LOCALLY AVAILABLE ADSORBING MATERIALS, SEDIMENT SEALING AND FLOCCULANTS FOR CHEMICAL REMEDIATION OF LAKE AND STREAM WATER

Report prepared for

Environment Bay of Plenty

by

Analytical & Environmental Consultants

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EXECUTIVE SUMMARY

This report examines a number of locally sourced (i.e. within New Zealand) inorganic and organic materials with a view to determining their actual or potential usefulness for reducing or removing nutrients from lakes, streams or groundwater in the Rotorua District. The major properties and nutrient removal potential of the various materials are examined, and an attempt is made to rank them in terms of potential utility.

A tentative ranking, in order of potential usefulness, is
1. Allophane
2. Zeolite
3. Bentonite
4. Steel slag
5. Limestone

A number of recommendations and cautions arise from the material reviewed in this report. They include the following:

- Before aluminium is released on a large scale into any of the Rotorua lakes, it would be very desirable to reliably determine the hypolimnetic pH during the period of anoxia.

- As flocculated material sinks the equilibrium conditions change as it passes through various physically and chemically distinct water strata before arriving at the lake bed. Therefore the results of bench tests may not necessarily reflect the reality in-lake.

- It is suggested that 'cost-effectiveness' should not be the prime characteristic used to choose a flocculating agent.

- Lakes that experience significant internal loading of phosphorus (P) or nitrogen (N) to their water columns may be the rule rather than the exception. In this type of lake, additional in-lake steps may be necessary, following diversion, in order to prevent a prolonged eutrophic state.

- In trying to manage the nutrient status of waterbodies it would be beneficial to know which of various abiotic and biotic processes has the potential to dominate the P release from sediments and, under what conditions.

- It should be emphasized that, in order to carry out successful phosphorus inactivation in any of the Rotorua Lakes, the chemical and physical nature of the sediments and the overlying water column will need thorough investigation.

- It is recommended that a biomonitoring procedure, using aquatic flora, be adopted should field trials with Phoslock™ or similar materials be carried out in the Rotorua Lakes (see Appendix 2).

- It has been shown that significant adsorption of lanthanum, as the free ion La^{3+} and also as an EDTA-La complex, occurred to membrane filters and to glass vessels. This finding should be kept in mind when conducting or assessing *in vitro* trials on toxicity or bioavailability of lanthanides. In addition, much of the lanthanide data obtained from laboratory studies is regarded by some authors as being of poor quality, probably due to analytical difficulties and insufficient attention to questions of solubility.

Appendix 1 summarises the aquatic chemistry of aluminium (an element central to a number of lakes remediation strategies). Appendix 2 briefly examines several overseas-derived modified mineral materials that have been used in lake remediation. Appendix 3, included for reader convenience, is a Periodic Table of the Elements. An Addendum proposes some less well-known methodologies or processes to remove nutrients from water or sediments.

INTRODUCTION

The purpose of this work is to report on locally sourced minerals and additives that can be used, either in their native state or modified, to remove nutrients from rivers, groundwater and lakes or to cap nutrients in lake sediments.

The report focuses on the properties of these materials, their availability and their possible relevance to problems of nutrient enrichment in the Rotorua Lakes.

Environmental issues and indicative costs of the materials, where available, have also been addressed.

In this document, the various sections have been arranged according to the procedures or materials being considered, rather than by nutrient type (i.e. N or P). Within these sections, the varied uses of a material (e.g. for sediment capping, permeable barriers etc.) are then considered. Materials have been arranged alphabetically. General considerations pertaining to sediment capping, stream treatment etc. are treated in their own sections, together with introductory sections dealing with various aspects of the problems of the lakes, their possible remediation and various technical matters.

Appendices and an addendum examine material that is considered peripheral to the main focus of the report. An attempt has been made to achieve a reasonable coverage of the relevant literature, however time and other constraints naturally mean that much material has not been examined. All references, whether in the main body of the report or in the Appendices and Addendum, are included in one block. The great majority of literature referred to has been examined, however a small minority referred to in works extensively cited have been included although not examined.

THE NATURE OF THE PROBLEM

A number of the Rotorua Lakes are undergoing the widespread problem of eutrophication (nutrient enrichment), with a resulting decline in water quality, cyanobacterial blooms and overall decline in amenity values. The lakes most affected at present are Rotorua, Rotoiti, Rotoehu and Okaro, but water quality trends in other lakes such as Okareka, Tarawera, Okataina and Tikitapu are also a cause for concern. These matters have been extensively discussed in a variety of reports, so will not be further treated here, other than to observe that nutrient inflows in groundwater and nutrient release from sediments during periods of hypolimnetic deoxygenation are considered to be a major component of the problem [1].

The nutrients of most concern are believed to be nitrogen and phosphorus. The sources of these nutrients include catchment sources such as:

- septic tank leachate
- stormwater runoff
- agricultural land uses, including runoff and enrichment of groundwater
- forest clearance
- geothermal inflows

and also internal recycling of nutrients from enriched lake sediments as well as natural diffuse sources such as rainfall, catchment runoff etc.

Action is being taken to reduce some of these nutrient inputs. For example, lakeside settlements are being successively sewered, farmers are being encouraged to reduce or

cap nutrient losses from their land, various major nutrient sources (Waiohewa Stream, Ohau Channel etc.) are being examined with a view to possible diversion around affected waterbodies.

However, alternative strategies may also be required and, to this end, Environment BOP is examining the use of various technologies and processes that may be used to remove nutrients from incoming surface water or groundwater, or to prevent the release of existing nutrients from lake sediments.

This quote from a recent CSIRO report [2] summarises the local situation very well:
> "The inevitable conclusion from this is that for management to have any rapid effect on water quality, it must be directed at the water body itself, rather than at the catchment. For short-term improvement there is no alternative. Thus research directed at environmental flow requirements, destratification processes, chemical treatment to remove P, etc. must receive significant support if any improvements are required over the next 10-20 years. This is not to downplay the importance of catchment-based works, which can be carried out for a variety of reasons that benefit the ecosystem, and is essential for long-term reduction of nutrient loads to waterways."

Principles of nutrient removal

This document largely considers the two macronutrients nitrogen and phosphorus. Scientific opinion is generally of the opinion that it is very desirable to reduce inputs of both of these elements in order to limit or reduce the degree of eutrophication of a water body.

Nitrogen may occur in waterways as a number of forms, both inorganic and organic. Inorganic nitrogen mostly occurs in oxic waters or pore waters as the major ions nitrate (NO_3^-) and nitrite (NO_2^-), which is less abundant but surprisingly often detectable. All nitrate salts are soluble, with solubilities of >5000 mg/l. Nitrite salts have similarly high solubility.

In anoxic waters or pore waters the ammonium ion, NH_4^+, dominates. Ammonium exists in a pH-controlled equilibrium with dissolved non-ionic ammonia, NH_3. Ammonia dissolves and ionises in water to form a weak base according to the equation:

Figure 1
Ionisation of ammonia in solution as a function of pH. From Kemmer [3].

$$NH_3 + H_2O \Leftrightarrow NH_4OH \Leftrightarrow NH_4^+ + OH^-$$

The addition of alkali will force this equation to the left, tending to favour the more toxic molecular ammonia form. Under the nearly neutral conditions found in most surface fresh waters, only a small proportion of the ammonia will be in the molecular form [3]. Figure 1 (*left*) illustrates this relationship.

Ammonium salts also are soluble, with solubilities of >5000 mg/l.
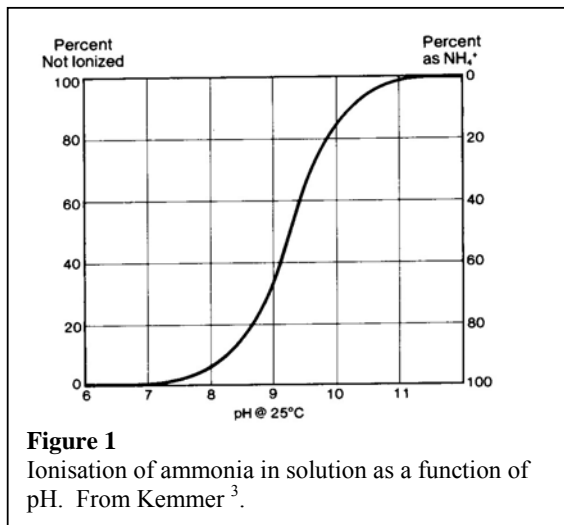
Nitrous oxide (N_2O) may be present as a dissolved gas in the water column or pore water at certain stages of the limnological cycle [4]. N_2O is an important indicator of the denitrification process. Nitrogen gas or dinitrogen, N_2, also is soluble in water, at concentrations similar to that of dissolved oxygen, and this dissolved nitrogen, although not directly available for utilisation by plants, may be taken up and 'fixed' to become plant-available ammonia by bacteria and cyanobacteria.

