which may be used to control internal P loads, and considered these in a decision-support framework aimed at identifying the key factors which may limit successful remediation. This approach was not intended to provide an exhaustive review for each of the management options, but includes key references to reviews or original material relating to the application. Because of the critical importance of lake processes affecting the successful implementation of management and remediation measures, we also incorporated an overview of relevant lake processes, particularly emphasising how New Zealand lakes differ from Northern Hemisphere ones.

The framework for the decision-support approach follows the three stages involved in undertaking an ERA—problem formulation, risk analysis, and risk characterisation (USEPA 1998), addressing options relating to the application of methods to reduce internal P loads in lakes. The legislative basis for the decision-making framework is ultimately based on the registration requirements for chemical capping agents of the Hazardous Substances and New Organisms (HASNO) Act, which is administered by the Environmental Risk Management Authority (ERMA), and the consenting for individual applications required by the Resource Management Act (RMA 1991).

The conceptual model within the decision-making framework was based on incorporating the key factors which affect the efficacy of an internal P load management process. For sediment capping agents, a main factor is the nature of lake sediments, particularly the sediment P concentration. The primary sediment characterisation for New Zealand lakes and sampling methods used were: (1) McColl (1977) used an Ekman dredge to sample the sediment surface layer and measured the total and "organic" phosphorus in 8 lakes in the Rotorua/Te Arawa lakes region in 1972; (2) Viner (1989) used an Ekman dredge to sample surficial sediment (1–2 cm) from 75 sites from Lake Taupo (Taupo volcanic zone); (3) Blomkvist & Lundstedt (1995) sampled depositional sediments in 12 lakes in the Rotorua/Te Arawa lakes region in 1995 using a Jenkins corer (Mortimer 1971), measuring sediment nutrients and metals concentrations; (4) Chittenden et al. (1976) used an Ekman dredge to collect surficial sediments (0–3 cm) from lakes Rotoroa, Rotoiti and Brunner (South Island, New Zealand) in 1973–74; (5) Trolle et al. (2008) collected surficial sediment (1–2 cm) using a cylindrical gravity corer from the deepest basins from 12 lakes in the Rotorua/Te Arawa region between March 2006 and January 2007.

We undertook a preliminary ecological risk assessment for application of a range of capping agents. We summarised a number of the potential adverse effects associated with the use of the different products and summarised human health, livestock and ecological guidelines where these are available. As part of this assessment, we generated standardised data sheets for different management options which may be used in lake nutrient and algal management. These datasheets provide effects-based information which may be used in the decision-making process (Appendix 1).

BACKGROUND—KEY LAKE PROCESSES AFFECTING P CYCLING

The general function and processes occurring in lakes are well known and the sediment-water interface processes have been described in numerous publications (e.g., Wetzel 2001; Spears et al. 2007; Beutel et al. 2008) since their first detailed study by Mortimer (1941, 1942).

New Zealand has a wide variety of lake types which reflect the diverse and dynamic landscape, and the turbulent and complex recent geological history of the landscape (Lowe & Green 1987). The maritime geographical location results in a high frequency of surface winds, which affects mixing in lakes, and a moderation of temperature changes which distinguishes New Zealand lakes from elsewhere (Green et al. 1987). However, the most marked deviations from the commonly occurring types of lakes are those of the Taupo volcanic zone of the North Island, which have waters dominated by sodium (Na) rather than calcium (Ca), with many of them dominated by geothermal fluids (Timperley 1987). The Taupo volcanic zone is a zone of volcanic and geothermal activity extending from Tongariro National Park (Mount Ruapehu) northwards and offshore to White Island in the Bay of Plenty, and includes Lake Taupo and the Rotorua/Te Arawa lakes. Because of the nature of the pumice soils in the Taupo volcanic zone, which have low metal (iron (Fe) and manganese (Mn)) but high P content, natural DRP concentrations in streams are high and DRP is often measurable in the lake water when DIN concentrations are low (Timperley 1983). The source of this P is dissolution of the pumice soil, and algae growing in many of the Taupo volcanic zone lakes may be growth-limited by N, i.e., they are considered to be N-limited lakes, at certain times of the year (White & Payne 1977). This tendency for N-limitation is in contrast to New Zealand lakes outside the Taupo volcanic zone and Northern Hemisphere lakes which often have a large surplus of N and where algal growth is limited by the availability of P, i.e., they are considered to be P-limited lakes (Lewis & Wurtsbaugh 2008). Because most of the worldwide research into lake restoration has been in the Northern Hemisphere, and it is preferable to enhance the P-limitation of a lake than to remove the N to control algal growth (Schindler et al. 2008), almost all remediation strategies for the reduction of internal nutrient loads in lakes focus on the management of P (Søndergaard et al. 2003, 2005; Jeppesen et al. 2005). This approach is also valid in the Taupo volcanic zone lakes of New Zealand (Burns et al. 2005). However, removing P from a lake, without regard to N, leaves potential for sudden algal blooms if P management is not maintained, with N playing a more important role in shallow (mean depth <5 m) lakes (Jeppesen et al. 2005).

The potential for wind mixing may be assessed by using the OSGOOD index (US Department of Agriculture 1999), which calculates the degree to which a lake or reservoir will mix because of wind forces. However, Davies-Colley (1988) found that although New Zealand lakes share the power law exponent of this relationship with Northern Hemisphere lakes, relating to the fetch length dependence on mixing depth, the coefficient of the equation was considerably larger. This analysis showed that in New Zealand's windy maritime climate, lakes mix more deeply than lakes in continental areas, which are characterised by relatively hot, calm summers. Davies-Colley (1988) classified New Zealand lakes in relation to their maximum depth and the predicted epilimnion depth and the likelihood of stable classification, intermittent stratification classes, and rare stratification. A number of shallow lakes are likely to have wind-induced resuspension of sediments, with often prolonged periods of high turbidity. For these lakes, the wind-induced resuspension may be the main mechanism for porewater nutrient transfer from the sediments (Søndergaard et al. 2003).

DEFINING THE GOAL

Of increasing worldwide concern are the symptoms of eutrophication, particularly the appearance of floating algal "blooms", and the development of nuisance algal blooms that may include toxic algal species of cyanobacteria (Schindler et al. 2008). The presence of cyanobacteria above 2000 cells/ml in potable water supplies can cause taste and odour problems, which increase the cost of water treatment (Ministry of Health 2005). Higher levels of cyanobacteria (>50 000 cells/ml) render surface waters unsuitable for contact recreation (Ministry of Health 2005). Very high levels, as occur in floating blooms, can result in fish kills and are potentially lethal to water fowl, dogs, and humans, especially children who may swallow the toxin if they fall into the water (Hamill 2001; Wood et al. 2006a). These cyanobacteria blooms often form unsightly surface scums which drift inshore with the wind, and their subsequent decomposition in the shallow near-shore waters (littoral zone) produces offensive smells (Wilding 2000). The planktonic cyanobacterial bloom effects include reduced transparency, increased pH and toxin production, with the bloom collapse causing potential hypoxia or anoxia and ammonia production (Havens 2008), with the potential for adverse effects on aquatic species, wading birds and humans.

Many factors have been linked to the success of planktonic cyanobacteria in lakes, including their ability to fix N and to control buoyancy, which favour cyanobacterial dominance of phytoplankton populations with P-limitation and calm conditions. Comprehensive theories to explain the success of these organisms have been difficult to resolve (Hyenstrand et al. 1998). In general, the potential for cyanobacterial dominance (i.e., >50% of the phytoplankton population) increases rapidly as total P increases from 30 to 100 μg/litre (Downing et al. 2001), however, long-term studies of the phytoplankton response to declining TP concentrations has shown greater response in deep (>5 m) compared with shallow lakes (Jeppesen et al. 2005). Jeppesen et al. (2005) acknowledge that conclusions derived from their analysis were based on correlation evidence, and interpretation of cause-and-effect relationships may therefore be complicated by other unmeasured factors. Because of the uncertainty in understanding the factors contributing to cyanobacterial blooms, it may not be possible to achieve the goal of eliminating cyanobacteria and a more realistic goal may be to have fewer or no toxic algal blooms in water bodies used for recreation. This goal of reduced planktonic cyanobacterial dominance would then be related to nutrient conditions which do not favour toxic algal bloom development (Downing et al. 2001), and the most effective management strategy to achieve this goal would be determined.

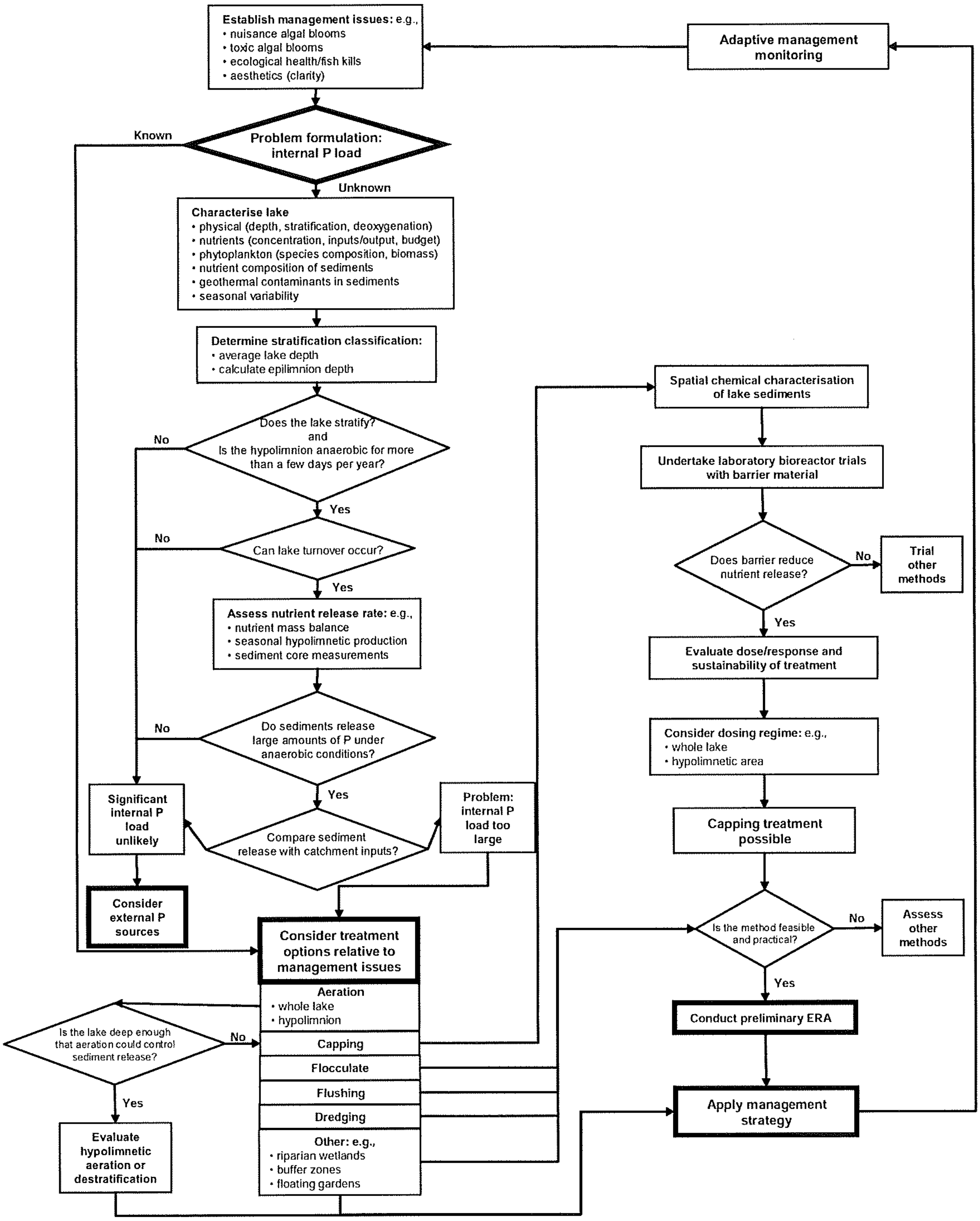

Fig. 1 Protocol for investigating the effectiveness of management options for reducing sediment nutrient release (phosphorus, P) in New Zealand lakes, and for undertaking an ecological risk assessment (ERA) of the treatment. Excludes consideration of physical manipulations (water levels or flood flows) (after Hart et al. 2003a).

The need to establish the management issues and to clearly identify management goals is the primary starting point in the process of implementing a decision-support framework for environmental management (RMA 1991; ANZECC 2000). We included identification of management goals, problem formulation and establishing the cause of a specific problem (i.e., a cause-effect linkage), as key components in a protocol for investigating management options for sediment P release management in New Zealand lakes (Fig. 1). The framework for the decision-support protocol follows an ERA approach (USEPA 1998), addressing options relating to the application of methods to reduce internal P loads in lakes.

A key component of resource management is that multiple environmental issues commonly occur in relation to stress effects on a specific aquatic environment. Often the "problem" which requires management action, may only be identified when marked changes have occurred from the historic condition, or be recognised based on comparisons with those conditions existing in similar local or regional water bodies (i.e., reference sites). The transition from a management issue (e.g., declining native fish populations), to a management "problem", is commonly difficult to prescriptively define, since monitoring programmes may involve infrequent sampling and measurement of parameters which may not be the primary issue of concern. Additional challenges may also result from an inability of regulatory agencies to provide rigorous statistical certainty to detect a "significant adverse effect" trend in a population response, which usually requires an extensive time-series to demonstrate that the natural seasonal variability of a stressed population exceeds the variability found historically or in other reference water bodies. The problem may either have a direct link to the management issue (e.g., fish kill caused by cyanobacterial toxins), or an indirect linkage (e.g., decline in fish catches). A key component before implementation of a management action is to establish a cause-effect linkage between the problem and the proposed management approach (USEPA 2000). This linkage may only target one of the stress factors linked to the management concern, recognising that multiple stressors and environmental factors frequently combine to cause the effects observed in aquatic ecosystems. Recognising both natural biotic variability and the multi-stressor nature of many environmental phenomena, the implementation of an integrated approach with multiple management measures is often required to holistically address ecological issues in lakes.