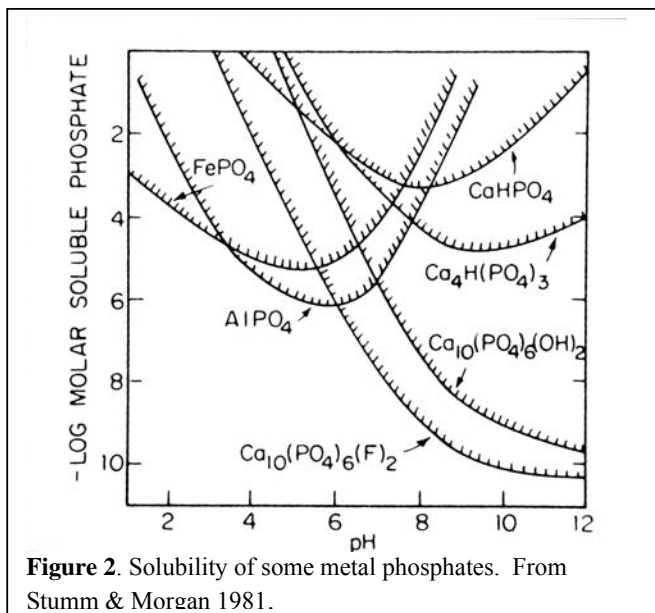The fact that nitrates, nitrites and ammonium all form soluble salts means that it is difficult to remove nitrogen from aquatic systems. The only really viable options are through some sort of ion exchange system, which may or may not be reversible, or through the microbially mediated process of denitrification. Ion exchange is discussed later in this report, but denitrification is largely outside the scope of this document, with the exception of the observation that it might be possible, under some circumstances, to practice environmental manipulation in such a way as to enhance denitrification rates in the water column or sediments of a water body. Electronically stimulated (or simulated) denitrification is briefly discussed in the Addendum to this report. Ammonia volatilisation is another route for transport of nitrogen to the atmosphere, however a high pH is required in order for a sufficient proportion of the ammonium nitrogen to be present as molecular ammonia.

Phosphorus occurs in natural waters as a wide range of inorganic and organic compounds. There are three major fractions of phosphorus compounds found in the water column of natural waters. These are Soluble Reactive Phosphorus (SRP), Soluble Organic (or unreactive) Phosphorus, (SOP) and Particulate Phosphorus (PP). Soluble Reactive Phosphorus was previously known as Dissolved Reactive Phosphorus (DRP) or Filterable Reactive Phosphorus (FRP). These fractions are differentiated by different analytical procedures.

Phosphorus compounds that are described as soluble and reactive are generally regarded as being the forms readily available for uptake by plants, algae and cyanobacteria. They are often referred to as 'phosphate'. Frequently 'phosphate' is regarded as being equivalent to the orthophosphate ion – a dangerous assumption. Orthophosphate is generally present at low concentrations in most natural waters and is very rapidly cycled due to biological and chemical activity [5]. However, orthophosphate has the ability to form a variety of salts and compounds of low or very low solubility, regulated to some degree by pH [6] (see Figure 2, *left*). Only its sodium, potassium, ammonium and hydrogen salts are soluble. It is this ability to form compounds of extremely limited solubility which makes 'phosphate' and phosphorus generally, a nutrient which is susceptible to being

Figure 2. Solubility of some metal phosphates. From Stumm & Morgan 1981.

manipulated, in terms of supply, in environmental systems. For this reason, the removal or 'inactivation' of phosphorus from the water column or sediments of water bodies is discussed at length. In addition microbially mediated 'dephosphatation' is briefly discussed in the Addendum to this report.

When considering solubilities, it should be kept in mind that the concept of the Solubility Product, although useful, is compromised by a number of factors that affect its ability to predict real-world outcomes in natural waters. These factors include:

- The formation of ion-pairs in solutions, in which more than one type of cation (or anion) takes part in the formation of a precipitate. Ion pairing frequently increases the solubility of a precipitate.
- A metal such as calcium may be present in water as Ca^{2+}, but it is also likely to be present as $Ca(HCO_3)^+$ or $Ca(OH)^+$. Such other ionic forms further complicate the situation.
- Water itself may become involved in ionic reactions. For example, iron in water may be present as Fe^{3+} but it may also be present as $Fe(H_2O)_6^{3+}$.
- Complexation reactions may occur, such as the reactions between copper and dissolved ammonia to form a whole range of cuprammonium complexes ranging from $CuNH_3^{2+}$ to $Cu(NH_3)_5^{2+}$. These different complexes may have different reaction behaviours.
- The presence of dissolved organic compounds also affects the solubility of precipitates, often by increasing the solubility.
- Precipitates are more soluble in the presence of dissolved 'foreign' ions of a type not involved in the precipitate.

Coagulation

Coagulation may be defined as the process of destabilising stable colloidal particles in suspension. It is a widely used practice in the treatment of water supplies and in wastewater treatment. A variety of materials, both inorganic and organic, have the ability to achieve this purpose.

Ion mobility

Various solutes, such as ions, have differing abilities to move through the soil and into (and through) the water table. Solute movement occurs through a combination of convection, diffusion and dispersion. In an ideal world, ions would move through the soil at the same rate as the water in which they are dissolved. In reality, other factors come into play, including:

- Cation exchange. Cations such as the ammonium ion, NH_4^+ may be adsorbed onto soil particles by ion exchange processes. Since the majority of soil particles carry a negative charge, anions such as the nitrate ion NO_3^-, do not usually undergo this process and move through the soil much more freely. This process is known as anion exclusion.
- Anion exchange. Phosphate in particular may be strongly bound onto soil particles by anion exchange and ligand bonding with the aluminium component of certain clay minerals such as allophanes. This is described in more detail later in this report.
- Transformations. The chemical and biological processes going on in soil and natural waters enable the transformation of various nutrient (and other)

compounds into alternative forms. For example, the transitions between nitrate, nitrite and ammonium forms of nitrogen, depending on redox and other conditions, are well known. Such transformations are also believed to occur with phosphorus.

- Plant uptake. Soil (or water) in which plant roots and soil micro-organisms are present will display the loss of some nutrient materials into the biomass of the soil or water.

To summarise this for the three major plant nutrient ions of interest to lake health in the Rotorua lakes region, nitrate-N may be expected to move readily freely through the ground (unless converted to ammonia by dissimilatory nitrate reduction), ammonium-N may be expected to be bound to soils to some extent (until converted to nitrate) and phosphate-P is readily bound to allophane in many of the local soil types. However, as was described at a recent public forum, the sandy nature of many of the Rotorua soils, and low phosphorus retention by some of the soil horizons, may allow leaching of phosphorus down the soil profile, and eventually into groundwater [7]. Phosphate has been long known to be present at significant levels in major springs (such as the Hamurana Spring) sourced from the Mamaku Plateau. A number of geothermal springs are significant sources of nitrogen (Professor Warwick Silvester, University of Waikato, pers. comm.)

CHARACTERISATION OF RAW MATERIALS EXAMINED

A brief summary of some major characteristics of the various minerals and other materials considered in this report is shown below in Table 1. More detailed descriptions of the various materials are given in the sections dealing with each.

Table 1
Comparison of physico-chemical properties of various mineral and non-mineral materials

Material	Density Kg/m^3	Surface area m^2/g	Ion exchange properties meq/100 g	Cost***	Local availability*	Major nutrient ions affected
Allophane	2000-2200	400 - 900	Anion/cation		Excellent	NH_4^+ NO_3^- PO_4^{2-}
Bentonite	2000 - 3000		Cation 70-100. Anion if modified		Good	PO_4^{2-}
Charcoal (activated)	Variable	300 - 2000	Very limited, but may be modified		Potentially excellent	Organically bound N and P
Chitin	Variable				Fairly good	NH_4^+
Pumice	600 - 800 **		Cation 5-8		Excellent	PO_4^{2-} NO_3^-
Steel slag	1490		Anion	$25/tonne		PO_4^{2+}
Wood wastes	Variable				Excellent	NO_3^- NH_4^+
Wool					Good	
Zeolite	~1700 – 2100	145	Cation 80->200. Some anion when modified		Excellent	NH_4^+ PO_4^{2+} NO_3^-

* in BOP/Central N.I.
** Taupo pumice soil
*** Cost is subject to a major variable – fuel costs

Materials for removing nutrients from surface water inflows or groundwater inflows

Trials are currently underway, or being planned, with a variety of materials that are intended to remove nutrients from surface water inflows such as streams and springs, or from groundwater. A variety of approaches are possible, including 'dosing' of the waterway with liquid or solid agents, placing aggregate solid material in a suitable

enclosure and allowing stream water to flow through the material, and placing materials in suitably located trenches to act as permeable reactive barriers. The various materials that may be of utility in such techniques are dealt with individually in their respective sections, rather than covered here.

Dosing streams or lakes with aluminium compounds

It has been suggested that dosing such inflows as the Hamurana Stream (which contains a high phosphorus load and an increasing nitrogen load) with an aluminium compound such as alum (aluminium sulphate) would possibly lead to a useful loss in phosphorus loading into Lake Rotorua (Dr Dell Bottcher, Keynote speaker, Rotorua Lakes 2003 Symposium, pers. comm.)