Lake characterisation is another key component of management of internal lake nutrient loads (Fig. 1). The assessment includes gathering information on the physical characteristics of the lake (especially depth, stratification and deoxygenation), current nutrient status (including epilimnion and hypolimnion nutrient concentrations, information on major inflow and outflow volumes and nutrient concentrations) and phytoplankton characteristics (species composition, biomass and lake macrophyte information). Geothermal effects are a specific aspect of New Zealand lakes which markedly affect lakes in the Taupo volcanic zone. The geothermal contribution of arsenic (As) is a specific factor which might be expected to affect treatments for internal P, because of the chemical similarity of As binding to sediments (Aggett & Roberts 1986; Smedley & Kinniburgh 2002).

LAKE CHARACTERISATION

Characterisation of New Zealand lakes has largely focused on water quality with an emphasis on nutrients and deoxygenation (Burns 1995; Burns & Rutherford 1998), and trends of nutrients and the TLI (Ministry for the Environment 2006). For 32 central North Island lakes, the major ion composition, including pH and bicarbonate alkalinity, has been characterised (Timperley & Vigor-Brown 1986; Timperley 1987). Timperley (1987) estimated that geothermal water may contribute up to 78% of the dissolved salts present in these lakes, forming a significant contribution to many of the larger lakes in the Taupo volcanic zone and especially the Rotorua/Te Arawa lakes region. Coulter (1977) found that geothermal fluid can contain high NH_4-N concentrations (>40 g/m^3) and was a significant nutrient source to Lake Ohakuri (Taupo volcanic zone region) (Coulter et al. 1983).

Blomkvist & Lundstedt (1995) identified 7 of the 12 Rotorua/Te Arawa lakes as being geothermally affected based on elevated sediment mercury and arsenic (As) concentrations. The geothermal content of the Rotorua/Te Arawa lakes increases the sediment As content, which varies 130-fold between lakes (Table 1), though with no significant correlation between sediment As concentration and lake geothermal water content. Some lakes have sediment As contents greater than 1.0% of Fe on a molar basis, with the highest being lakes Rotomahana

Table 1 Sediment data for New Zealand lakes from the Rotorua/Te Arawa region of the Taupo volcanic zone from Trolle et al. (2008), Blomkvist & Lundstedt (1995) and McColl (1977). Names in bold indicate lakes with >1.0% arsenic (As) in relation to sediment iron (Fe) content. (WW, wet weight; TOC, total organic carbon; TKN, total Kjeldahl nitrogen; TP, total phosphorus; OrgP, organic phosphorus; *n*, number of core samples.)

		Trolle et al. (2008)						Blomkvist & Lundstedt (1995)										McColl (1977)						
Lake	Geothermal water %	*n*	TOC %	Fe mg/kg	TN mg/kg	TP mg/kg	TP/Fe Mole%	*n*	WW %	TOC %	Fe mg/kg	As mg/kg	As/Fe Mole%	TKN mg/kg	TP mg/kg	As/TP Mole%	TP/Fe Mole%	*n*	pH	TOC %	TKN mg/kg	TP mg/kg	OrgP mg/kg	OrgP/TP %
Awaatua								3	84.5	4.7	8270	28	0.3	3810	870		19.0							
Ngapouri	16																	10	6.5	5.2	4910	1780	330	18.5
Okareka	6	2	5.4	13 120	7020	1450	19.9	3	89.5	7.9	21 100	89	0.3	5875	1154		9.9	10	6.7	3.2	3380	810	290	35.8
Okaro	6	2	12.0	17 300	15 760	1950	20.3	3	93.7	10.8	10 500	78	0.6	9392	2247	3.2	38.6	10	6.6	7.9	8310	1600	350	21.9
Okataina	21	2	4.3	26 800	6590	2750	18.5	3	90.2	7.7	16 200	228	1.0	6390	2288	1.4	25.5	10	6.8	3.8	4120	1400	290	20.7
Rerewhakaaitu	16	3	14.0	36 970	17 870	1280	6.2	3	93.3	9.2	20 400	36	0.1	9165	1240	4.1	11.0							
Rotoehu	69	2	7.1	24 720	12 600	2060	15.0	3	91.1	9.4	7930	71	0.7	9513	1148	1.2	26.1							
Rotoiti	38	2	10.2	8890	18 870	3430	69.6	6	92.6	10.2	3835	53	1.0	9382	2200	2.6	103							
Rotokakahi	7	4	7.0	13 230	10 470	1870	25.5	3	92.6	8.5	8400	52	0.5	7775	1222	1.0	26.2	10	6.4	3.7	3940	690	290	42.0
Rotoma	64	3	5.5	19 120	8200	1440	13.6	3	90.9	8.3	20 400	318	1.2	6303	2015	1.8	17.8	10	7.1	4.6	4970	1510	370	24.5
Rotomahana	53	2	3.8	13 940	7950	1200	15.5	3	94.3	6.9	11 200	1390	9.3	5067	1440	6.5	23.2							
Rotorua	43	8	4.4	9490	6810	1050	20.0	9	95.0	11.3	3237	42	1.0	10 006	1726	39.8	96.1							
Tarawera	37	2	4.7	25 990	6900	3480	24.1	3	92.5	8.0	30 800	3010	7.3	5672	3300	1.0	19.3							
Tikitapu	13	2	5.2	7440	5160	470	11.4	3	90.0	7.2	8270	23	0.2	4548	641	38.0	14.0	10	6.1	4.0	3380	710	310	43.7
Mean	30		7.0	18 084	10 350	1869	21.6		91.5	8.5	13 119	417	1.8	7146	1653	9.1	33.1		6.6	4.6	4716	1214	319	29.6
SD	22		3.3	8934	4772	936	16.0		2.7	1.8	8075	862	2.9	2152	733	14.7	30.6		0.3	1.6	1710	462	32	10.6
Min.	6		3.8	7440	5160	470	6.2		84.5	4.7	3237	23	0.1	3810	641	1.0	9.9		6.1	3.2	3380	690	290	18.5
Max.	69		14.0	36 970	18 870	3480	69.6		95.0	11.3	30 800	3010	9.3	10 006	3300	39.8	103.0		7.1	7.9	8310	1780	370	43.7
Max./Min.	11.5		3.7	5.0	3.7	7.4	11.0		1.1	2.4	9.5	130.9	70.3	2.6	5.1	40.1	10.5		1.2	2.5	2.5	2.6	1.3	2.4

(9.3%) and Tarawera (7.3%) (Table 1), with these lakes having geothermal water contents of 53% and 37%, respectively. Notably, Lake Rotoehu has the highest geothermal water content (69%), but a low sediment As content in relation to Fe (As/Fe mole% = 0.7, Table 1), and Lake Rotorua a 43% geothermal water content and a low sediment As content (As/Fe mole% = 1.0), indicating the high variability of geothermal water composition between lakes. The calculated molar fraction of As compared with P is generally low (<5%), with the exceptions of lakes Rotoma (6.5%), Rotomahana (40%), and Tarawera (38%) (Table 1). High concentrations of sediment As are important considerations in relation to P binding to sediment minerals, as both As and inorganic P are expected to competitively bind to similar binding sites. Thus, As bound to sediment Fe can be released under anoxic conditions with DRP (e.g., Lake Ohakuri, Coulter et al. 1983), potentially leading to high concentrations in lake or reservoir waters (McLaren & Kim 1995). As will also competitively bind with sediment capping agents and reduce the efficiency of the P-binding capacity. However, the use of remediation processes to reduce internal P loading would also provide additional benefit in geothermally contaminated lakes of decreasing sediment As release (Tokunaga et al. 1999), and improving water quality for both ecological, human, and animal health uses. These data indicate that the sediment composition of some geothermally influenced lakes may be a significant consideration when selecting a remediation technique, if active capping agents are to be used.

The phosphorus content of surficial lake sediments is also highly relevant to the degree of internal nutrient cycling and the application of active capping agents (Cooke et al. 2005). However, although substantial limnological information is available about New Zealand lakes (e.g., Jolly & Brown 1975; Viner 1987), detailed sediment chemistry data are limited, with the most comprehensive data being for the Rotorua/Te Arawa lakes (McColl 1977; Blomkvist & Lundstedt 1995; Trolle et al. 2008) (Table 1), and for Lake Taupo (Viner 1989). Chittenden et al. (1976) measured surficial sediment nutrients (TN, TP) and mineralogy (by X-ray fluorescence) in three large South Island lakes (Brunner, Rotoroa, Rotoiti). Stoffers et al. (1983) made a "reconnaissance survey" of the mineralogy and geochemistry of sediments from different aquatic environments in New Zealand, including 3 North Island and 17 South Island lakes. No measurements of sediment organic or nutrient concentrations were undertaken in this study.

Trolle et al. (2008) compared sediment core data from 2006 with results from a 1995 survey (Blomkvist & Lundstedt 1995) and found that mean TP concentration increased in surficial sediments in seven of the 12 lakes studied, with deep sediments in three lakes (Rotoiti, Rotokakahi and Okareka) exceeding the highest concentration recorded in 1995 (Table 1). The sediment TP concentrations between these lakes ranged 7.4-fold, from 470 to 3489 mg/kg (dry weight), with a 5.0-fold range in total Fe content in the 2006 study (Trolle et al. 2008), compared with a 5.1-fold range in TP and a 9.5-fold range in total Fe in 1995 (Blomkvist & Lundstedt 1995) (Table 1). Lake Tarawera had both the highest Fe and TP content in 1995, with the highest Fe content found in Lake Rerewhakaaitu in 2006. Lake Rotorua had the lowest Fe content and a relatively elevated TP level in 1995, with Lake Tikitapu having the lowest Fe content in 2006. Viner (1989) reported an average TP for Lake Taupo (Taupo volcanic zone) of 700 mg/kg, which is markedly lower than all of the Rotorua/Te Arawa lakes, with the exception of Lake Tikitapu (Table 1). Similarly, the sediment TP concentrations for the South Island lakes Rotoiti, Rotoroa and Brunner (mean ± SD; 963 ± 173 mg/kg; 784 ± 266 mg/kg; 1330 mg/kg, respectively) (Chittenden et al. 1976), were lower than the mean TP concentrations for the Rotorua/Te Arawa lakes (Table 1). Trolle et al. (2008) found that 68% of the variation in net sedimentation rates across the Rotorua/Te Arawa lakes could be explained by lake trophic state and catchment area, and concluded that between-lake variations in sediment TP and TN concentrations are influenced by a range of complex interacting factors, such as sediment redox conditions as well as variations in sediment mineral composition. The high variability of sediment TP, Fe and geothermal As content in the Taupo volcanic zone lakes, indicates that individual lake sediment characterisation and site-specific assessments of the efficacy of active capping procedures are required.

ASSESSING SEDIMENT P LOADS

Only part of the TP in the sediment can be released under anoxic conditions and that proportion is considered to be "bioavailable P", i.e., P that can be released from the sediment as DRP (Psenner et al. 1984). Thus, although the TP content provides an upper (conservative) estimate of the P load to be managed, the proportion of bioavailable P should be considered when estimating minimum treatment rates and costs, if active capping agents are to be used. Spatial variability of sediment P content and redox conditions across the lake bed each affect the mass of P which is released (Syers et al. 1973). Consequently, the sediment P content should be estimated from multiple surficial sediment (0 to 4 cm layer; Cooke et al. 2005) samples from the area of lake bed which experiences anoxia beneath the hypolimnion during summer stratification. The permanently aerobic littoral zone is unlikely to release significant quantities of P and thus does not require remedial action with sediment capping.

Options for estimating the proportion of bioavailable P include using the seasonal proportion of DRP released from the sediment while the hypolimnion is anoxic, or sequential chemical extraction methods (Psenner et al. 1984; Cooke et al. 2005; Spears et al. 2007). McColl (1977) estimated the "organic phosphorus" content in sediment by measuring the difference in $0.5M$ H_2SO_4-extractable phosphorus before and after ignition in a muffle furnace, finding organic phosphorus averaged 30% of TP (range 18.5–43.7%) in 11 Rotorua/Te Arawa lakes (Table 1). Continuous flow incubations of sediment cores in a laboratory can provide estimates of the release rate or efflux of DRP and NH_4-N under anoxic conditions (e.g., Miller-Way & Twilley 1996). This technique can also be used to assess the suitability and efficacy of sediment capping materials on the sediments of the lake to be managed (Gibbs et al. 2007; 2008).

IDENTIFYING INTERNAL NUTRIENT CYCLING RELEVANCE

Estimating a whole lake nutrient budget requires derivation of N and P loads from different land-use types and from point sources. Nutrient sources to New Zealand lakes have been reviewed for diffuse and riverine sources (McColl & Hughes 1981; Rutherford et al. 1987; Vant 1987; Elliott et al. 2002); point sources (Hickey & Rutherford 1986); and agricultural sources (Wilcock 1986). Combined, these publications provide information that allows an integrated mass budget estimate, however, such estimates have not been undertaken for many New Zealand lakes.

If lake water has low DRP and TP concentrations throughout the year and does not thermally stratify producing an anoxic hypolimnion during the summer, it is unlikely that the internal nutrient cycling of P is the main cause of any algal blooms which might occur. Shallow lakes are generally considered unlikely to have significant internal P loads because they are generally well mixed and oxic throughout the water column. The exceptions are lakes with high Fe and Mn concentrations in the sediment, high DIN concentrations in the lake water, and with hypolimnion dissolved oxygen (DO) concentrations that fall below 50% saturation at night. For example, Lake Horowhenua is a shallow (maximum depth 1.8 m) iron-sand dune lake which has high DIN water concentrations in winter, and experiences low-DO-induced P releases from the sediments each morning in summer (Gibbs & White 1994). These releases are sufficient to produce prolific cyanobacteria blooms and remove almost all of the DIN, leaving free DRP in the lake water (Gibbs & White 1994). DRP may not always be measurable in lake water if there is a high uptake rate by algae as DRP is released from the sediment, and rapid turnover of the P by the algal assemblage as senescing algae leak nutrients back into the lake water.

Water quality measurements in lakes with high algal production that show relatively high DRP (>20 mg/m^3) and low DO (<5 g/m^3) concentrations in the bottom waters or hypolimnion during stratified periods indicate that sediment release is likely to be a main nutrient source for algal growth (Vant 1987; Spears et al. 2007). A rapid rate of oxygen depletion in the hypolimnion during the onset of thermal stratification leading to anoxia is an indication of high sediment oxygen demand (SOD) (Burns 1995), which may also indicate high internal nutrient loads. High TP concentrations (>2000 mg/kg, Table 1) with an N:P ratio of <6 in the upper 4 cm of the sediments of these lakes indicate a potential for significant internal nutrient cycling of P from the sediments to support algal growth in the lake water. Higher sediment N:P ratios would be similar to the planktonic ratios of about 10 given by White et al. (1985), whereas lower N:P ratios would reflect an inorganic P addition to the planktonic input and a potential for release under anoxic conditions.

Internal N-cycling may also result in sediment N release to the overlying water. Despite the nitrification-denitrification microbial removal of N from the lake, there may still be a substantial accumulation of DIN in lake water from sediment release when lakes have received waste water and other effluent discharges in the past (Burger et al. 2007). High DIN concentrations (>500 mg N/m^3) imply P-limitation to algal growth (Vant 1987), thus even small DRP input from the catchment stimulates an algal bloom (e.g., Schindler et al. 2008).

REMEDIATION TECHNIQUES

For any particular lake, there may be several options for reducing algal blooms, and using more than one remediation technique will improve the prospects for successfully reducing nutrient concentrations to below critical thresholds. Wherever possible, both N and P should be targeted together (Lewis & Wurtsbaugh 2008). Management strategies may also use short-term controls together with long-term remediation techniques to reduce water nutrient concentrations. Remediation techniques can be grouped into those that physically manipulate the lake environment without chemicals (e.g., aeration/oxygenation; enhanced flushing, dredging, and discing the sediments) (Klapper 2003; Ashley et al. 2009) and those that use chemical additions (e.g., shading, flocculation, and sediment capping using passive or active capping agents) (Cooke et al. 1993, 2005; Douglas et al. 2004). However, both the internal and external nutrient loads need to be managed concurrently for successful remediation of a degraded lake (Vant 1987; USEPA 1999; Elliott et al. 2002).

We outlined a decision-support process for addressing options for reducing lake sediment nutrient release targeting phosphorus (Fig. 1). The situation leading to a decision to undertake an ERA would be one where a management agency has a lake experiencing regular algal blooms, and has undertaken preliminary work to establish that a sediment capping approach is a feasible option for reducing the frequency and severity of algal blooms. The preliminary work would involve: (1) characterising the main drivers likely to be responsible for the algal blooms occurring in the lake. Specifically, information would be needed on: physical characteristics of the lake (including volume, depth, clarity, stratification, deoxygenation-including duration of anaerobic conditions); annual variation in the concentrations of major nutrients (TP, DRP, NH_4-N, NO_x-N); input/output budgets for the major nutrients); annual changes in algal biomass and species (chlorophyll *a*, floating bloom assessment); information on geothermal inflows (including water and sediment As concentrations); (2) determining the stratification classification and the potential for mixing of epilimnion and hypolimnion water; assessing whether the lake forms a stable stratification (depth, wind fetch) (Davies-Colley 1988; US Department of Agriculture 1999); (3) determining that sediments will release nutrients (P, N) under realistic conditions, particularly anaerobic conditions (sediment core measurements or hypolimnetic nutrient measurements); (4) considering other potential treatment options to address internal P loading (includes: lake aeration, hydraulic flushing, dredging of sediments, other source control measures); (5) determining that the active capping material will reduce sediment nutrient release under lake hypolimnetic conditions (laboratory bioreactor trials); (6) considering dosing regime of a/the capping agent. Dosing of the hypolimnetic area of a lake will target the main source area of sediment P release and minimise exposure of sediment-dwelling biota to the capping agent.

A preliminary ERA framework (Fig. 2) considers the types of receptors which may be adversely affected, and incorporates the problem formulation component addressing the nature of the stress effect(s). The supply of human and stock drinking water are a primary consideration in relation to the potential for release of chemicals into the lake water. A number of potential ecological effects may occur with both physical and chemical approaches, including smothering of the benthos, toxicity to water and sediment-dwelling species, turbidity and acidification (Table 2). Although many of these effects will be acute (i.e., relatively short-term), such as during the lake dosing period, some may be more chronic in nature (e.g., turnover of hypolimnetic waters with elevated ammonia and sulfide concentrations), with a potential for adverse effects on the whole lake ecosystem.

Physical techniques

Aeration

As the level of oxygen in the water immediately above the sediments is a key regulating factor for P release in most lakes (Smolders et al. 2006; Spears et al. 2007), a common remediation technique is the use of aeration, either with full lake mixing or hypolimnetic aeration without mixing (Klapper 2003). Maintaining an oxygenated hypolimnion also limits the release of ammonia, which may otherwise increase to potentially toxic concentrations (Beutel 2006). Aeration is a short-term management strategy that regulates both N and P concentrations in the water column (Beutel & Horne 1999), and may also limit dominance of cyanobacteria and surface scum formation owing to the resulting turbulence.

Whole lake aeration

Artificial mixing or destratification can be used in deep lakes (>10 m) to mix the thermally stratified hypolimnion with the epilimnetic waters. Full lake

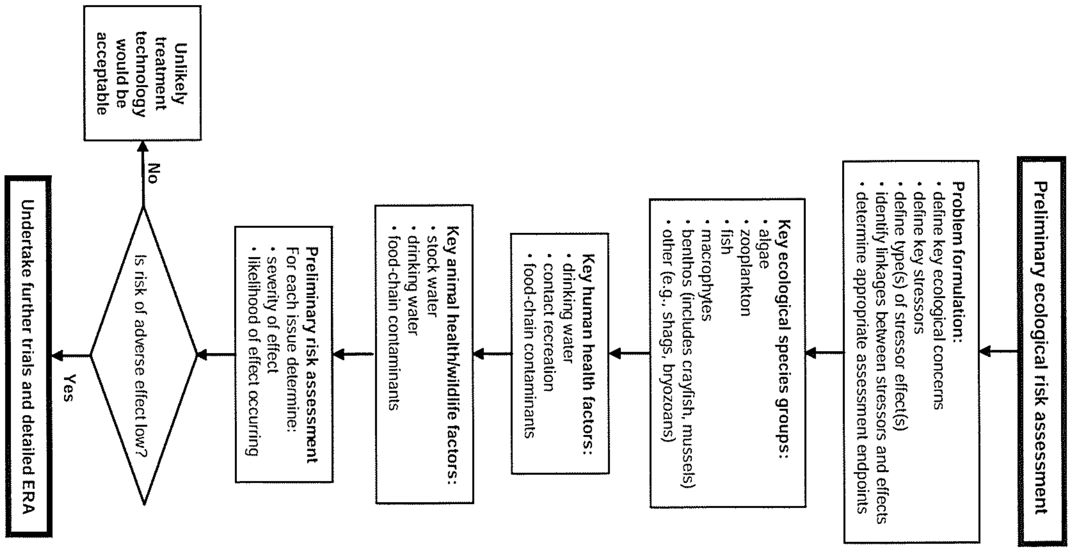

Fig. 2 Preliminary ecological risk assessment (ERA) for sediment nutrient release management in New Zealand lakes (after Hart et al. 2003a).

Table 2 Summary of chemical and physical management options for reducing sediment nutrient release (phosphorus, P), and undertaking an ecological risk assessment (ERA) in New Zealand lakes. (NR, not required; NA, not applicable; ND = no data; DW, drinking water; SW, stock water; ?, unknown; S, smothering; T, toxicity; Turb, turbidity by resuspension; A, acidification.)

Method	Product (CAS No.)	Available in NZ?	Registered in NZ for application to natural waters?	Current use in NZ lakes?	Phosphorus binding capacity (w/w %)	Basis for method	Key factors for success	Human health concerns when used as directed	Potential adverse environmental effects	Application method
Physical										
Aeration: whole lake		Y	NA	Y	NA	Iron oxide binding of P	Initiate when lake naturally mixed; sufficient iron in sediment to retain P	Tainting, odour if initiated when lake stratified	T, thermal alteration	Blower(s) and diffuser(s)
Aeration/ oxygenation: hypolimnion		Y	NA	N	NA	Iron oxide binding of P	Sufficient iron in sediment to retain P			Purpose-build system(s)
Hydraulic flushing		Y	NA	Y	NA	Increase inflow volume; may be linked with	Available water supply; ability to divert intake		T, SW (downstream)	Engineering

Method	Product (CAS No.)	Available in NZ?	Registered in NZ for application to natural waters?	Current use in NZ lakes?	Phosphorus-binding capacity (w/w %)	Basis for method	Key factors for success	Human health concerns when used as directed	Potential adverse environmental effects	Application method
						hypolimnetic outflow (if practicable)	(and outflow) to hypolimnion			
Dredging		Y	NA	Y	NA	Removal of sediment	Shallow depth to allow operation	DW	T, SW, Turb	Dredging devices
Riparian wetlands/ Shoreline restoration		Y	NA	Y	NA	Reduce sediment and nutrient loadings to lake	Nutrient source identification; treatment efficiency	NA		Engineering
Chemical										
Capping: calcite	Crushed limestone (471-34-1)	Y	NR	N	ND	Surface binding of P	Binding capacity, dose calculation		S, Turb or hypolimnion	Slurry to surface
	SoCal™	N	N	N	3	Surface binding of P	Binding capacity, dose calculation		S, Turb	Slurry to surface or hypolimnion
	ESCal™	N	N	N	1	Surface binding of P	Binding capacity, dose calculation		S, Turb	Slurry to surface or hypolimnion
Capping: zeolite	Modified (Scion)	Y	Y	Y	1.6 – 2.3	Aluminium (Al) precipitation of P	Binding capacity, dose calculation	DW	S, T	Granules to surface
Capping: bentonite	Phoslock™ (LaCl$_3$: 20211-76-1)	Y	Y	Y	1	Lanthanum (La) precipitation of P	Binding capacity, dose calculation	DW	S, T, Turb	Granules to surface
Capping: alum	Alum (7784-31-8)	Y	N	N	4.90	Al precipitation of P	Binding capacity, dose calculation, pH/alkalinity	DW	S, T, A, SW	Liquid to surface or hypolimnion
Capping: allophane		Y	NR	N	0.6-1.9	Surface binding of P	Binding capacity, dose calculation		S, Turb	Slurry to surface or hypolimnion
Capping: iron	Iron slag	Y	N	N	ND	Iron oxide binding of P	Binding capacity, dose calculation	DW	S, T	Granules to surface
Alum (flocculation)	Alum (7784-31-8)	Y	N	N	4.90	Al precipitation of P	Binding capacity, dose calculation, pH/alkalinity	DW	T, A, SW	Liquid to surface
Alum + smectite + buffer + algaecide	Baraclear™ (Bentonite: 1302-78-9)	?	N	N	ND	Al precipitation of P	Binding capacity, dose calculation	DW	T, SW	Granules to surface
Iron	Ferric chloride (7705-08-0)	Y	N	N	56	Iron oxide binding of P	Hypolimnetic oxygen		S, T, Turb	Liquid to surface
Polyaluminium silicate chloride	PASC	Y	N	N	ND	Al precipitation of P	Binding capacity, dose calculation	DW	T, SW	Liquid to surface

mixing uses a compressor to blow air through a perforated tube along the lake bed and the rising bubbles cause upwelling of the bottom water which disrupts any thermal stratification and mixes the lake (Klapper 2003). Applied at one end of a lake, the rising bubbles induce a strong circulation pattern through the whole lake. For example, the Auckland city water supply reservoir Mangatangi (depth 60 m; area 1.7 km^2) is maintained fully mixed with one aerator near the dam wall (M.M. Gibbs pers. obs.). Ideally, the lake should remain fully mixed throughout the year, and depending on the lake characteristics, aeration may only be required during summer. Aeration is important and should be started when oxygen concentrations fall below 6 g/m^3 in the hypolimnion in spring. This technique is often used in smaller lakes and reservoirs (Ashley & Nordin 1999). The main advantages are that reoxygenation of the lake is rapid (days to weeks) and expands the habitat range of benthic biota and fish where bottom waters were previously anoxic. A significant potential for adverse effects can be where long-term stratification in a lake has accumulated high concentrations of hydrogen sulfide (H_2S), As, DRP and NH_4-N in the hypolimnion, and vigorous aeration and mixing may cause a sudden release of these toxic constituents through the epilimnion, with resulting significant ecological impacts, including fish kills. A disadvantage of whole-lake aeration is that it treats the symptoms only and, if stopped, the lake will rapidly revert to its previous condition.