There is a potential source of confusion in that a number of compounds are referred to as 'alum'. One is aluminium sulphate, and this is what is usually referred to when lake (or stream) dosing with 'alum' is discussed, and this meaning is generally used in the water treatment industry also. Another one commonly encountered is a double salt of aluminium, potassium aluminium sulphate, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, also known as potash alum.

However, in chemical nomenclature 'Alum', is a term given to the crystallized double sulphates of the alkali metals (lithium, sodium, potassium, rubidium, caesium, or francium), and one of the trivalent metals aluminium, chromium, or ferric iron [8]. Potash alum is the common alum of commerce, although both soda alum and ammonium alum are manufactured.

In this report 'alum' means aluminium sulphate, although this is not a strictly correct use of the term.

The questions which must be asked before engaging in such an exercise include:
- What dosage rate of aluminium compounds will be needed to precipitate an adequate amount of phosphorus from the stream?
- How long after dosing before precipitation of a floc commences?
- Where will the precipitated floc settle out?
- What will be the impacts of lake water, with possibly different chemistry, on the dosed stream water as mixing with lake water occurs?
- How chemically and physically stable will the floc be?
- What will be the environmental impacts of the floc?

Some practical experience of this process has been obtained overseas. An example is Lake Rockwell, Ohio. This eutrophic water supply reservoir receives about 90% of its water supply from the Cuyahoga River, which drains a large agricultural and forested catchment area[9]. Phosphorus was considered to be the main limiting nutrient for algal growth in the reservoir.

Aluminium sulphate was added to the stream over summer and autumn. An alum solution was dispensed through a perforated manifold which spanned the main river channel. The dose rate varied according to the river flow. The Al concentration in the river was maintained at 1 to 2 mg/l.

This treatment removed 50 to 60% of the SRP (Soluble Reactive Phosphorus) in the river, but the total P loading to the reservoir was not significantly reduced. Some P was apparently added to the river from a wetland between the dosing point and the reservoir, and some of the aluminium floc was transported into the reservoir, carrying sorbed P with it. No changes in algal biomass were observed in the reservoir.

There was a rapid build-up of aluminium hydroxide floc on the river bed, which interfered with river flows. There was a significant fall in pH to about 4.0 in the immediate vicinity of the dosing manifold, but the pH rapidly recovered to 7.5 within a few metres downstream. There was a significant mortality of aquatic invertebrates in this area. When dosing was stopped at the end of the trial, the floc was dispersed into the reservoir and the area was re-colonised with invertebrates.

Cooke et al [9] do not recommend such an approach. Rather they recommend a fixed-bed system (Bernhardt 1980) or a pump-storage basin, or alternatively, direct dosing with less toxic calcium hydroxide or ferric chloride. These latter options, however, do require the maintenance of aerobic conditions (both in the stream and in the lake).

Some local experience has also been gained in the use of 'alum' in a lake. The small, hyper-trophic Lake Okaro was dosed with alum (at $0.45g/m^3$ aluminium) in December 2003. The alum solution was applied to the lake surface At the time of dosing, and throughout the sampling period, the lake was stratified with an anoxic hypolimnion. In the hypolimnion the pH dropped from 5.9 to 5.5. From 12 to 22 December, 2003, the TN:TP mass ratio in the epilimnion increased from 12:1 to 34:1, indicating phosphorus limitation. In the hypolimnion, the TN:TP ratio increased from 8:1 to 9:1 over the same period. The TN:TP ratio increase was mostly produced by increased ammonium. Ammonium release after the alum treatment was weakly correlated with bacterial productivity. It was surmised that bacteria may have used flocculated organic matter as a source of nutrients. Environment Bay of Plenty's principal aim for this trial was to reduce phosphorus in the epilimnion through adsorption by aluminium hydroxide, produced by a series of reactions following aluminium sulphate application. Toxicity of aluminium sulphate to biota was a concern for Environment BOP, thus a very low dose was used. As chemical reactions of aluminium may be prolonged, toxicity due to decrease in pH and increase in soluble aluminium is possible. On the other hand, low aluminium sulphate dose and poor coverage may mean changes in TN:TP ratio and pH are short-lived. It was concluded that further sampling would be required to determine any longer term effects [10]. This work appears to have provided some very useful experience and background information in this particular aspect of lake restoration.

Since aluminium compounds, in general, are not considered as locally sourced, they are not extensively treated in the main body of this report. However, Appendix 2 to this report examines the chemistry of aluminium in aquatic systems, due to its relevance to the possible modification of minerals.

Observations on flocculation/precipitation of phosphorus

There is much debate on which compounds should best be used for removing phosphorus from water by flocculation or precipitation. The most commonly used materials are salts of iron or aluminium. Aluminium has the advantage that under anoxic conditions (i.e. if the hypolimnion becomes anoxic in summer and autumn)

phosphorus is less likely to be released from an aluminium-phosphorus complex than from an iron-phosphorus complex.

On the other hand, the solubility, at pH 7, of iron phosphate is about 0.4% of that of aluminium phosphate, so that the iron is more efficient at removing phosphorus from the water column. In addition, aluminium is only effective over a relatively limited pH range of 5.5 to 8. Below pH 5.5, soluble aluminium ions (Al^{3+}) are released. Above pH 8, soluble $Al(OH)_4^-$ is formed. There is a large body of literature detailing the toxicity of 'free' aluminium in the aquatic environment, whereas the toxicity of 'free' iron is believed to be significantly lower.

Before aluminium is released on a large scale into any of the Rotorua lakes, it would be very desirable to reliably determine the hypolimnetic pH during the period of anoxia in addition to the pH of any stream inflows to which alum might be added. In relatively lightly buffered waters such as those in many of the Rotorua lakes, the accumulation of carbon dioxide during anoxia, coupled with geothermal inflows of low pH, could well result in a low-pH situation where aluminium was released on a large scale. If the aluminium was **strongly** bound to a suitable mineral carrier, such as zeolite, this could ameliorate the situation.

The adsorption of P by alum can be enhanced by the presence of organic polyelectrolytes, such as tannin and synthetic anionic polyelectrolytes, and also clay [13]. This may explain some reported cases of better P adsorption occurring on Al-based substrates when organic compounds are present in the water (and see later in this report). Addition of aluminium salts to wastewater in the presence of tannic acid forms aluminium hydroxyphosphate, hydroxy-alumino-tannate and aluminium complexes containing both phosphorus and tannic acid [13].

The chemistry of aluminium in natural waters is complex and not fully understood. It has been proposed that aluminium be dosed directly into streams flowing into Lakes Rotorua. There are certain difficulties associated with this option. It appears that the earlier hydrolysis products of alum tend to present a different array of potentially toxic aluminium species than does an aged solution with lower concentrations of toxic monomeric species and intermediate polymers. For this reason, continuous exposure to these early hydrolysis products, such as would occur in a treatment of flowing waters, may be more damaging to aquatic biota than would a whole-lake treatment.

Inorganic solid phosphate phases are formed by direct precipitation with calcium, aluminium and iron. It should be noted that many of these solid-liquid phase equilibria can reach completion in the time required for the particle to sink. However, as the particle sinks the equilibrium conditions change as it passes through various physically and chemically distinct water strata before arriving at the lake bed [11]. Therefore the results of bench tests may not necessarily reflect the reality in-lake.

Iron is generally applied as a soluble salt of the ferrous (Fe^{2+}) form, as salts of ferric (Fe^{3+}) iron tend to be relatively insoluble. Work carried out in a reservoir in Germany[12] showed that ferrous iron was slower at forming insoluble phosphate compounds, and that the flocs formed were much slower to settle out of the water table than those formed using ferric iron. However the ferrous iron persisted longer in the water column, and was thus able to 'scavenge' phosphorus over a longer period of time and

thus over a larger volume of the water column. This lead to roughly equal overall efficiency in phosphorus removal between the ferrous and ferric forms of iron. In addition, ferrous iron was shown to produce a smaller reduction on the overall buffering ability of the water column.

Iron precipitation can work in concert with Ca, Cu and Zn ions to also remove more complex phosphorus compounds such as mono- and polyphosphonates (widely used in industrial and household products). The presence of these other metal ions was shown to considerably enhance the adsorption of phosphorus compounds [13].

It is suggested that 'cost-effectiveness' should not be the prime characteristic used to choose a flocculating agent.

Passing stream water through enclosed porous materials

This is not a technique that appears to have had wide application, and is unlikely to be practicable in the case of larger inflows. However, many of the Rotorua Lakes have small streams or seepage areas which are frequently high in nutrients, and for such inflows this technique seems to be worth investigating. Initial trials are underway and are discussed in the sections dealing with individual materials.