Hypolimnetic oxygenation

Hypolimnetic oxygenation without mixing requires a higher level of specialised capital equipment than whole-lake aeration (Beutel & Horne 1999; Klapper 2003; Cooke et al. 2005). This technique injects pure oxygen as fine bubbles into a confined column of hypolimnetic water so that the oxygen dissolves and oxygenated water is then returned to the hypolimnion. Because there are no free gas bubbles rising to the surface, the thermocline is not disturbed, which may be important where a lake has long-term stratification and build-up of high concentrations of toxic contaminants in the hypolimnion. The limitations, advantages, and disadvantages are similar to those for aeration with whole-lake mixing. The oxygenation efficiency is likely to be lower than whole lake aeration and the running cost will be higher because pure oxygen is used. The use of air would be less efficient than using pure oxygen and a different equipment design would be required to deliver the excess air to the lake surface without causing lake mixing (Ashley & Nordin 1999; Ashley 2000; Ashley et al. 2009). A management strategy might be to reoxygenate the hypolimnion to remove the potentially toxic components and lower the P concentrations before using aeration with whole lake mixing for longer term management. However, hyperlimnetic oxygenation may be more important where cool bottom water temperatures are required for water supplies (Ashley & Nordin 1999).

Hydraulic flushing

Manipulation of the hydrology of a lake with engineering structures can remove both nutrients and algal biomass through enhanced flushing (Klapper 2003). The introduction of additional water to a lake increases flushing and reduces the natural residence time of water in the lake. Flushing requires a source of water currently not entering the lake, which may be achieved by diverting or piping water from a river in an adjacent catchment into the lake. In addition to exchanging low-nutrient for nutrient-enriched water, less pristine water sources may be used with a weir on the lake outlet to skim off algal material produced in the lake and thus remove both N and P as particulate material.

Hypolimnetic siphoning selectively removes nutrient-enriched water from the lake and allows the lake to fill with higher quality nutrient-depleted water. For example, a weir on the lake outlet has a pipe that draws water from the bottom of the lake, so that low-nutrient water entering at the surface displaces the nutrient-enriched bottom water which is removed from the lake via the siphon (Klapper 2003). This technique requires the lake to remain thermally stratified to isolate the inflow and outflow waters which have different chemistries. Consideration needs to be given to the impact on the downstream environment as nutrient-enriched water discharged via the siphon may be anoxic and contain potentially toxic concentrations of NH_4-N or H_2S. Incorporating an aeration baffle below the outlet could reduce the impact of high NH_4-N and low DO concentrations on fish downstream by enhancing aeration and nitrification.

The advantages of enhanced flushing, including the hypolimnetic siphon, are that after the initial cost, running costs are minimal and these remediation processes actively restore a lake. However, the impacts on the downstream environment need to be considered, because of the potential to release toxic contaminants and to adversely affect food-chains, which may be reliant on the particulate organic matter from the lake or reservoir waters (e.g., Doi et al. 2008).

Dredging

Physically removing lake sediments is another engineering option that also targets both N and P. Dredging is the direct removal of sediment to reduce the internal load, but requires knowledge of the sediment structure to ensure that an adequate depth of high-nutrient sediment is removed (Klapper 2003). Although dredging works for small lakes, there are practical considerations of how much sediment to remove (including depth and spatial extent in a lake), where to put contaminated sediment following removal, and the feasibility and cost of moving considerable amounts of sediment.

The advantages of this approach include permanent removal of small areas of highly enriched or contaminated sediments, which may be adversely affecting the lake ecosystem. The disadvantages of this approach include: (1) the high cost of disposal of sediments if local agricultural use is not possible and if chemical contaminants are present in the sediments (e.g., urban runoff, geothermal contaminants); (2) the requirement for large and specialised machinery for large-scale excavations; and (3) the potential for significant disturbance and release of contaminants into lake water during dredging operation. Cost recovery may be possible for non-geothermally influenced lakes where the sediment becomes a source of fertiliser for agriculture.

Discing

Physical disturbance oxygenates sediments and enhances nitrification of pore-water NH_4-N to NO_3-N and thus the removal of N through denitrification. The RIPLOX method of sediment oxidation focuses on decreasing the P-release from sediments, using a combined surface sediment treatment by calcium nitrate ($Ca(NO_3)_2$), ferric chloride ($FeCl_3$) and lime ($CaCO_3$) (Ripl 1976). The $FeCl_3$ added to the sediments increases the binding capacity for P, and the $Ca(NO_3)_2$ increases the redox potential and also leads to oxidation of Fe bound on sulfide, which is also capable of binding P (Ripl 1976). The lime is added to increase the pH and optimise the lake sediment for denitrification. The application is usually in late spring, with chemicals applied by direct injection with discing of the upper sediment layer, as used in the treatment of Lake Lillesjön, Sweden (Ripl 1976).

The advantage of this approach is that the method can be directly applied to target high nutrient sediments to reduce both N and P internal loads, with minimal disturbance to sediments. The disadvantages include the cost of chemicals, the expensive application and the need for relatively shallow (<5 m) and flat lake bottoms.

Chemical techniques

Capping

Remediation treatments that use flocculation and sediment capping, passive or active, use similar products and are designed to enhance nutrient limitation for the growth of algae or to change the nutrient balance in favour of one group of algae over another. Flocculation and sediment capping should be regarded as short- to medium-term management strategies, as the treatment will become buried with fresh material from the catchment (Lewandowski et al. 2003). Consequently, it is important that concurrent catchment remediation action is also implemented to extend the longevity of each in-lake treatment.

Capping agents are used to reduce sediment nutrient release rate by permanently blocking the release of N and P from the sediments below the capping layer. Passive or active, the capping layer becomes buried by detritus after a few years and the decomposition of this organic matter fuels the release of nutrients from the sediments (Welch & Cooke 1999). However, if catchment input loads have also been subjected to remedial actions, the internal nutrient loads are likely to be reduced and the lake may become less eutrophic. Treatment at the recommended dose is expected to remain effective for several years before repeat treatment is needed (Welch & Cooke 1999; Cooke et al. 2005).

Passive capping agents

Passive capping agents, such as sand, gravel and clay, are designed to enhance burial of organic matter thus reducing SOD and the efflux of nutrients, both N and P, from the sediment (Jacobs & Förstner 1999; Cooke et al. 2005). This technique relies on reducing the diffusion rate of nutrients into the overlying water. The thicker and finer the layer of passive material, the lower the diffusion rate, and hence the greater the reduction in sediment-water exchange. Typical sediment capping thicknesses are >5 cm which limits this technique to smaller ponds and reservoirs owing to the large quantities of capping material required.

An advantage of this approach is that the new capping sediment can provide an improved habitat for sediment-dwelling species. However, a disadvantage is the potential for extensive smothering of benthos with addition of the thick capping layer. Targeting of capping to areas where hypolimnetic anoxia occurs will reduce possible adverse effects on the benthos.

Active capping agents

Active capping agents are chemically active barriers (Jacobs & Förstner 1999), available for the reduction of either NH_4-N (Besser et al. 1998; Nguyen & Tanner 1998) or DRP (Cooke et al. 2005), from sediments. Active P capping agents are designed to replace the reversible P-binding of Fe and Mn with an irreversible P-binding to the capping agent. These active agents include the natural products, allophane and aluminium sulfate (alum), and modified natural products such as, Phoslock™, a bentonite clay modified with a rare metal, lanthanum (La), and a zeolite modified with Al (Table 2; see Appendix 1 for key aspects of the active capping agents for sediment P reduction).

Alum

The most common flocculation agent is alum which binds with DRP in the lake water, even under anoxic conditions, and settles to the lake bed. Because alum is applied as a solution to the water column, it is critical that it is buffered to maintain a pH above 6.5 to prevent the formation of highly toxic Al^{3+} ions and to facilitate flocculation (additional information on pH limitations in Appendix 1) (Cooke et al. 2005). As the floc settles, it can also trap algae and other suspended solids resulting in clearer lake water. Provided the guidelines of application rates and pH are considered, alum can successfully sequester sufficient DRP to cause P-limitation and shift an algal assemblage dominated by potentially toxic cyanobacteria toward one dominated by non-toxic diatoms (Downing et al. 2001). There are also non-targeted effects to consider, including potential Al toxicity, acidification, smothering of the bed and effects on stock and human water supplies (Table 2). An unexpected pulse of NH_4-N in lake water after alum application was observed both in laboratory studies (Gibbs et al. 2008), and in a low-dose whole lake trial on Lake Okaro (Taupo volcanic zone) (Paul et al. 2008), where there was a post-treatment algal bloom. Although alum can also be used as a sediment capping agent (Cooke et al. 2005), its primary function is as a flocculation agent which requires the DRP to be freely available in the water. Thus alum should be applied towards the end of the stratified period when the hypolimnion is anoxic and the DRP from sediment release has accumulated to a maximum level. Used at the correct dose, alum treatment that settles as a capping layer on the sediment is expected to remain effective for at least 5 years and up to 20 years in some lakes (Welch & Cooke 1999) before repeat treatment is needed. The decline in treatment effectiveness over time is dependent on bioturbation and burial of the alum floc (Cooke et al. 2005).

No published sediment toxicity studies are available which provide tolerance thresholds for sediment-dwelling species in response to various thicknesses of alum floc. However, Narf (1990) studied five mesotrophic and eutrophic alum-treated lakes, finding increases in faunal density and diversity in nearly all treated lakes. Injection of an alum slurry into the hypolimnion is recommended to minimise whole-lake benthos exposure to the floc, although the increased complexity of the application method is expected to raise the cost of application, and may limit the use of alum to smaller lakes and reservoirs.

The main disadvantages of using alum as a sediment capping agent are: potential for pH reduction (may require buffer dosing); potential Al toxicity; uncertainty of where the floc will deposit on the lake bed—with potential for adverse affects on littoral benthic communities if alum is applied to the epilimnion; potential resuspension of floc in shallow lakes; and a restriction period for drinking water, irrigation and stock water (Table 2, Appendix 1). The advantages include: low material cost, flocculation of particulates and P-removal from water column; and applications to many lakes with documented sustained efficacy.

Modified zeolite

Modified zeolite is a new granular P-inactivation agent, "Z2G1", that has been developed as a capping agent (Scion, Rotorua, manufactured by Blue Pacific Minerals Ltd., Matamata, New Zealand) is an Al-based P-inactivation agent that uses a zeolite clay as a carrier for the Al and does not require buffering to avoid lake water acidification as can occur using alum in poorly buffered lakes (Cooke et al. 2005). Zeolites are known to have a high affinity for ammoniacal-N (NH_4-N) and other cations (Wen et al. 2006), and the modified zeolite retains the NH_4-N absorption properties of the base material. Z2G1 has been designed to be applied as a sediment capping material with a granular formulation that improves the settling rate and thus accuracy of treating specific areas of lake bed. The modified zeolite has the added capability of sequestering NH_4-N and thus is presently the only active capping agent that targets both N and P.

The toxicity of modified zeolite has been assessed for infaunal sediment-dwelling species and has undergone elutriation tests as part of the product registration process (Martin & Hickey 2007). Sediment testing of a range of modified zeolite doses was determined for 2 species (amphipod, *Phreatogammarus helmsii*; and clam, *Sphaerium novaezelandiae*), with elutriate testing to 3 species (algae, *Pseudokirchneriella subcapitata*; crustacean, *Daphnia magna*; fish, rainbow trout, *O. mykiss*). The sediment toxicity tests found significant effects for clam reburial at 700 g/m^2 and amphipod survival at 2100 g/m^2, but no detectable effects for amphipods or clams at a dose of 350 g/m^2 (Martin & Hickey 2007) The modified zeolite tested had a grain size of 1–3 mm. Finer grain size (<1 mm) provides a more consistent sediment coverage enabling a lower dose rate of around 200 g/m^2.

The advantages of the use of modified zeolite for sediment capping include: particulate granules (1–3 mm) at the recommended dosing (350 g/m^2) do not completely smother the bed, it is not susceptible to resuspension, both P and NH_4-N are locked-up, minimal effects on pH and on water column turbidity (Appendix 1). The disadvantages include: minimal P removal from water column, restriction period for drinking water, irrigation, and stock water; sinking and burial in low density (nepheloid) sediment will reduce efficiency; potential smothering and toxicity for high-dose applications (Table 2, Appendix 1).

Phoslock™

Phoslock™ is La-modified bentonite clay (developed by the Australian Federal Government-owned Commonwealth Scientific and Industrial Research Organization (CSIRO) and the Australian Water and Rivers Commission) to redress the fluxes of P that contributed to the occurrence of eutrophic conditions in the Swan River Estuary, Western Australia (Douglas et al. 1998). The mechanism of P removal by Phoslock™ involves the reaction of phosphate anions with La, leading to formation of a single insoluble species of lanthanum phosphate, or rabdophane (National Industrial Chemicals Notification and Assessment Scheme 2001; Douglas et al. 2004).

Douglas et al. (2004) consider that the use of La to remove phosphate was superior to the more conventional Fe and Al salts in five ways: (1) La is effective over a wider pH range (c. 4.5–8.5) than Fe (III) (c. 3.5-4.5) or Al (c. 5.0–6.5); (2) La precipitates polyphosphates equally well as orthophosphates; (3) the reaction of La with phosphate is stoichiometric; (4) almost total removal of phosphates can be obtained; (5) the solubility product of La-phosphate is extremely low (K_{sp} = c. –24.5 to –25.8).

Potential solute toxicity was largely overcome by the incorporation of La into clay minerals with high ion exchange capacity clay, such as bentonite. Large-scale field trials of the La-substituted bentonite Phoslock™, showed a substantial reduction in P released from bottom sediments when applied as a thin (c. 1 mm) capping layer (Douglas & Adeney 2001; Robb et al. 2003).

The toxicity of Phoslock™ to infaunal sediment-dwelling macroinvertebrates and trout (*O. mykiss*) has been assessed as a component of the product registration process in New Zealand (Clearwater 2004; Clearwater & Hickey 2004). Sediment testing included a range of Phoslock™ doses and determined effects on four species (amphipod, *P. helmsii*; oligochaete worm, *Lumbriculus variegates*; midge larvae, *Polypedilum parvidum* and *Chironomus zealandicus*), with juvenile rainbow trout exposed in the overlying water during the sediment-dosing and exposure procedure. The results showed that amphipods were the most sensitive species to Phoslock™, with a lowest observed effect threshold (LOEC) of an estimated sediment thickness of Phoslock™ of <0.4 mm resulting in a 15% reduction in survival (Clearwater 2004; Clearwater & Hickey 2004). Some trout mortality occurred with an increased dose from 40 to 200 g Phoslock™/m^3, which simulated dosing to a shallow (1 m depth) lake. The small increase in dissolved La in the overlying water, from 0.010 g La/m^3 to 0.014 g La/m^3, between these doses suggested that La was not primarily responsible for the increased trout mortality, which was probably largely owing to the high suspended solids concentration in the treatment system (Clearwater & Hickey 2004).

Whole-lake applications of Phoslock™ in New Zealand have been undertaken on three occasions in Lake Okareka (Taupo volcanic zone) (Environment Bay of Plenty 2007). Phoslock™ dosing gave a maximum dissolved La concentration of 0.010 g La/m^3 and took several months for the finest particles of Phoslock™ to sink to the lake bottom, with no adverse effects noted in the lake chemistry or fish and freshwater crayfish (koura, *Paranephrops planifrons*) health following treatment (Environment Bay of Plenty 2007). Significant bioaccumulation of La released from the Phoslock™ occurred in both koura and rainbow trout liver and hepatopancreas tissues, but the accumulation in flesh of both species was low (Landman et al. 2007). Physiological measurements did not demonstrate effects attributable to the increased La exposure.

The advantages of Phoslock™ for sediment capping include: the choice of granule or slurry application; and rapid dispersion of granular formulation in the lake water as a flocculent (Appendix 1). The disadvantages include: potential smothering of the benthos; slow settling of fine particles; and a restriction period for drinking water, irrigation and stock water (Table 2, Appendix 1).

While comparative laboratory tests (Gibbs et al. 2007; 2008) show that each of these products (alum, allophane, Phoslock™, and modified zeolite) remove DRP from the lake water and have the capacity to block the efflux of DRP from the sediments, the efficacy of each product is a function of its P-binding capacity (g P/kg product), the application rate, the product grain size (which affects sediment coverage and sinking into soft sediments), the stability of the capping layer on the sediment surface, and the pH of the sediment and overlying water.

A key factor affecting the success of a capping agent application is timing. In contrast to flocculation when the DRP needs to be in the lake water, the DRP needs to be in the sediments for effective capping, so that the capping agent can bind P and prevent its release under anoxic conditions. Thus capping agents should be applied when the lake is fully mixed and there has been time for DRP to be sequestered by Fe and Mn in the sediments so that DRP concentrations in the lake water are low.

A more practical factor to consider is the spatial accuracy and evenness of application to a lake bed. Although alum can be used as a capping agent, alum flocs are slow to settle out of the lake water which could allow it to drift beyond the target zone. In contrast, the more granular products (i.e., allophane, Phoslock™, and modified zeolite), will rapidly settle after application. Phoslock™ may be applied as a slurry which disperses into the water and offers some degree of flocculation but less accurate application as it slowly settles to the sediment. Because high treatment rates of these three granular products may form a gelatinous or cohesive layer across the sediment surface, it is important to estimate the appropriate dose rate for each lake sediment to minimise the thickness of the capping layer which affects natural sediment processes (Vopel et al. 2008).

DISCUSSION

The restoration of a lake through management of sediment nutrient release is only one part of what should be an integrated approach including catchment nutrient management. The reduction of internal nutrient loading may be achieved by either physical or chemical approaches, or by a combination of both approaches. The management of internal nutrient loads is often only a short-term measure and the period between treatments varies from daily to seasonal, for aeration options, up to several years for active capping agents. The longevity of the treatment effectiveness using sediment capping is reduced if the external nutrient loads are not managed concurrently. Consequently, an important consideration for management of internal nutrient loads is the annual cost to treat the lake to achieve the desired goal.

The successful implementation of internal nutrient management measures requires site-specific consideration of a range of factors affecting the success and sustainability of the approach(es) used, together with an assessment of the potential for adverse effects on ecology, livestock and humans. For example, the release of toxic Al^{3+} ions into the water column may occur where the dose rate of alum or aluminium-based capping agents is excessive and the pH is low or where alum was incorrectly buffered and failed to form a floc (see Appendix 1) (Cooke et al. 2005). Also, laboratory studies have shown that, although sediment capping agents sequester P, they can also affect the benthic microbial processes of nitrification and denitrification under aerobic conditions (Gibbs et al. 2008), with the increased thickness of the diffusive boundary layer being a significant factor contributing to these effects (Vopel et al. 2008). The consequence of these effects is that N concentrations may increase in the water column for several weeks immediately after treatment (Paul et al. 2008).

The four most common P-inactivation agents available as active sediment capping agents in New Zealand are alum, allophane, Phoslock™, and modified zeolite. These capping agents function optimally in well buffered (high alkalinity) lakes, through different pH ranges and thus, the sediment and water column pH is an important factor in determining the dose rates of these products for a specific lake. Although our information on New Zealand lake sediments is limited to relatively few lakes, the available data indicate a relatively large variability in Fe content (about 10-fold, Table 1), with a similar range in the TP/Fe percentage, and a 5-fold range in sediment TP content. No information is available on the fraction of "bioavailable-P" in sediments for New Zealand lakes, though the organic-P content ranges over 2.4-fold, indicating additional variability which influences the estimation of treatment requirements. Although TP may be used as a conservative estimate for initial treatment rate calculations, measurement of bioavailable P will enable those treatment rates to be reduced along with the costs. A lack of buffering in soft-water lakes of the Taupo volcanic zone make it important to establish P-binding efficacies in the laboratory before undertaking whole-lake treatments.

The variable Fe content affects the ability of sediment to bind P under aerobic conditions, and thus the potential efficacy of aeration alone as nutrient reduction treatment. Capping agent P-binding capacity ranges from 0.6% to 4.9% on a dry weight basis (Table 2), requiring that the dosing loading is calculated on a site-specific basis. Combined, these factors require a systematic approach for the lake assessment and management implementation process.

The framework for the decision-support approach follows the three stages involved in undertaking an ERA—problem formulation, risk analysis and risk characterisation (USEPA 1998). The ERA process seeks to: identify the key ecological issues and key stressors; identify the linkages between the key stressors (drivers) and each ecological consequence (based on conceptual models or quantitative ecological models); determining the best assessment "endpoints" to use in the risk assessment; and identifying the risks associated with various management actions to control the issue of concern. A tiered approach is used to address the various components of the ERA.

The initial tier of the ERA is the problem formulation, in this case related to the possible application of measures to control internal nutrient (P) loads in lakes (Fig. 1). Here we assumed that the key issue of management concern is the production of algal (cyanobacteria) blooms, which are supported by high internal nutrient (P) loads from sediment release, and that a realistic P-reduction goal has been set, which can be achieved through management of those internal P loads. This process includes establishing objectives for the restoration programme. Once the problem is identified, knowledge of the cause-effect linkage may be used to determine the best approach for management of internal nutrient load. For sediment capping agents, the assessment process also includes undertaking laboratory trials with the capping material using the lake water and the lake sediment as part of the initial feasibility studies.

The following components are also required for standardised active capping agent evaluation procedure: (1) adoption of a standardised calibration procedure for lake sediment characterisation and capping agent evaluation; (2) use of a calculation procedure based on readily determined sediment parameters and known capping agent characteristics to determine theoretical minimum dose requirements; (3) application of an experimental approach for laboratory testing which is designed to derive a minimum dose for binding released P and response to higher application rates (i.e., a dose-response design); (4) an adjustment procedure to the theoretical basis which may be required to allow for efficiency (e.g., non-stoichiometric binding) and formulation (e.g., particle size or slurry) differences affecting product performance under anticipated lake conditions; and (5) field-dosing estimation to include "application factors" (AFs)—i.e., margins for factors reducing efficiency (e.g., physical disturbance, bioturbation, retention/saturation in lake water, sediment and water column pH, geothermal influence), sustainability (e.g., total binding capacity, burial) and lake seasonality (e.g., the optimal time to treat).

Understanding of the relative importance of both product-specific factors and lake-specific factors is required to develop: (1) a minimum dose requirement; (2) a field-dose requirement; and (3) a basis for estimating the expected sustainable efficacy period. Cooke et al. (2005) provide a dose estimation procedure for alum based on chemical measurements of sediment P. Previous studies used a laboratory-based flow-through system with cores and natural and nutrient-amended lake water to quantify the dose requirements for different capping agents, including modified zeolite to Lake Okaro sediment (Taupo volcanic zone) (Gibbs et al. 2007), and alum, modified zeolite, Phoslock™ and allophane to Lake Rotorua (Taupo volcanic zone) sediment (Gibbs et al. 2008). The advantage of the flow-through approach is that it permits long-term measurements of efficacy for P-binding under steady-state nutrient conditions in the overlying water and for testing under aerobic and anoxic conditions. Nutrient flux measurements for N and P, together with heavy metals and metalloids, permit assessment of potential adverse effects on sediment microbial processes (e.g., nitrification, denitrification) and the release of potentially toxic contaminants (e.g., As, Al^{3+}, La^{3+}). A continuous flow-through incubation system has also been used to demonstrate the effects of temperature, a lake-specific seasonal factor, on P release from natural eutrophic lake sediments (Søndergaard 1989). This temperature dependence on P-release rate indicates that the field dose requirement for capping agents may need to consider the effects of seasonal temperature changes on the internal P loads.

The use of alum provides a key example of the need for site-specific adjustment of the capping dose. The precipitation of P can be achieved with aluminium salts because the newly formed aluminium hydroxide ($Al(OH)_3$) strongly binds inorganic P. In contrast to ferric hydroxide, $Al(OH)_3$ complexes are not sensitive to redox changes, however, low as well as high pH results in dissolution of $Al(OH)_3$ due to the amphoteric nature of Al (Appendix 1). While the optimum pH for P precipitation occurs at about pH 7, with a cation:P molar ratio of 1:1, the efficiency declines at other pH values (Peterson et al. 1976). Peterson et al. (1976) used sodium aluminate in pond water and achieved maximum removal efficiency over a narrow pH range (pH 4 to 6) and required a 7.2:1 cation:PO_4-P molar ratio to achieve a 90% reduction of the water phosphorus. A molar ratio of 12.6:1 was determined for 6 lakes in Washington (United States) (Rydin et al. 2000), with a ratio of 5.7:1 for Lake Delavan (United States) (Rydin & Welch 1999), and 2.1:1 for hypereutrophic Lake Süsser See (Germany) (Lewandowski et al. 2003) based on profiles of measured P and Al in sediments. In an evaluation of the effectiveness of reducing TP and longevity of alum treatments in 21 dimictic lakes across the United States, Welch & Cooke (1999) found that the internal loading rate was reduced by c. two-thirds and TP was reduced by c. one-half for a period of 5 to 11 years. Cooke et al. (2005) conservatively recommend a molar ratio of 100:1 (Al:P) based on the lowest ratio achieved in three Wisconsin (United States) lakes. Together, these trials and field application studies indicate that substantial additional Al above the theoretical stoichiometric quantity is required if P concentrations are to be reduced and then maintained at low levels for a range of lake pH conditions. In contrast, the binding efficiency of rare earth elements (e.g., La) is not affected by redox conditions and is only minimally affected by pH, so these elements may be more suited to lake dosing over a wider range of water quality conditions.

The product P-removal efficacy is affected by the formulation used and the method of field application. For example, solid products may be applied using a particle spreader or as a liquid slurry, while alum may include a buffer to minimise pH reduction in soft-water lakes (Table 2). Products with a large particle size (e.g., modified zeolites), are expected to have a critical threshold for sediment cover which must be reached to achieve an effective capping layer. The particle size and density are also important where the sediment has a nepheloid layer, which would allow differential sinking of the particles instead of the formation of a coherent capping layer. Smaller particle size would be less likely to sink, owing to higher surface tension at the sediment interface. The overall efficiency of all capping products is dictated by the lake-surface spreading precision of the applicator. Only hypolimnetic alum dosing may provide the exception, since its slow floc settling is expected to provide a greater opportunity for dispersion before settling to form a sediment capping layer.

The field application also requires inclusion of an AF to the laboratory-derived or theoretical dose. The AF is a "safety factor" from the perspective of P removal and sustainability of the capping barrier. The margin for the AF is arbitrary but needs to consider a range of site-specific factors which might be expected to reduce the *in situ* efficacy of the barrier. These factors include: physical disturbance (e.g., sediment degassing); bioturbation; burial; and application and composition variability within the lake. Together, these factors will individually or cumulatively act to reduce the efficiency of the barrier and the sustainability of a given application over time, thus requiring either greater quantities of capping material for each application, or more frequent dosing. Once the P is bound to the capping agent, it is not released, but more recent P from sediment on top of the layer is released under anoxic conditions to become the new source of P for the lake.

Implementation of an active management regime for internal nutrient management will require an ERA, with this two-tier assessment addressing possible adverse ecological effects (Fig. 2). In addition to the beneficial effects of significantly reducing the proliferation of cyanobacterial blooms, there are potential adverse ecological effects. The primary stressors in this situation would be the sediment capping agents, though consideration should be given to possible secondary effects (e.g., deoxygenation caused by alum precipitation of planktonic algae). The primary concern of a preliminary ERA would include identifying key ecological species or groups which may be affected, and identifying routes for potential livestock and human health exposure and effects (Fig. 2).