Treatment trenches or permeable reactive barriers

An example of the above method is the work being carried out in New Zealand on 'denitrification walls', in which a trench filled with sawdust (as a carbon source) is placed across a nitrogen-rich groundwater flow. Recent studies carried out near Cambridge (New Zealand) showed that the nitrate removal rate may be limited due to the denitrification rate being constrained by nitrate supply (despite large nitrate inputs to the groundwater). This effect is believed to be due to nitrate predominantly moving in groundwater through zones of greater hydraulic conductivity (than the trench) or by slow diffusion of nitrate to the immobilised regions where denitrification occurs [14]. Possible 'work-arounds' to this problem could include incorporation of local soil into the trench fill, to improve hydraulic connectivity between ground and trench, or by direct dosing of water-borne carbon compounds or other electron donors into the ground. Further discussion on this occurs in the section on wood wastes

SEDIMENT CAPPING AND TREATMENT

Nuisance algal blooms can be reduced or eliminated if nutrient concentrations are lowered to levels where algal growth is nutrient–limited. This can be carried out by diversion or pre-treatment of incoming nutrients, by dilution, or a combination of these methods. In cases where a significant reduction in nutrient loading is achieved, where the lake has a limited retention time, and where recycling from sediments is not significant, the trophic state can be significantly and rapidly improved. Nutrient diversion is being planned for Lake Rotoiti.

In many cases, even though diversion removes a significant fraction of nutrient loading, long retention times and/or internal nutrient release may indefinitely prolong the lake's enriched state and support continued algal blooms. Lakes that experience significant internal loading of phosphorus (P) or nitrogen (N) to their water columns may be the rule rather than the exception, particularly lakes with extensive littoral and wetland areas [15], or with close proximity between the epilimnion and anoxic sediments [16]. Such

phosphorus release from the sediments may be a major source of nutrients in many lakes [17]. In this type of lake, additional in-lake steps may be necessary, following diversion, in order to prevent a prolonged eutrophic state.

P inactivation is a lake restoration/improvement technique. Its purpose is to lower the lake's phosphorus (P) content by removal of P from the water column (P precipitation) and/or by retarding P release from lake sediments (P inactivation). Usually an aluminium salt, either aluminium sulphate (alum), sodium aluminate, or both, is added to the water column to form aluminium phosphate and a colloidal aluminium hydroxide floc to which certain P fractions are bound. The aluminium hydroxide floc settles to the sediment and continues to sorb and retain P within the lattice of the molecule, even under reducing conditions [18]. Iron, lanthanum and calcium salts have also been used to precipitate, inactivate or sorb P. P inactivation by reducing the loss of P from sediments may also be referred to as sediment capping. The potential to reduce N loss from sediments via a capping procedure has been little investigated, due to the high solubility of virtually all nitrate and ammonium salts. In addition, denitrification processes during periods of hypolimnetic anoxia are thought to be a significant route of N-loss from such lakes as Rotorua [1].

Minerals such as sand, soils, fly ash, clays and hydrous metal oxides may be used to provide a partial physical barrier between nutrient-rich sediments and the water column. Such techniques are not widely used, due to a variety of reasons, such as toxicity, cost, lack of effectiveness or reluctance to pioneer 'new' approaches. More commonly used is a range of salts of metals such as aluminium, iron, calcium and zirconium. A more recent development is the modification of minerals by incorporating, within their physical structure, salts of various metals such as lanthanum, aluminium or iron.

An alternative approach is the oxidation of sediments to bind phosphorus to iron already present in the sediments [34]. These various developments are further discussed later in this report. The removal of nutrient-rich sediments by dredging is also under active consideration [19], but this matter is outside the scope of this report.

Phosphorus and sediments

Understanding the nature of the sediments is vital in any consideration of P inactivation. Sediments in different lakes do not necessarily behave in the same way or have similar properties. The behaviour of P in lake sediments is governed by the nature of the sediments, the nature of the overlying water column, the forms of P present, and other factors.

It is important that these relationships not be overlooked. To quote from Harris [20]:
> "We have discovered time and time again in ecology that simplification of a complex problem (usually in ignorance) leads to unexpected and surprising (even tragic) results.......There are no "Magic bullets" in ecology and there probably never will be......As the years have gone by we have slowly begun to realise that the ecological world is much more complex than we think, and that simplistic models and simplistic prescriptions for research topics do not realistically describe what common sense tells us is happening. We sorely lack good practical recipes for many severe environmental problems."

It is encouraging that it appears that recent work on the Rotorua Lakes is being undertaken with this philosophy in mind.

For many inland waters, phosphorus constitutes a limiting nutrient determining its biological productivity. This is due to the role of this element in the binding of carbon in living organic matter, as summarised in the simplified equation:

$$106CO_2 + 16NO_3^- + HPO_4^- + 122\,H_2O + 18H^+ \quad \overset{P}{\underset{R}{\underset{\leftarrow}{\rightarrow}}} \quad C_{106}H_{263}O_{110}N_{16}P + 138O_2$$
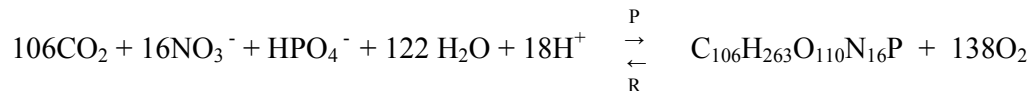
where, associated with the arrows, P stands for photosynthesis and R for respiration.

Phosphorus is introduced into the aquatic environment in a number of different chemical forms, and has been described in general as being present in the aqueous phase as a small fraction of the total and in the solid phase as a large fraction of the total. Each fraction is made up of a large number of different components, most of which may change between their dissolved or particulate state according to a dynamic equilibrium:
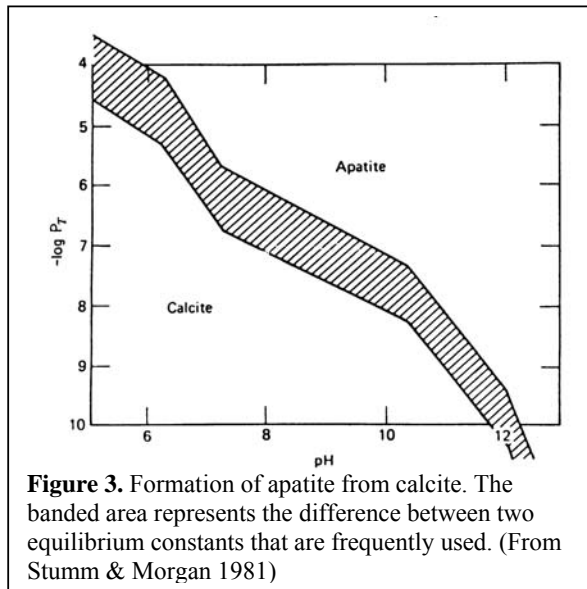
$$P_{\text{dissolved}} \leftrightarrow P_{\text{particulate}}$$
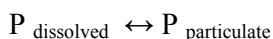
The most common soluble forms of phosphorus are orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}), under the pH conditions normally encountered in natural waters, and organic phosphorus compounds. Orthophosphates are readily available for assimilation by organisms; they may, however, be removed from the dissolved phase by chemical precipitation with Al^{3+}, Fe^{3+}. and Ca^{2+}, plus certain other metal ions.

Iron (III) phosphates or Fe(III) complexes which absorb phosphorus, play an important role in the cycling of phosphorus in the environment. The association of both orthophosphates and organic phosphorus compounds with iron, manganese and aluminium occurs as surface sorption on freshly precipitated oxyhydrate gels of these metals; post-depositional processes (diagenesis), however, produce a large number of well-defined chemical species, the most often encountered ones being vivianite $Fe_3(PO_4)_2 .8H_2O$ and ludlamite $(Fe,Mn,Mg)_3(PO_4)_2 . 4H_2O$; a variety of others are to be expected as well according to the local redox conditions [21]. A common feature of these compounds is that they will release considerable quantities of phosphorus under anaerobic conditions. Strong pH increases have been shown to prompt phosphorus release as well. Low redox conditions (approximately –250 mV) in the sediments lead to these nutrient releases.

Until recently it was thought that this was a purely physico-chemical reaction, where phosphorus-adsorbed iron oxide was released as iron was reduced under anoxic conditions. However, it is now becoming clear that much of the release of phosphorus is mediated by sediment microbial communities, because sediments which have had their microbial communities killed release different quantities of phosphorus when compared to normal sediments (Mitchell, 1997, in Robertson 1999 [22].) It is possible that fermentative Fe^{3+}-reducing bacteria are involved in this process [23], but a number of different microbial types are likely to be implicated.

> "It appears that release of P from sediments can be the result of abiotic processes
> (i.e. redox-induced chemistry), the indirect action of bacteria, or the direct
> release of P from Bacteria. While more than one of these processes can be

operating at the same time, in trying to manage the nutrient status of waterbodies it would be beneficial to know which of these processes has the *potential* to dominate the P release from sediments and, under what conditions." [24]

Figure 3. Formation of apatite from calcite. The banded area represents the difference between two equilibrium constants that are frequently used. (From Stumm & Morgan 1981)

Apatitic phosphorus compounds (i.e. apatites), which contain significant amounts of calcium, are more resistant to dissolution under anoxic conditions. In these mineral compounds, phosphorus is present essentially as tricalcium phosphate, on combination with a range of other calcium compounds. The formation of apatites from calcite (calcium carbonates) is governed by pH and the availability of phosphorus (see Figure 3, *left*).