A common stressor effect of sediment capping agents is smothering of benthos, with the potential for adverse effects increasing with increased layer thickness. All capping agents raise the oxic/anoxic boundary depth within the sediment towards the

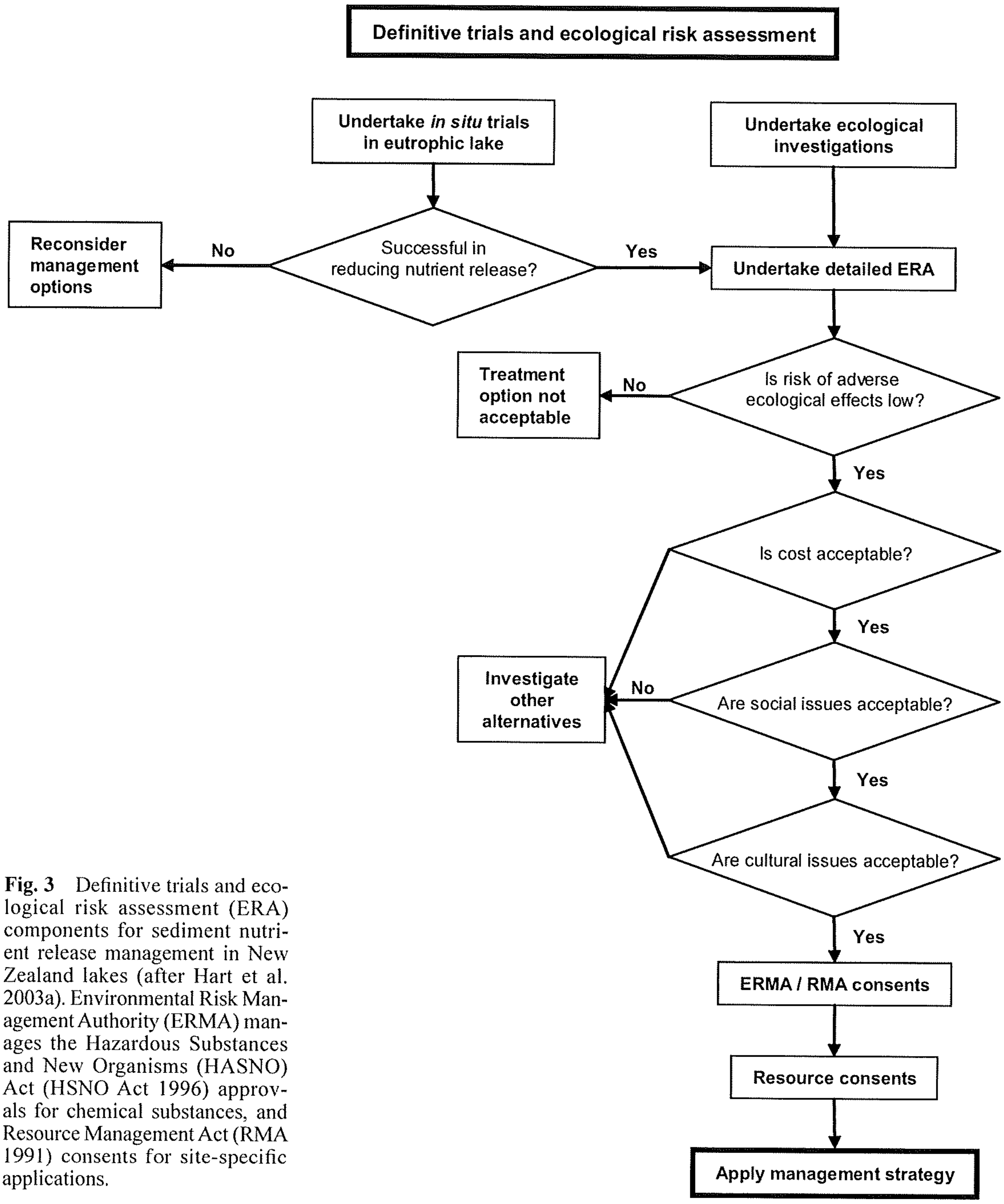

Fig. 3 Definitive trials and ecological risk assessment (ERA) components for sediment nutrient release management in New Zealand lakes (after Hart et al. 2003a). Environmental Risk Management Authority (ERMA) manages the Hazardous Substances and New Organisms (HASNO) Act (HSNO Act 1996) approvals for chemical substances, and Resource Management Act (RMA 1991) consents for site-specific applications.

natural sediment/water interface, and potentially to levels within the capping material layer (Gibbs et al. 2008; Vopel et al. 2008). This effect is caused by the combined effects of increased diffusion resistance and a longer diffusion path to reach the sediment interface. The susceptibility of a given macrofaunal species is dependent on its ability to exchange oxygen with the overlying water, either directly or through irrigation of burrows. Availability of microbial and meiofaunal food supply is also affected to some extent by the capping material. A low density floc material, such as alum, may pose a high physical risk in that many invertebrates are unlikely to be able to support themselves above the capping layer. We are unaware of any sediment toxicity thresholds for alum floc, though sediment-dwelling and freshwater species have been used in effects studies for other sediment capping product registrations (Clearwater 2004; Clearwater & Hickey 2004; Martin & Hickey 2007). These dose-response effects studies provide quantitative information for use in risk assessments. A key component of an integrated risk assessment is to assess the ecological risks for the whole lake and consider a range of time scales appropriate to sustainable management. Although some short-term effects may occur during the treatment phase, the ERA must balance these effects with the ecological improvements and other beneficial uses.

Definitive product trials and a detailed risk assessment may be required before application of a capping barrier. A range of components are incorporated in this tier of the ERA (Fig. 3). One component of these investigations may be to undertake *in situ* trials in the lake, which may have specific objectives which are not readily addressed in laboratory-scale trials (e.g., disturbance, reburial rate), specifically addressing efficacy, ecological effects and sustainability. These studies would refine the stress exposure and ecological response under more realistic, and often longer-term (chronic) exposure conditions. A number of methods become cost or logistically infeasible once the lake size exceeds a threshold. These size thresholds will differ between treatment types depending on the cost of product and the logistics of application. These components form part of the detailed ERA and assessment of environmental effects (AEE). The AEE needs to include social and cultural values which need to be considered on a case-by-case basis with public and multi-agency consultation. The result of this consultation process may be concerns with a specific product or approach, and the selection and decision-making process may need to be modified accordingly.

Application of capping products in New Zealand requires approval under the Hazardous Substances and New Organisms (HSNO) Act, which is administered by the Environmental Risk Management Authority (ERMA), and consent for individual applications under the Resource Management Act (RMA) (RMA 1991; HSNO Act 1996). At present, alum is not approved for application to natural waters (S. Scobie, ERMA pers. comm.), whereas Phoslock™ and modified zeolite (Z2G1) have approvals. Application of a natural product for capping (e.g., allophane) would not require ERMA approval. All capping and chemical treatment products require site-specific AEE and RMA consents for the application and associated effects and compliance monitoring. For some lakes, additional approval may be required from the New Zealand Government, Department of Conservation, where threatened or endangered species are present or the lakes are in conservation land. Special consideration for protection of native or indigenous species may be made under the provisions of the RMA (1991).

Chemical and physical remediation methods are not the only techniques that can be used to improve the water quality of a lake. Much research has been done on the use of biomanipulation in Northern Hemisphere lakes (e.g., Søndergaard et al. 1990). The main difference between Northern Hemisphere lakes and New Zealand lakes is the lack of piscivorous fish in the native fish food chain (Howard-Williams & Kelly 2003). However, the introduction of exotic fish (e.g., perch) to many New Zealand's lakes has seen their rapid decline in water quality, mostly associated with destabilising the sediments as these exotic fish forage (e.g., Rowe 2007). Biomanipulation to remove or introduce exotic fish species was beyond the scope of this paper, but illustrates the need for an integrated and site-specific approach to managing lake water quality.

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Appendix 1 Decision support and risk assessment information for chemical and physical methods for sediment nutrient (phosphorus, P) release management in New Zealand lakes. Appendix is organised into separate sections for each treatment option, to provide a profile for each chemical or physical treatment. Chemical Abstract Service (CAS) Numbers are reported for some chemicals. CAS Numbers are unique identifiers for individual chemicals, used to avoid confusion of systematic chemical nomenclature and common chemical names.

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1 General treatment—alum

1.1 Compounds

Alum

1.2 Synonyms/formulations

Alum granules; alum solution (40%); buffered alum

1.3 Active ingredient

Aluminium sulphate, $Al_2(SO_4)_3.16\ H_2O$, CAS No. 7784-31-8; buffer (calcium carbonate, calcium bicarbonate)

1.4 Mechanism

Alum may be used to treat the water column for solids and phosphorus removal and/or to provide sediment capping to control internal loading. It is usually applied in the form of aluminium sulphate that dissociates in water forming ions which are hydrated. A subsequent series of hydrolysis reactions leads to the liberation of hydrogen ions and, in the appropriate pH range (c. pH 6 to 8), the formation of aluminium hydroxide, $Al(OH)_3$, a colloidal, amorphous floc with high coagulation and P adsorption properties that settles through the water column to the sediment surface.

To form flocs, aluminium sulphate requires the presence of alkalinity, which, if naturally present in the form of bicarbonate, would lead to the following reaction:

$$Al_2(SO_4)_3\_xH_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + xH_2O + 6CO_2 \qquad (1)$$

In the presence of phosphate, the following reaction also occurs:

$$Al_2(SO_4)_3\_xH_2O + 2PO_4^{2-} \rightarrow 2AlPO_4\downarrow + 3SO_4^{2-} + xH_2O \qquad (2)$$

Alum has been widely used for phosphorus removal in lakes (Cooke et al. 2005). The stoichiometric equation (2) indicates a molar ratio of 1:2 (alum:P; or 1:1 cation:P), and that each kg of P requires 0.87 kg of aluminium for complete precipitation. Thus for hydrated alum ($Al_2(SO_4)_3.16\ H_2O$) with an aluminium content of 4.3% the P precipitation will maximally be 4.9% of the mass of alum added. Additional alum will be required to allow for reduced precipitation efficiency at different pH values

1.5 Application techniques

Liquid application to surface or hypolimnion

1.6 Application rates

Based on: (1) water column dissolved reactive phosphorus (DRP); (2) surficial (0-4 cm) sediment readily available P; (3) seasonal hypolimnetic P production; or (4) sediment flux rate. Additionally, an "application factor" adjustment to the calculated stoichiometric quantity of alum is required to adjust for other factors affecting P-binding efficiency

All dosing is limited by lake alkalinity to maintain pH above 6.5 (see dose estimation in relation to alkalinity, Cooke et al. 2005). Buffer (calcium carbonate) may be added to alum to allow increased dose

1.7 Key issues

- acidification of lake to pH <6 when unbuffered alum used in low alkalinity waters → no floc formation and

formation of highly toxic Al^{3+}
- low concentration alum addition to waters at high pH (e.g., during algal bloom) resulting in no floc formation
- disruption of floc by wind mixing or high bioturbation activity
- hydraulic flushing causing floc disturbance

1.8 Environmental effects
- water column Al toxicity
- water column pH reduction (if unbuffered)
- sediment smothering of benthos
- sediment toxicity

1.9 Registered/available in New Zealand
Not registered by Environmental Risk Management Authority (ERMA) for use in natural waters.

1.10 Source
Orica Chemicals Ltd, New Zealand

1.11 Human and livestock health
Drinking water: 0.1 g Al/m^3 (aesthetic determinant) (Ministry of Health 2005)
Livestock: 5 g Al/m^3 (ANZECC 2000)

1.12 Ecological guidelines
Freshwater: pH <6.5, "insufficient data"; >6.5, 0.055 g/m^3 (ANZECC 2000)
Sediment: no guidelines. Vopel et al. (2008) provide thickness measurements in relation to dose

1.13 Environmental fate/degradation
- sediment and burial if precipitation occurs
- elevated water concentrations if precipitation is incomplete (i.e., pH <6; >9)

1.14 Advantages
- low material cost
- liquid application
- can be applied to either lake surface or hypolimnion
- flocculation of particulates and P removal from water column
- applications to many lakes with documented sustained efficacy (Cooke et al. 2005)

1.15 Disadvantages
- aluminium toxicity
- pH reduction
- low floc stability
- need to measure dosage rate
- smothering of benthos
- restriction period for drinking water, irrigation and stock watering

1.16 Comments
Alum dose optimisation. Aluminum hydroxide flocs are least soluble at a pH of approximately 7.0. The solubility of $AlPO_4$ is related to the pH and the equilibrium constant for the salt. Stumm & Morgan (1995) state that the solubility of aluminium phosphate is pH-dependent, and the optimum pH for phosphorus removal is in the range of 5.5 to 6.5. Peterson et al. (1976) found that sodium aluminate in pond water achieved maximum phosphorus removal efficiency over a narrow pH range (pH 4 to 6), and required a 7.2:1 cation:PO_4-P molar ratio to remove 90% of the phosphorus at circum neutral pH. This finding contrasts with the stoichiometric expectation of an equimolar relationship for phosphorus precipitation (equation 2) and indicates the increased predominance of the hydroxide precipitation (equation 1) as pH increases. Thus, the efficiency of precipitation varies with the ambient pH, and is higher in an acidic environment, such as an anoxic hypolimnion, or in contact with sediments (Vopel et al. 2008).

Alkalinity. Cooke et al. (2005) provide calculations to estimate the amount of aluminium which may be added to water for a given alkalinity to maintain pH above 6.5. They recommend a minimum alkalinity of 35 g $CaCO_3/m^3$ to allow for addition of sufficient Al to lakes for long-term control of P release and to undertake a trial titration of the lake water with alum prior to dosing. Care must also be taken that pH is in the range for floc formation following dosing when using low-dose alum in eutrophic lakes with a high pH (e.g., see Paul et al. 2008). For lakes with low alkalinity, or those requiring high Al doses, a buffer (sodium carbonate) must be added to maintain pH in the range suitable for floc formation and to provide some residual buffering capacity for photosynthetic activity effects on pH (Cooke et al. 2005).