The overall reaction may be summarised as:

$$10CaCO_3 + 2H^+ + 6HPO_4^{2-} + 2H_2O \leftrightarrow Ca_{10}(PO_4)_6(OH)s = 10HCO_3^-$$
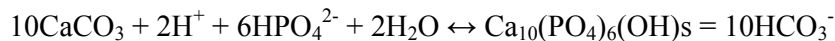
Some semiquantitative characteristics extracted from the pertinent literature suggest that:

- the content of inorganic phosphorus in sediments and water is considerably higher than that of organic phosphorus;
- the inorganic fraction consists mainly of non-apatitic phosphorus, but in sediments from calcareous regions apatitic phosphorus might be dominant;
- diagenetic processes (where calcium is available) seem to act towards a partial conversion of other phosphorus forms into apatitic phosphorus in deeper sediments, hence reducing phosphorus availability to remobilization through redox processes [21].

To quote Hendy [25]:

> "Seston is the light fluffy material that accumulates on the bottoms of the lakes. It possesses a density very close to that of water and it's made up of a combination of washed-in materials, silt and clays, and the organic debris from dying organisms. As this falls to the bottom of the lake it plays a very important part in removing material from the lake, especially the nutrients and adsorbed material such as trace elements, and much of this is assisted by the adsorption of trace elements onto the surfaces of the seston, rather than a chemical reaction itself, and in particular we look at manganese and iron as these adsorption agents. While the water from which the seston is falling contains dissolved oxygen in sufficient quantities, the iron and the manganese remain in an oxidised state which provides the binding agent between the solid material that's falling and the phosphate, the arsenate and other trace elements that are adsorbed onto those solids.

"We have a surface that in itself is not going to do very much unless we have the binding agents and those binding agents could be aluminium, iron, or manganese. In the case of the iron and the manganese they have to be in their oxidised state and they provide the link between the anions such as phosphate and arsenate and that surface. As the lakes become more eutrophic the accumulation rate of this falling organic matter to the seston will eventually exceed the supply of dissolved oxygen in the water into which they are falling and as the micro organisms break down that organic matter, they first utilise the dissolved oxygen and then when that's run out they start to reduce the manganese and the iron. When that happens the iron and the manganese become soluble, released into the pore waters and the adsorbed materials that they are holding are let go. Once they are let go they are free to move with the water and through the water and back into the bottom of the lake. Now in a lake that is oxygenated, as they approach the bottom waters, they are approaching a zone in which there's oxygen and once more the iron and the manganese will start to oxidise and readsorb the nutrients, the phosphate, the arsenate and other trace elements.
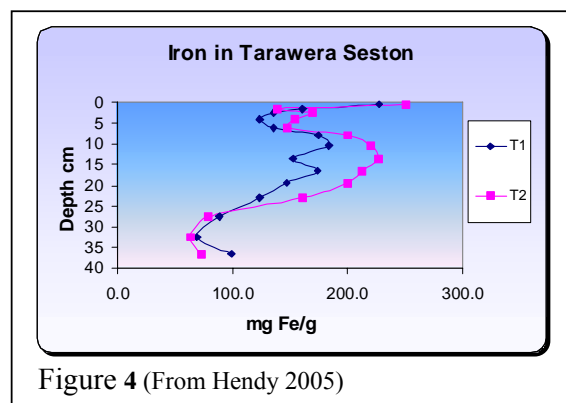
Figure 4 (From Hendy 2005)

"Geochemists have been sampling lake cores for decades and seeing profiles like this (*left*), and up until very recently they have looked at these and have thought that there had been a sudden rapid increase in the amount of that material going into the lake. But that, I think, is actually wrong. What is happening is the material in the seston is being remobilised and materials are moving up, striking the oxygen in the lake and re-precipitating

"The phosphate is doing the same thing. Right at the very top in the pore waters there are concentration gradients like this and those gradients are the driving
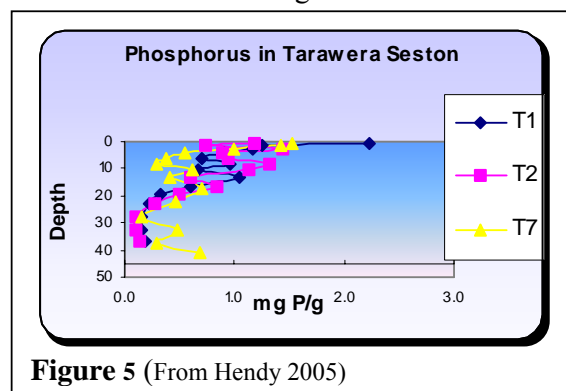
Figure 5 (From Hendy 2005)

force driving these ions out of the seston and into the overlying lake. From the slope of those, and once we know how fast materials can diffuse through this material, we can calculate the rate at which these trace elements and nutrients are being re-released back into the lake. So the iron, the manganese, the phosphate and the arsenic continue to accumulate in that intermediate zone where the seston meets the lake, and in Tarawera that accumulation has given a total of about 1 mg P/square cm. Now that doesn't sound very much, but if you multiply that up by the area of the lake,

that's 800 tonnes of phosphorus. Compare that to what's flowing out of the lake which is about 8 tonnes per year."

It is therefore apparent, that in order to arrest this process of P release from the sediments under conditions of anoxia, one of two things must be done:
- The overlying waters may be prevented from going anoxic. This may be done by various means, but discussion of them is outside the scope of this report.
- The adsorption mechanisms which retain P in the sediments must be altered in such a way that they continue to operate under anoxic conditions. There are various means of achieving this, which will be discussed in more detail below.

In addition, the loss of nitrogen from sediments is also deserving of consideration. Under anoxic conditions, nitrification (the oxidation of ammonia to nitrate by certain bacteria) is stopped, resulting in an abundance of ammonia. This may in turn result in reduced rates of denitrification (the reduction of NOx to atmospheric nitrogen by some bacteria), and hence influence the rate of loss of nitrogen to the atmosphere. In the case of nitrogen, there may be some long-term storage in the form of humic substances.   However, sediments are regarded as more important long-term sources of P than of N.   If external sources of nutrients are removed, N will be depleted from sediments before P is, owing to the relatively high denitrification rates in sediments (and lower initial concentrations of N) [22].

It should be emphasized that, in order to carry out successful phosphorus inactivation in any of the Rotorua Lakes, the chemical and physical nature of the sediments and the overlying water column will need thorough investigation. Extensive studies have been carried out, in recent years, of the water columns of many of the local lakes. A detailed chemical and physical study of sediments in lake Rotorua is well underway, and it is anticipated that this will shortly be extended to Lake Rotoiti [19].

Sediment oxidation

A different method to control internal P loading from anaerobic lake sediments, called sediment oxidation, was developed by Ripl [26]. With this procedure, $Ca(NO_3)_2$ is injected into lake sediments to stimulate denitrification. Nitrate acts as an electron acceptor. Ferric chloride also is added to remove H_2S and to form Fe^{+3} to which P is sorbed. The improved redox conditions in the sediment assist in reducing the release of phosphorus from the sediments. In a recent advance of this approach, a specialised compound, Depox® has been developed [27]. This material is based on a three-dimensional macromolecular complex produced by incremental hydrolysis of a ferric iron solution under conditions of increasing pH. This matrix is able to bind iron, and the incorporated nitrate is released only slowly. A further modification of the product, Depox®Al/Fe, also contains aluminium, although the original paper on these products does not clarify the additional benefits (if any) of incorporating aluminium. Such materials are often mechanically incorporated into the sediments by a process similar to harrowing, which is more suited to use in shallow lakes. It may be observed that seeking to deliberately introduce further nitrogen into lakes which are perceived by the public to be nutrient-enriched would need a skilful programme of persuasion.

P inactivation (sediment capping)

A variety of materials have been used to treat sediments in order that they may retain P under a wider range of environmental conditions (for example, an anoxic hypolimnion). Examples include:

- The use of zirconium tetrachloride in a pond [17]. The cost of carrying out this on a whole-lake scale may be expected to be very high. The environmental impacts could also be of concern.
- The use of fly ash residue (from the coal industry) [17]. Problems with this option include heavy metal contamination and (these days) availability of the material.
- The use of mineral materials, either in original or modified form. This will be discussed in more detail below. A number of the modified materials are imported and are covered in Appendix 2 to this report.
- The use of aluminium salts. This will be discussed in more detail below.

Practical aspects of sediment capping

In general, practical considerations suggest that sediment capping materials be supplied and transported as a solid material. For example, early versions of Phoslock were supplied as a slurry, but it is now available as granules, which makes it much easier and cheaper to distribute and transport. Materials that can be readily converted to a slurry, preferably on board the barge or other vessel that is being used to transport them across the lake being treated, would have an advantage.