Sediment capping dose estimation. There are three procedures for determining the dose of alum to inactivate sediment P (Cooke et al. 2005). These alum doses are based on: (1) the lake alkalinity; (2) the estimated rates of net internal loading from the sediments as determined from a mass balance equation; and (3) direct determination of mobile inorganic P in sediments. The first method may be generally limited in New Zealand Taupo volcanic zone lakes because of low alkalinity. For the second method, Cooke et al. (2005) cite an example for Eau Galle Reservoir, Wisconsin, United States, where the summer internal P load was calculated and multiplied by 5 with the goal of controlling P release for

Appendix 1 (*continued*)

5 years as a desirable target. The amount was then doubled to account for any underestimate in internal loading. A variation of this procedure is to use direct flux measurements of anoxic sediment cores to estimate the summer internal loading for dose calculations. For the third procedure, representative surficial sediment samples are collected and mobile P as iron (Fe)-P (or bicarbonate dithionite) and loosely sorbed P (according to Psenner et al. 1984) in the top 4 cm of each core. However, the residual-P pool was found in 6 Washington (United States) lakes to represent only a relatively small fraction (10–20%) of the total phosphorus (TP) (Rydin et al. 2000), indicating that TP may be a useful indicative measure of dosing requirement. The dose in g Al/m^2 is determined by the product of the mobile P content and a ratio of Al added:Al:P formation expected. This ratio was 100:1 as observed in *in vitro* experiments performed in three Wisconsin lakes (Rydin & Welch 1999; Cooke et al. 2005). Combined, these trials and field application studies indicate that substantial additional Al is required above the theoretical stoichiometric quantity if P concentrations are to be reduced and maintained at low levels for a range of lake pH conditions. A factor of 5 to 7 times appears to be required as a minimum "adjustment factor" to allow for reduced binding efficiency and other factors affecting efficacy of P-removal in natural lakes.

Toxicity. Whole-lake alum dosing may result in significant adverse effects on the lake ecology as a result of changes in water quality (pH reduction, aluminium toxicity) and smothering of the benthos. The pH of lake water may be maintained in an appropriate physiological range by: (1) addition of alum within the alkalinity buffering capacity of the lake; or (2) dosing with a mixture of alum and sodium aluminate; or (3) inclusion of additional alkalinity (e.g., sodium carbonate) with the alum dose (Cooke et al. 2005). Water column toxicity is of concern with aluminium, the chemical form of which is dictated by the pH. Between pH 6 and 8, most of the Al is in the form of floc as $Al(OH)_3$. As the pH declines below pH 6.0, the concentration of the more toxic Al^{3+} becomes increasingly important. The United States Environmental Protection Agency's (USEPA) acute water quality criteria for pH 6.5–9.0 waters is 750 mg/m^3 and a chronic criterion of 87 mg/m^3 based on total recoverable metal in the water column (USEPA 2006). For the chronic guideline, the document notes that the use of a water-effects ratio, to modify this criteria for site-specific application, might be appropriate as the chronic guideline was based on a fish test in acidic and low hardness water (pH 6.5–6.6 and hardness <10 g/m^3). USEPA (2006) further state that: (1) "the total recoverable metal procedure might measure aluminium associated with clay particles, which might be less toxic than that associated with aluminium hydroxide"; and (2) "EPA is aware of field data indicating that many high quality waters in the United States contain more than 87 mg aluminium/m^3, when either total recoverable or dissolved is measured." The Australian and New Zealand Environment and Conservation Council (ANZECC 2000) water quality guideline for aluminium is 55 mg Al/m^3 for pH >6.5 for chronic exposures. Everhart & Freeman (1973) found that rainbow trout (*Oncorhynchus mykiss*) could tolerate chronic exposure to 52 mg/m^3 of dissolved Al with no significant changes in behaviour or physiology. Gensemer & Playle (1999) provide an updated review of Al toxicity to fish, with a focus on mechanisms of toxicity, and the role of Al speciation in controlling bioavailability. These two studies indicate that the bioavailability and toxicity of Al is strongly influenced by ambient water quality, including pH and organic matter, and site-specific studies may be required for sites where high doses are applied.

There are additional exposure and dosing factors which should be considered in a lake treatment exposure to Al in the water column. Whole-lake dosing, unlike a continuous exposure bioassay, produces a single maximum dose exposure to organisms, followed by a rapid decline in concentration as the floc settles through the water column (1-2 h) (Cooke et al. 2005). This short exposure duration is likely to markedly decrease the risk compared with the acute water quality criteria. However, although dissolved Al concentrations may not result in toxicity during this dosing period, some effects on planktonic species may occur because of entrainment in the floc (C. Hickey pers. obs.). The overall effects of this entrainment are not expected to result in a long-term reduction in the populations of zooplankton in a lake, but may require site-specific consideration. Dosing may also be restricted to the hypolimnion. Cooke et al. (2005) summarise alum doses for 19 United States lakes, with c. half dosed in the hypolimnion. The advantages of dosing the hypolimnion are that it reduces the total quantity of alum required, targets the area producing the internal nutrient release and can markedly reduce the biota exposure. However, the disadvantage of dosing during lake stratification is that the mass of phosphorus contained in the epilimnion will not be reduced, which may result in a sustaining of the existing bloom situation. If the hypolimnion is anoxic for extended periods of time, then the numbers of exposed biota is likely to be minimal compared with whole-lake dosing.

Settling of floc on the lake bed significantly alters the chemical environment and may adversely affect the benthos. A main disadvantage of alum floc over other sediment capping agents is its low density, which will not physically support most macroinvertebrate species. Deoxygenation of the overlying floc layer can result in anoxic conditions within the capping layer (Vopel et al. 2008), and exceedance of this threshold is expected to significantly reduce survival of many infaunal species.

No published sediment toxicity studies that provide tolerance thresholds for sediment-dwelling species in response to various thicknesses of alum floc are available. However, Narf (1990) studied five mesotrophic and eutrophic alum-treated lakes, finding increases in faunal density and diversity in nearly all treated lakes.

Timing of dosing. The timing of dosing for any sediment capping is a critical consideration relative to maximising efficiency and the sustainability of treatment. Whole-lake dosing when the lake is fully mixed and at the end of the winter period maximises the mass of phosphorus held within the sediment, and the capping layer includes the flocked material from the overlying water column. Importantly, dosing at that time minimises algal biomass that forms during the growth season and is deposited as detritus following lake turnover. This detrital material ultimately buries the capping layer to a depth where its nutrient removal ability does not significantly contribute to P cycling in the overlying lake water. This burial process, rather than the inherent phosphorus binding capacity of the capping material, may then be the main factor defining the sustainability of the treatment process.

Low-dose application to Lake Okaro, Taupo volcanic zone (Paul et al. 2008).

2 General treatment—Phoslock™

2.1 Compounds

Lanthanum modified bentonite clay

2.2 Synonyms/formulations

Phoslock™; 1-3 mm granules + dispersant

2.3 Active ingredient

Lanthanum (La)

2.4 Mechanism

The mechanism of P-removal by Phoslock™ involves the reaction of phosphate anions with La, leading to formation of a single insoluble species of lanthanum phosphate, or rabdophane (National Industrial Chemicals Notification and Assessment Scheme 2001; Douglas et al. 2004).

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

The stoichiometric equation (3) indicates that 1 kg of P requires 4.5 kg of La.

The P uptake capacity of La-substituted clays typically exceeds 1 kg P/100 kg (1%) (Douglas et al. 2004).

2.5 Application techniques

Granule spreader or slurry

2.6 Application rates

- calculation from stoichiometry based on measured sediment P concentrations
- experimentally measured capping efficiency

2.7 Key issues

- release of La to overlying water—potential toxicity and food-chain accumulation
- turbidity in lake during application period

2.8 Environmental effects

- sediment smothering of benthos
- potential sediment toxicity

2.9 Registered/available in New Zealand

Registered by ERMA

2.10 Source

Primaxa Ltd, New Zealand

2.11 Human health and livestock

No drinking water guidelines

2.12 Ecological guidelines

Water: no guidelines

Sediment: <0.4 mm thickness (Clearwater 2004; Clearwater & Hickey 2004)

2.13 Environmental fate/degradation

- largely sediment accumulation and burial
- some residual La in lake water
- some food-chain accumulation of La

2.14 Advantages

- application as either granular or slurry to lake surface
- rapid granular dispersion to provide even bed distribution

2.15 Disadvantages

- partial smothering of benthos
- restriction period for drinking water, irrigation and stock watering
- burial with sediment reduces efficacy
- cost

2.16 Comments

Ross et al. (2008) found that Phoslock™ was most effective at binding P at pH values between 5 and 7, and the P

Appendix 1 (*continued*)

adsorption capacity decreased above pH 9 (by about 30%). A large increase in Phoslock™ dose (from 230:1 to 450:1) was not found to improve P removal at high pH (>pH 9), suggesting that lakes with algal blooms may require pH adjustment to improve P removal (Ross et al. 2008). The bound P was not released from Phoslock™ under anoxic conditions.

The toxicity of Phoslock™ to infaunal sediment-dwelling macroinvertebrates and trout (*O. mykiss*) has been assessed as a component of the product registration process in New Zealand (Clearwater 2004; Clearwater & Hickey 2004). Sediment testing included a range of Phoslock™ doses and determined effects on four species (amphipod, *P. helmsii*; oligochaete worm, *Lumbriculus variegates*; midge larvae, *Polypedilum parvidum* and *Chironomus zealandicus*), with juvenile rainbow trout exposed in the overlying water during the sediment-dosing and exposure procedure. Amphipods were the most sensitive species to Phoslock™, with a lowest observed effect threshold (LOEC) of an estimated sediment thickness of Phoslock™ of <0.4 mm resulting in a 15% reduction in survival (Clearwater 2004; Clearwater & Hickey 2004). Some trout mortality occurred with increasing the dose from 40 to 200 g Phoslock™/m^3, however, the small increase in dissolved La from 0.010 g La/m^3 to 0.014 g La/m^3 between these doses suggested that La was not primarily responsible for the increased trout mortality (Clearwater & Hickey 2004).

Few reports are available addressing the potential physiological and organism health effects of La bioaccumulation. Persy et al. (2006) reviewed the clinical data for La bioaccumulation and effects on humans when oral dosing of lanthanum carbonate was used for phosphate reduction in association with renal failure. The authors concluded that bioavailability of La is extremely low and noted that in clinical studies, no toxic effects had been reported after a 4-year treatment period. Persy et al. (2006) also noted that the liver is the main route of excretion, and hence elevated concentrations may be expected in it. We are unaware of references relative to physiological effects of La bioaccumulation on fish or other aquatic species.

Multiple applications to Lake Okareka, Taupo volcanic zone (Environment Bay of Plenty 2007).

3 General treatment— modified zeolite

3.1 Compounds

Aluminium modified zeolite mineral

3.2 Synonyms/formulations

Modified zeolite was developed by Scion in New Zealand by treating raw zeolite—crystalline, hydrated aluminosilicates that contain alkali and alkaline-earth metals—with hydrochloric acid (to remove residual inorganic salts) and Al-based substances.

The formulation used in efficacy and toxicity trials has the code "Z2G1"

0.3–3.0 mm granules

Al + zeolite

3.3 Active ingredient

Aluminium (Al)

3.4 Mechanism

See alum section 1.4

3.5 Application techniques

Granule spreader

3.6 Application rates

- nominal dose of 350 g/m^2 (T. Stuthridge, Scion pers. comm.)
- calculation from measured sediment P and binding efficiency (1.6-2.3%)
- experimentally measured capping efficiency

3.7 Key issues

- low concentration of Al added to water at low or high pH when no floc or precipitation of P occurs
- turbidity associated with fine zeolite material

3.8 Environmental effects

- water column Al toxicity
- sediment toxicity
- sediment smothering

3.9 Registered/available in New Zealand

Registered by ERMA for use in natural waters

3.10 Source

Blue Pacific Minerals, New Zealand

3.11 Human health

Drinking water: 0.1 g Al/m^3 (aesthetic determinant) (Ministry of Health 2005)

Livestock: 5 g Al/m^3 (ANZECC 2000)

3.12 Ecological guidelines

Freshwater: pH <6.5, "insufficient data"; >6.5, 0.055 g/m^3 (ANZECC 2000)

Sediment: no guidelines. Vopel et al. (2008) provide thickness measurements in relation to dose.

Multi-species sediment toxicity tests (amphipods and clams) found no detectable effects for a dose of 350 g/m^2 (Martin & Hickey 2007).

3.13 Environmental fate/degradation

- sediment burial
- dissolved Al, particularly at low or high pH

3.14 Advantages

- particulate granules at recommended dosing rate do not completely smother the lake bed
- not susceptible to resuspension
- both P and ammonia are removed by modified zeolite
- minimal effects on water column pH
- minimal effects on water column turbidity

3.15 Disadvantages

- care required to achieve even distribution on lake bed
- minimal P removal from water column
- restriction period for drinking water, irrigation and stock watering
- burial with sediment reduces efficacy
- potential pH reduction at high dose rates
- cost

3.16 Comments

Owing to its high cation exchange capacity, zeolite is widely used in water and sewage treatment, ion exchange in radioactive wastewater treatment, and removal of ammonia and heavy metals from water, and for capping of chemically contaminated sediments (Jacobs & Förstner 1999). A characteristic of the zeolite structural framework is that it shows infinite three-dimensional systems of tunnels and cages, where exchangeable cations as well as water molecules are situated (Jacobs & Förstner 1999).

One of the advantages of zeolites is that they can be chemically modified to enhance removal of a wide variety of contaminants in aquatic systems (Jacobs & Förstner 1999). The pre-treatment of zeolite surfaces with cationic surfactants additionally facilitates the adsorption of non-polar contaminants (e.g., chlorinated hydrocarbons) and anionic contaminants (e.g., phosphate, arsenate). Depending on the nature of the chemical modifier, either only the external surfaces may be modified, or both the external and internal cage and tunnel structure are modified to change affinity for contaminant types (Jacobs & Förstner 1999).