Potential problems with sediment capping

Bioturbation

It might be assumed that once in place, a sediment capping layer would remain indefinitely, unless disturbed by ebullition of sediment gases or some major seismic or climatic disturbance. However, the phenomenon of bioturbation should also be considered. Bioturbation may be defined as:

> "an in-bed particle translocation phenomenon driven by the activity of bottom-living animals that moves sediment-bound pollutants and homogenises surface layers." [28]

This phenomenon has been proposed as a possible explanation for observed failures of sediment contaminant-release models. These failures are manifested as unexpectedly high contaminant release rates reported during field studies in a number of waterways. The conclusion arose from these studies that a further chemical release process was operating. Bioturbation has been proposed as supplying this additional process. It has also been recognised as a potential explanation for delayed recovery at a number of sites where contaminated sediments were covered with clean material which was expected to act as a 'cap' to the contaminated sediments. Oligochaetes (worms) were recognised as one potential causal group, but other aquatic animals are also potentially implicated [28].

A recent study carried out on Lake Tarawera investigated the possible role of in-lake fauna in distributing trace elements [29]. The effects of bioturbation *per se* were not examined but it was found that bottom dwelling fauna such as koura, freshwater mussels and bullies contained high concentrations of certain trace elements.

The main potential candidates for causing bioturbation in the Rotorua lakes are the kakahi (freshwater mussel), the koura (freshwater crayfish), and possibly the common bully and certain bottom dwelling smaller invertebrates.

Kakahi (*Hydridella menziesi*) attain sizes over 100 mm and reported maximum ages ranging from 13 to 33 years. They are filter feeders, travelling around on lake beds and leaving distinctive tracks behind them in the lake sediments. They are abundant in some of the Rotorua lakes, including Rotorua and Rotoiti. Wells and Clayton [30] studied the impacts of diquat spraying of aquatic weed beds in Lake Rotorua and found that kakahi were abundant (at densities up to 550/m^2) in water depths of 0.5 to 9 metres. They hypothesised that hypolimnetic deoxygenation may exclude kakahi from the hypolimnion in summer.

Koura (*Paranephrops planifrons*) are abundant in some of the Rotorua Lakes, including Lake Rotoiti (although numbers are believed to be falling) and are common in Lake Rotorua. They are the largest bottom-living crustacean in these lakes, growing up to 70mm long (excluding antennae). They may shelter under rocks or in burrows (substrate permitting) during the day, emerging at night to feed. They are omnivores, feeding on small invertebrates, organic detritus and plant material [31, 32]. In Lake Rotoiti they have been shown to live at depths of 7 to 10 metres in the summer, but after the lake destratifies they become widely dispersed across the lake bottom at depths of up to at least 50 metres. Lack of hypolimnetic oxygen is the cause of these summer migrations. They probably play a role in nutrient cycling, in that their feeding activities result in the breaking down of larger pieces of organic detritus and plant material [31]. Their feeding activities and burrowing habits render them a probable candidate for causing bioturbation.

The common bully (*Gobiomorphus cotidianus*) is abundant in most of the Rotorua Lakes, and is a bottom-dwelling species. Most specimens occurring in lakes reach a maximum length of 70-80mm. They are opportunistic carnivores, feeding on a variety of invertebrates, small fish etc. [33]. Both their feeding and breeding habitats give them a certain potential to cause bioturbation, particularly when present in large populations which may reach up to 500/m^2. They do occur in deep water, especially the large adults (they have been recorded at depths down to 70 m in some lakes [34]), but these will presumably migrate into shallower waters to avoid hypolimnetic deoxygenation during the warmer months. The possible advent of larger bottom-feeding fish, such as koi carp, could be expected to greatly increase the disturbance of sediments. For these and other reasons, the accidental or deliberate introduction of such species to the Rotorua Lakes should be avoided at all cost.

Certain smaller invertebrates are also potential candidates. Oligochaete worms are deposit feeders that live in, and ingest, sediments. They tend to achieve high densities and biomass in fine, nutrient-rich sediments where the degree of eutrophication is high [35]. Population densities may be as high as 50,000/m^2, and they may burrow into sediments to a depth of 10 cm or greater [28]. Some oligochaetes, particularly tubificids, have the ability to withstand anaerobic conditions for a month or more, but activity largely ceases during this period [36]. It is probable that oligochaete populations would be low in the deeper sediments (below approximately 15 m) of a lake such as Rotoiti, which stratifies and undergoes prolonged hypolimnetic anoxia. However, in the case of

Lake Rotorua, which stratifies for short, erratic periods and undergoes rather brief hypolimnetic anoxia, oligochaetes may be present in significant numbers in the deep sediments. Work carried out by Forsyth in the early 1970s supports this opinion, with oligochaetes being less numerous at depth in those lakes with a degree of hypolimnetic deoxygenation [37]. Lake Okaro, which even then experienced major deoxygenation (with all the lake bottom below the thermocline at 6 metres becoming anoxic by February) was described as having 'negligible' numbers of macroinvertebrates at the deepest part of the lake (15 m) throughout the year.

Wetzel [36] comments that tubificids have been shown to alter the stratigraphy of surface sediments by their activity. Chironomid (midge) larvae also inhabit lake sediments and are described as one of the main insect groups involved in bioturbation of sediments [38]. Like oligochaetes, they may tolerate lower concentrations of dissolved oxygen than most aquatic fauna, and they show similar distributions patterns in stratified lakes. They will tend to disappear from the deeper areas of lakes that experience hypolimnetic deoxygenation.

It may be concluded that bioturbation, with possible disturbance or loss of a nutrient 'capping layer' is more likely to be significant in lakes which do not experience prolonged periods of deoxygenation. This effect has been recognised in at least one paper [20]. However, even a lake such as Rotoiti, which contains large koura and bully populations (which periodically migrate to and from deeper waters) may well experience disturbance of the sediment capping layer, and this factor should be considered.

Wave action

Internal resuspension of sediments should also be considered as a potential problem with sediment capping projects. For this and other reasons, there appears to be little advantage in attempting to cap sediments in shallow waters, where wave action may well render such attempts futile. However, the presence of large internal waves (seiches) in lakes such as Rotoiti may also have a potential for disturbing sediment caps (Professor David Hamilton, University of Waikato, pers. comm.) These internal waves are believed to represent considerable amounts of energy. The question is whether their long periods means that this energy is released sufficiently slowly (at any one location) as to avoid disturbing sediments or sediment caps.

The use of mineral materials to cap sediments

This approach has been attracting considerable attention in recent years, particularly in Australia. A number of proprietary products have been developed for the purpose, including the following:
- Phoslock, a lanthanum-modified bentonite clay.
- Bauxsol, a chemically and physically modified waste product from the aluminium smelting industry.
- AlgalBLOCK, a precipitated calcium carbonate.
- Baraclear, an aluminium modified smectite clay.

These materials are all imported, and therefore outside the strict scope of this report, however, they are considered in moderate detail later in Appendix 1 to this document.

There are a number of local minerals which offer potential for this purpose. The major requirements of a suitable material include:

- Reasonably high specific gravity in order that the material may sink to the lake bed and remain there.
- Ability to bind major nutrient ions, such as phosphate, nitrate and ammonium (the latter two are more difficult).
- Ability to retain bound nutrients under anoxic conditions.
- Ability to trap nutrients which might otherwise diffuse upwards from the underlying sediments.
- Ability to be chemically or physically modified, if necessary, at reasonable cost.
- Ease of application.
- Relatively low cost of purchase and application.

Intellectual Property considerations.

There are a number of locally sourced materials which show promise for the purposes of lake remediation. Most are suitable in their own right, and some of these have the potential for further improvement by modification. An initial study of the US Patent (US 6,350,383 B1) for Phoslock suggests that it is written in such broad terms as to make the commercialisation of some such materials (even if locally developed) difficult without reaching an agreement with the patent holder. The patent covers a variety of mineral materials (including bentonite, other clays, zeolite etc..) and a variety of modifying processes and materials, including elements from Groups IIIB and IVB (CAS version) of the Periodic Table, together with the lanthanides. It does not, however, appear to cover the modification of mineral materials with elements, such as aluminium or calcium, which are outside these groups. However, the US Patent for Baraclear (US 2003/0213753) covers a wide range of possibilities for aluminium-modified smectite-type minerals (including bentonites). Certainly any local developments of modified materials will need to be carried out with the IP ramifications clearly in mind.

An interesting comment was received that for research organisations and small to medium sized commercial enterprises which have developed a modification process for a material, it makes much sense to come to an intellectual property agreement with a multinational corporation and draw licence fees from the multinational in return for the use of the invention. This way, a reasonable return can be secured from the intellectual property, whereas the multinational has the financial and human resources to protect the ensuing patent from 'piracy' (Dave Martin, Director, Terrane Minerals Ltd., pers. comm.)

Materials of interest for lakes remediation

Possible locally sourced materials are described below, listed alphabetically. Relatively little research appears to have been conducted on the relative abilities of different materials to take up nutrients. However, one such study compared the ability of a variety of natural and synthetic minerals to take up phosphate when used as a substrate in constructed wetlands. Of the materials bauxite, shale, burnt oil shale, limestone, zeolite (unmodified), light expanded clay aggregates (LECA), and fly ash, fly ash and shale had the highest P adsorption values, followed by bauxite, limestone and LECA [39].

This section of the report discusses materials that may be sourced within New Zealand. In many cases, if chemical modification is required, the substances needed to carry out modification may need to be imported, but the bilk material is sourced in this country.

A tentative ranking, in order of potential usefulness is given below. Where two materials show similar promise, the material that may be obtained more cheaply is given preference. Considering the current rapid increase in fuel prices, proximity to the Rotorua Lakes is considered to equate to 'cheapness' to a substantial degree. Not all of the materials studied have been included in this order of preference, which includes only those materials considered likely to be appropriate for large-scale use. The fact that a material does not appear does not, however, mean that it would not find use in small-scale applications.

Tentative order of preference

Order	Material	Pros	Cons
1	Allophane	Locally abundant, easily worked, strong P-adsorber, anion/cation abilities, may be modified	Slow to settle on dispersal
2	Zeolite	Locally abundant, easily worked,	Needs modification for best results
3	Bentonite	High cation exchange ability, may be modified to provide anion capability	Not quarried in Rotorua District, adsorbed ammonium may be microbially removed
5	Steel slag	Effective at P removal, good substrate for microbial and macrophyte communities, can be regenerated, dense so resists hydraulic disturbance	High transport costs
4	Limestone	Readily available at moderate cost. Has been shown to retain P in sediments under anoxic conditions	Not quarried in Rotorua District,

Allophane
A definition of allophane may be given as [47]:
> 'Allophane is the name of a group of clay-size minerals with short-range order which contain silica, alumina and water in chemical combination.'

Silicic acid in solution has a marked tendency to polymerise as the pH rises so that colloidal silica gels can occur as cementing agents in the lower B and C horizons of leached soils. Amorphous (microcrystalline) silica also occurs in soils formed on recent deposits of volcanic ash, as has been observed in Japan, New Zealand and Hawaii. Indeed, the bulk of the clay fraction in such soils may consist of a microcrystalline compound of silica and alumina called **allophane**. Allophanes have extremely high

negative charge densities because approximately one-third of the Si atoms are replaced by aluminium[40].

Figure 6 A schematic presentation of the structure of an allophane (From Wada 1985)
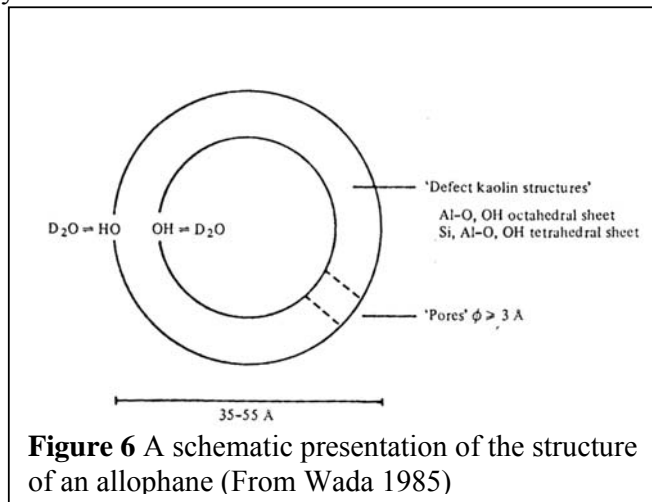
Allophanes form from volcanic ash materials and are major components of volcanic- derived soils. They may also be found in the clay fraction of non-volcanically derived soils[41]. Volcanic soils containing allophane usually have low bulk densities and may have significant organic matter content. The SiO_2: Al_2O_3 ratio of allophane varies from 0.84 to nearly 2. The aluminium may be in both tetrahedral and octahedral coordination. Al-rich allophane consists of spherical particles 3 to 6 nm in diameter (see Figure 6 *above*). These spherules have been shown to have micropores with a diameter ranging from 0.3 to 2.0 nm. These micropores may also be referred to as 'defect sites'. Allophanes have the empirical composition $Al_2Si_2O_5.nH_2O.$, but with a variability in the Al:Si ratio.

In New Zealand allophane tends to be particularly associated with the yellow-brown loams derived from old volcanic ash beds, such as the Tongariro and Taranaki deposits. These cover wide areas of the North Island but in many places they have been buried under later volcanic deposits [42]. Allophanic minerals are extremely important in soils derived from volcanic ash, for example the yellow-brown pumice soils and yellow-brown loams[43]. Allophane may persist in tephra beds for at least 250,000 years under favourable conditions, and is therefore a mineral which is relatively stable in soils [47].

There are three types of allophane found in New Zealand [44]:
- Al-rich allophane with an Al:Si molar ratio $\geq\approx2.0$ This is known as proto-imogolite allophane.
- Si-rich allophane with an Al:Si ratio ≈1.0. This is referred to as a halloysite-like allophane.
- Stream deposit allophane with an Al:Si ration $\approx0.9-1.8$. This is referred to as hydrous feldsparthoid allophane.

The Al-rich and Si-rich types of allophanes are both found in soils, but the predominant type in New Zealand is the Al-rich form. The third form (stream deposit allophane) has only a very localised distribution in New Zealand. The dominant conditions influencing the formation of allophane are the activity of silicic acid in the soil solution, the availability of aluminium, and the opportunities for co-precipitation of Al and Si. These conditions are, in turn, affected by pH, the presence of organic compounds and the leaching regime. The highest concentrations of allophane found in New Zealand soils are in the New Plymouth and Ohaewai soils, where allophane may constitute up to 38% of the soil in the lower horizons.

Allophane is in the group of minerals described as short-range order aluminosilicates. The materials described in this section, **allophane, proto-imogolite allophane and imogolite,** are often loosely referred to as 'amorphous' aluminosilicates, which implies that they have random, or non-crystalline structures. More correctly they could be referred to as 'X-ray amorphous' since it was the failure to observe sharp, intense peaks on X-ray diffractograms from these materials that led to their classification as 'amorphous'. Other techniques of analysis, particularly electron microscopy, infra-red spectrometry, nuclear magnetic resonance spectrometry and thermal analysis, have shown that these materials do in fact have some structural order, but only over a 'short--range'. The structures are not regular enough, and the particle sizes too small, to give anything but broad, low intensity peaks in X-ray diffractograms. In recent years the term short-range order, rather than amorphous, has been used to describe these particular aluminosilicate minerals.

The most characterized and best ordered of these materials is **imogolite**. This is shown by transmission electron microscopy to consist of bundles of long tubes. There is a viewpoint that holds that imogolite is not a short-range order (SRO) material because it has long-range order in one dimension (along the tubes)[44]. According to the definition given above, imogilite would not be classified as an allophane.

Allophane, although consisting of similar structural units to imogolite and kaolinite, is less ordered than either of these minerals, and its elemental composition is much more variable. At one extreme, its elemental composition is similar to that of kaolinite with an Al : Si ratio of 1: 1, and at the other extreme it resembles imogolite with an Al : Si ratio of 2: 1. A clear definition of allophane would therefore seem difficult to achieve. However, a useful approach is to regard the short-range order aluminosilicates in soils as constituting an allophane series of minerals, with kaolinite and imogolite as end members. Kaolinite and kaolin are discussed later in this report.

Some allophanic material in soil is referred to as **proto-imogolite** allophane. The reason for this is that it is considered to have similar properties to aluminosilicate gels, prepared in the laboratory, which, on heating, form imogolite.

Soils dominated by allophane have physical and chemical properties known as **andic** and such soils are generally classified as **andisols**. Andic soil properties include:
- very porous and friable nature, greasy when moist
- low bulk density
- strong interaction with organic matter
- high water retention, rapid permeability
- high oxalate extraction of Al and Fe, high pH in NaF
- high phosphorus retention
- weak strength, sensitive
- high surface area, variable charge

Soils containing allophane (and imogolite) form very complex and stable associations with organic matter in soil. These complexes appear to protect the organic fraction from degradation by soil organisms. It appears that the aluminium component of the allophane is primarily responsible for forming such complexes.

The very high surface area of allophane (typically $\approx$400 to 900 $m^2.g^{-3}$) means that even quite small proportions of allophane in a soil have a significant effect on the properties of the soil – 1 % of allophane may contribute 85% of the surface area of the soil.

Andosols generally are noted as soils with variable electric charge.   The degree of these charges (positive or negative) may be affected by factors such as pH and electrolyte concentration[45]. In allophanes negative charges are believed to be derived from Si-OH groups in the Si-O tetrahedral sheet that constitutes the walls of the spherules, with additional negative charges possibly arising from the substitution of Si with Al in allophanes with higher Si:Al ratios.