The modified zeolite is a granule formulation (c. 0.5–2.0 mm) and a density of 2.2 which results in rapid settling through the water column. It is applied at a nominal dose of 350 g/m^2 which results in a cover of c. 80% of the sediment surface (Martin & Hickey 2007). The binding capacity is c. 1.6–2.3% at pH 7 (Gibbs et al. 2008). Laboratory testing for sediment toxicity was undertaken to provide information for product registration (Martin & Hickey 2007), and dose/response trials were conducted to measure nutrient flux reduction before treatment of Lake Okaro (Taupo volcanic zone) (Gibbs et al. 2007) and to assess Lake Rotorua (Taupo volcanic zone) for potential treatment (Gibbs et al. 2008).

The toxicity of modified zeolite (Scion, Z2G1) to sediment-dwelling species was assessed and elutriation tests were conducted as part of the product registration process (Martin & Hickey 2007). Sediment testing to different modified zeolite doses was conducted for two species (amphipod, *Phreatogammarus helmsii*; and clam, *Sphaerium novaezelandiae*), with elutriate testing of three species (algae, *Pseudokirchneriella subcapitata*; crustacean, *Daphnia magna*; fish, *O. mykiss*). The sediment toxicity tests found significant effects for clam reburial at 700 g/m^2 and amphipod survival at 2100 g/m^2, with no detectable effects for amphipods or clams at a dose of 350 g/m^2. (Martin & Hickey 2007).

Application to Lake Okaro, Taupo volcanic zone (Wright-Stow et al. 2008).

4 General treatment—calcite

4.1 Compounds

Limestone

4.2 Synonyms/formulations

(i) Crushed limestone
(ii) SoCal™
(iii) ESCal™

Appendix 1 (*continued*)

4.3 Active ingredient
Calcium carbonate ($CaCO_3$)

4.4 Mechanism
P adsorption

4.5 Application techniques
Slurry

4.6 Application rates
- based on calculated binding for surficial sediment P (1–3% by weight)
- experimentally measured capping efficiency

4.7 Key issues
- low binding efficiency of some product
- turbidly associated with dosing

4.8 Registered/available in New Zealand
Crushed limestone available in New Zealand

4.9 Source
Various

4.10 Human health
No concerns

4.11 Ecological guidelines
Physical smothering

4.12 Environmental fate/degradation
- burial in sediments reduces efficiency

4.13 Advantages
- potentially low cost product
- sediment smothering (but could be restricted to hypolimnion)

4.14 Disadvantages
- period of water column turbidity

4.15 Comments
Precipitation of phosphate with calcite commonly occurs in hardwater lakes during summer, and is favoured by increased pH (Stumm & Morgan 1995). The use of calcite barriers was compared for three forms of material (crushed limestone and two forms of precipitated calcite, SoCal™ and ESCal™) in laboratory reactors for natural lake sediment in Australia (Hart et al. 2003b,c). These trials demonstrated that the two precipitated calcites could effectively reduce P release from sediments under anaerobic conditions, whereas the limestone was ineffective. The maximum binding capacity for SoCal™ and ESCal™ were 3% and 1% (by weight), respectively, at high external P concentrations (Hart et al. 2003b,c).

The long-term effectiveness is determined by the stability of calcite barriers and the binding capacity for P. The calcite barriers dissolve in systems where the water is undersaturated with $CaCO_3$. A speciation computer modelling programme (e.g., PHREEQC) (United States Geological Survey 2009) may be used to calculate the saturation indices for lake waters at various pH and temperature conditions, which indicate whether the calcite would dissolve or precipitate under these ambient conditions.

No known New Zealand applications.

5 General treatment— iron salts

5.1 Compounds
Ferric chloride

5.2 Synonyms/formulations
Various

5.3 Active ingredient
Iron (Fe^{3+})

5.4 Mechanism
Ferric chloride has been successfully used to remove phosphates from sewage effluent by precipitation with a mixture of ferric salt and lime. It has also been used in lake waters (Cooke et al. 1993). The reactions of ferric chloride with bicarbonate alkalinity and phosphate are respectively:

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaCl_2 + 6CO_2 \quad (4)$$

$$Fe^{3+} + PO_3^{3-} \rightarrow FePO_3 \downarrow \quad (5)$$

The stoichiometric equation (5) is believed to predominate at pH above 7 and indicates that 1 kg of P requires 1.8 kg of ferric iron. However, addition of ferric iron will also result in reduced lake water alkalinity with precipitation of ferric hydroxide (equation 4) and the efficiency of water column phosphate removal may be low with both reactions occurring. Addition of a suitable buffer may be required for low alkalinity lakes.

5.5 Application techniques

- liquid to surface or sub-surface to hypolimnion

5.6 Application rates

- calculation from stoichiometry and measured water P concentrations (equations 4 and 5)
- alkalinity measurement required

5.7 Key issues

- reduction in lake alkalinity associated with dosing (may require alkalinity addition)
- optimise timing of dosing when maximum P in lake water
- binding efficiency may be lower than anticipated based on stoichiometry

5.8 Environmental effects

- physical smothering of lake bed
- pH change of lake

5.9 Registered/available in New Zealand

Not registered for use in natural waters

5.10 Source

Various

5.11 Human health

0.2 g Fe/m^3 (aesthetic determinant) (Ministry of Health 2005)
0.3 g Fe/m^3 (human health consumption) (USEPA 2006)

5.12 Ecological guidelines

Water: no guideline (ANZECC 2000); 1 g Fe/m^3 (USEPA 2006)
Sediment: no sediment quality guidelines

5.13 Environmental fate/degradation

- precipitation of P to sediment
- elevated concentration in water

5.14 Advantages

- readily available
- considered a "natural" product
- hydrogen sulfide binding and precipitation
- low cost

5.15 Disadvantages

- reversible binding of P (redox-dependent)
- low floc retention in turbulent conditions
- alkalinity reduction

5.16 Comments

The performance of an active capping layer may be influenced by the biogeochemical environment in which the absorbent is going to be deployed. A significant factor in the effectiveness of different iron-containing absorbents is their high content of Fe (III) oxyhydroxides. Under reducing conditions, which exist in anoxic sediments of the hypolimnion of seasonally stratified lakes, Fe (III) is reduced microbially to Fe (II), with the release of adsorbed P. Thus, Fe (III) absorbents are likely to be ineffective in the long term (weeks to months), unless the treatment is combined with sufficient aeration to maintain oxic conditions in the hypolimnion. Addition of Fe to the anoxic hypolimnion, or sediments, provides the additional benefit of precipitating the highly toxic H_2S as insoluble FeS. Potential adverse effects on whole-lake waters on turnover and sediment microbial processes may be mitigated by this treatment.

No known New Zealand applications.

6 General treatment—allophane

6.1 Compounds

Alumino-silicates

6.2 Synonyms/formulations

Various natural and synthetic minerals

6.3 Active ingredient

Aluminium (Al^{3+})

Appendix 1 (*continued*)

6.4 Mechanism

As for Al but modified by mineralogy and surface properties

6.5 Application techniques

Slurry or powder spreader

6.6 Application rates

- calculation from measured binding efficacy (0.6-1.9%) and measured surficial sediment P
- experimentally measured capping efficiency

6.7 Key issues

- turbidity of lake during application
- large quantity to be applied
- consistency of quality of mineral source

6.8 Environmental effects

- sediment smothering of benthos
- potential sediment toxicity

6.9 Registered/available in New Zealand

No ERMA registration required as allophane is a natural product. Resource consent required for site-specific applications (RMA 1991)

6.10 Source

Various natural sources (Parfitt 1990)

6.11 Human health

Unknown, but expected to be low. Possible concerns with leaching of contaminants if collected from impure mineral source

6.12 Ecological guidelines

Water: possible concerns with leaching of contaminants from impure mineral sources. Assessment relative to water quality guidelines (ANZECC 2000)

Sediment: assessment of contaminants relative to sediment quality guidelines (ANZECC 2000). No known dose/response data for sediment toxicity

6.13 Environmental fate/degradation

- sediment burial

6.14 Advantages

- natural product
- readily available mineral
- no pH/alkalinity alteration expected
- low sediment toxicity expected

6.15 Disadvantages

- relative large quantities required for dosing because of low binding efficiency
- ecotoxicity unknown
- large sediment thicknesses increase the probability of adverse effects on sediment-dwelling species if the product is inherently ecotoxic
- low P-binding at high pH

6.16 Comments

Allophanes occur in nature as secondary aluminosilicate minerals formed during weathering processes of rocks and soils (Douglas et al. 2004). They can also be synthesised in the laboratory, typically from stoichiometric addition of pure Al and Si solutions (Douglas et al. 2004).

Anion (phosphate) uptake capacity has been demonstrated in laboratory studies to vary strongly as both a function of surface charge, and hence pH, and ionic strength. Above pH 8–9, anion uptake is minimal with cation uptake the predominant reaction. The maximum phosphate adsorption typically occurs at or below pH 6. Typical uptake capacity of allophane is between c. 6 and 19 g/kg (0.6–1.9%) (Douglas et al. 2004).

The low binding of allophane at high pH results in reduced performance under some natural lake conditions. These conditions are likely to occur during algal blooms, however, the lower pH in the hypolimnion of stratified lakes will result in improved P-binding in those environments. A key component warranting consideration is the relatively low binding capacity of allophane, which results in thicker capping layers to achieve the equivalent binding compared with other materials. The requirement for using large quantities has application cost implications and may result in greater potentially adverse effects on benthic communities if applied to oxic areas of the lake.

A recent laboratory trial showed effective P binding for a natural allophane under cycled anoxic and aerobic-anoxic conditions (Gibbs et al. 2008). This product has not been trialled in a New Zealand lake.

No toxicity information is available for New Zealand allophane effects on freshwater aquatic species.

No known New Zealand applications.

7 General treatment—aeration

7.1 Compounds

a. artificial circulation
b. hypolimnetic aeration

7.2 Synonyms/formulations

Hypolimnetic oxygenation with compressed or liquid oxygen may also be used

7.3 Active ingredient

Air and oxygen

7.4 Mechanism

a. whole-lake mixing and aeration
b. hypolimnion mixing apparatus

7.5 Application techniques

a. surface spray; paddle wheel; air diffusers
b. moored hypolimnetic aerator

7.6 Application rates

Oxygen transfer rates in excess of 7 kg/kW/h; pumps in excess of 1600 litres/min/kW; 1 to 3 kW aerating units per 5000 m^2 surface

Surface spray: best circulation in lakes less than 5 m deep owing to the creation of convection currents.

Surface mixer/aerator: wind and solar powered aerators and mixers may also be used.

Paddle wheel: most suited for shallow (<5 m) lakes; low above-surface spraying; creates strong current.

Air diffuser: best mixing for deep (>10 m) lakes; diffuser on lake bottom; supplied by an air compressor.

A hypolimnetic aerator may be used in stratified lakes to maintain thermal stratification. These systems have the advantage of requiring a lower mass of oxygen transfer to control sediment phosphorus release.

7.7 Key issues

- capital installation costs
- ongoing maintenance and operational costs
- need to ensure adequate oxygen transfer to result in continuously aerated water

7.8 Cost

a. NZ$500 to >NZ$10,000
b. site-specific

7.9 Registered/available in New Zealand

No registration required for use. Resource consent (RMA 1991) may be required for site-specific applications

7.10 Source

Various

7.11 Human health

Iron, tainting and odours possible in water supply systems at start-up

7.12 Ecological guidelines

Exceedance of surface water quality guidelines may occur on start-up of aeration in a stratified lake system

7.13 Environmental fate/degradation

Not applicable

7.14 Advantages/benefits

- provides oxygen for aerobic decomposition of organic matter
- prevents fish kills
- controls blue-green algal scums and flocs
- prevents build-up of harmful dissolved gasses (NH_3, H_2S)
- wind or solar power may be suitable for some systems

7.15 Disadvantages

- currents may entrain sediments
- power requirements
- equipment maintenance
- mooring systems required

Appendix 1 (*continued*)

7.16 Comments
Practical approach for reduction of sediment nutrient release in small lakes. Energy and logistic requirements increase with size of waterbody.

Complementary method to be used in conjunction with other nutrient management techniques.

Application to water supply reservoirs in Auckland region (M.M. Gibbs pers. obs.).

8 General treatment—Dredging

8.1 Compounds
Mechanical

8.2 Synonyms/formulations
Bucket, drag-line, suction and other systems

8.3 Active ingredient
Mechanical activity

8.4 Mechanism
Physical removal from waterbody

8.5 Application techniques
Various (e.g., suction, bucket)

8.6 Application rates
Site-specific consideration

8.7 Key issues
- access to target area
- transport and disposal of material
- habitat disturbance
- release of toxicants (e.g., NH_3, H_2S, As) from sediments and turbidity from increased turbulence

8.8 Cost
Suction dredging—c. NZ$7,000/ha (includes removal and disposal of uncontaminated sediment)

8.9 Registered/available in New Zealand
Resource consent (RMA 1991) may be required depending on the scale of activity. Dredge disposal guideline may apply if material is disposed of within the waterbody

8.10 Source
Various

8.11 Human and livestock health
Drinking and livestock guidelines during activity

8.12 Ecological guidelines
Appropriate water quality guidelines for contaminants released during activity

8.13 Environmental fate/degradation
Land disposal

8.14 Advantages
- can deepen lake
- targeted removal of specific sedimentation areas (e.g., from bank erosion, agricultural inputs, construction areas, stormwater outfalls)
- limits nutrient cycling
- reduction of macrophyte nuisances
- removal of toxic sediments
- can be effective for several years
- can be cost-effective

8.15 Disadvantages
- release of nutrients
- resuspension of contaminants and turbidity
- destruction of benthic organisms
- availability of adequate disposal facility
- cost for large areas
- may need to be repeated

8.16 Comments
No known New Zealand applications.