The charge of allophane particles is strongly governed by pH. The most reactive groups in the allophane structure are probably the $Al(OH)H_2O$ groups. Under acid conditions these become $Al(OH_2)^+H_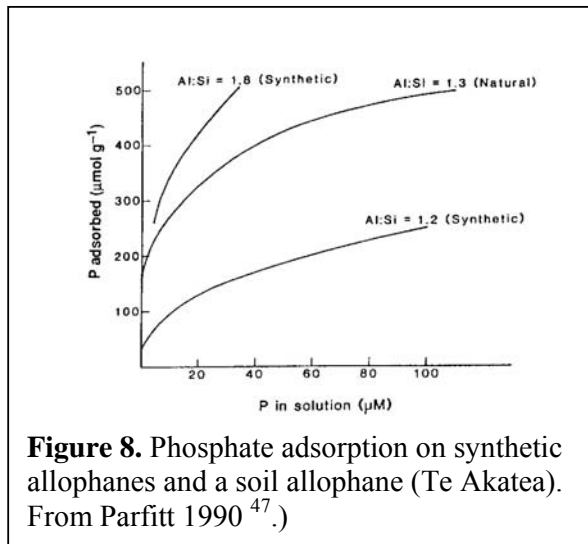2O$ and under alkaline conditions they become $Al(OH)(OH)^-$. In the pH range 5 to 7, both positively and negatively charged species are present on the surface of allophanic particles [47]. The negative sites have the ability to adsorb cations and the positive sites can adsorb anions, giving allophane the ability to take up a fairly wide range of dissolved ionic species. The accompanying diagram(*left*) demonstrates this ability. As may be seen, at lower pH more anions are adsorbed, and at higher pH more cations are adsorbed.
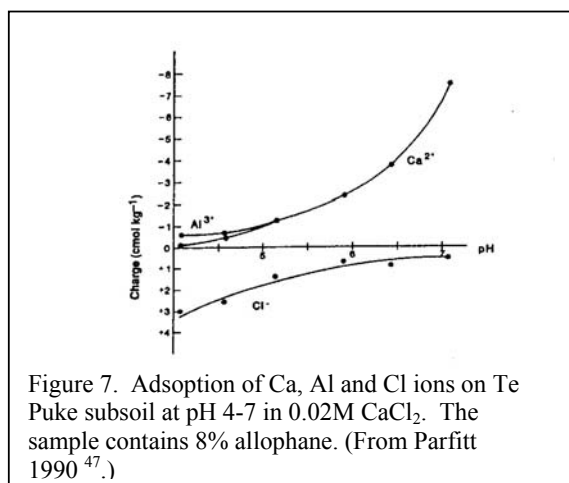
Figure 7. Adsorption of Ca, Al and Cl ions on Te Puke subsoil at pH 4-7 in 0.02M CaCl₂. The sample contains 8% allophane. (From Parfitt 1990 [47].)

The interaction of allophane with organic matter, which carries a negative charge, increases the negative charge on allophane and decreases the positive charge, thus increasing the ability to adsorb cations and decreasing the ability to adsorb anions. The subsoil shown in Figure 7 (*above*) contains 1.8% C, some of which is probably associated with the allophane. The negative charge carried by the organic matter contributes to the relatively high negative charge (and associated ability to adsorb cations) shown at pH 7.

In highly allophanic soils, the organic matter appears to react rather slowly with allophane, but once allophane/organics complexes are formed they account for the slower rate of mineralisation of carbon and nitrogen in these soils, compared with non-allophanic soils.

When phosphate solutions are added to allophane at pH 5-6 with $CaCl_2$ present, the first increments of phosphate are rapidly and strongly adsorbed. As surface coverage increases, the later increments of phosphate are more weakly adsorbed [46].   These phosphorus adsorption reactions involve ligand exchange with AlOH and AlH_2O groups at defect sites on the surfaces of the allophane spherules. These initial adsorption reactions are followed by a slow reaction where the allophane structure is disrupted and aluminium phosphate precipitates may be formed. The extent of the P adsorption

Figure 8. Phosphate adsorption on synthetic allophanes and a soil allophane (Te Akatea). From Parfitt 1990 [47].)

increases as the Al:Si ratio of the allophane increases, with the amount of phosphate that is strongly adsorbed varying between 50 and 200 $\mu mol.g^{-1}$. This is equivalent to 2 to 8 phosphate ions per spherule of allophane.

Figure 8 (*left*) shows the impact of the Al : Si ratio on phosphate adsorbance.

Phosphate is usually associated with naturally occurring allophane, and it can be extracted with either 0.5M H_2SO_4 or acid-oxalate reagent. In other words, strongly acidic conditions will displace this adsorbed phosphate. Up to 120 $\mu mol P.g^{-1}$ has been extracted from allophanic subsoils. Allophane spherules interact strongly, particularly if they are dried, to form both silt-size and sand-size aggregates. The interaction between undried aggregates is weak. The strongest interactions occur at a pH close to 6, where the positive and negative charges on the allophane are present in approximately equal amounts. On drying, the spherules tend to coalesce, giving rise to stable aggregates. Obviously, if allophane was to be used in a permeable reactive barrier or similar installation, the use of sand-size rather than silt-size particles would be preferable.

Allophane will also adsorb other anions, particularly sulphate, with the amount adsorbed increasing as the pH decreases from 7 to 4. Sulphate is adsorbed by displacing the H_2O and OH groups held at defect sites. Allophanic soils adsorb up to 100 μmol S per g of allophane.

Allophane has been the subject of considerable research in New Zealand, because allophanes are very widespread in their distribution here. This is due to the frequent occurrence of tephra falls, and a suitable environment and climate for the production of allophane [47].

Work is currently underway to study allophane as a potential N-adsorber, but the research is still confidential. Allophane is an excellent natural P-adsorber. It is possible that for best results the mineral may need some modification. Such modification could, for example, include additional bound aluminium, but care would be needed to avoid patent infringements. Alternatively, advantage might be taken of the fact that allophanes may possess both anion and cation exchange properties to modify them in such a way that other nutrient ions, such as NH_4^+ might be taken up and retained in anoxic sediments.

Theoretically allophane is the cheapest of all of the minerals under consideration in this study, being available locally in large quantities. Considerable work has been carried out by AgResearch staff in investigating and classifying local soil types, and their work should be referred to.

Allophane, being a clay mineral, has a tendency to disperse into very fine particles when discharged into water. This would aid in removing dissolved phosphorus from the water column but may cause an increase in turbidity for prolonged periods. Consideration might need to be given to pelletising the material for release into lakes and other waterways. Allophane that is naturally low in P would be preferable for such uses.

Initial research into the use of natural and modified allophanes for water quality improvement is underway by Landcare Research (Palmerston North). Dr Mark Cleaver is running the project. Dr Gudong Wang is carrying out the R & D work (his speciality is clay mineralogy and nanoclay systems). Ballance Fertilisers have an interest also and are providing some financial support. This project is in its initial phase only. The work is underway but has not progressed as quickly as was initially hoped, and no results are yet available (Dave Martin, Director, Terrane Minerals Ltd., *pers. comm.*)
.
As with other clay minerals, allophane is generally mined by selective open pit methods using heavy machinery. Where processing is required it may be carried out by one of two methods:
- A dry process, involving crushing, drying, pulverising and then air flotation to remove the grit particles (mostly quartz and feldspar)
- A wet process, by forming a wet slurry then removing the grit by means of hydrocyclones or other installations, centrifuging the cleaned material, thickening in a settling tank, filtering then drying. This is the more costly process but generally produces a higher quality product.

Bentonite

Bentonites are a group of clays consisting predominantly of smectite (montmorillonite) minerals. Smectites have a 2:1 sheet structure where two tetrahedral sheets (each sheet is a plane of silica tetrahedral) are linked by an alumina octahedral sheet. Water may be sandwiched between the triple layers so that the lattice structure swells. These are expanding lattice clays which usually swell in water, are thixotropic (i.e. they form a gel on wetting, which reverts, reversibly, to fluid on stirring) and possess high cation-exchange capacities [48]. There are two main types of naturally occurring bentonites:
- A swelling bentonite which has a high sodium:calcium ratio, typically associated with marine sediments. Known as sodium bentonite.
- A non-swelling bentonite with a low sodium:calcium ratio, typically associated with freshwater sediments. Known as calcium bentonite.

Bentonites occur in a number of localities around New Zealand. Marine-deposited bentonites occur in a number of areas along the east coasts of both the North and South Islands. The major North Island deposits occur in Gisborne, Hawkes Bay and Wairarapa. The most readily accessible deposit (from the Rotorua District) would be those at Mangatu (north of Gisborne) and Paraheka, south of Gisborne. These are both swelling bentonites, with calcium carbonate content ranging from 4.5 – 8.3% (Mangatu) to 2 –4 % (Paraheka). Only the Paraheka deposits are currently worked (intermittently).

A deposit of some interest is the Coalgate deposit in the Harper Hills, 65 km west of Christchurch. This is a non-swelling bentonite formed by weathering of glassy basaltic

ash deposited in a lake [48]. It is a calcium-magnesium type, but may be processed to form a swelling type by treatment with soda ash. Measured resources total about 10^6 tonnes, but potential resources are believed to be much larger. It is high in iron.

There is some interest in the possible modification of this iron-rich bentonite from the Coalgate deposit by the addition of further iron (Dave Martin, Director, Terrane Minerals Ltd., pers. comm.) This project is in the initial stages only i.e. it is under consideration. Mr Martin is of the opinion that the Coalgate material is the most promising type for lake remediation work. Bentonite of the swelling type is used as the basis for Phoslock.

Unmodified bentonites have high cation exchange capacity, which makes them of interest in ammonium adsorption. However, once adsorbed it is believed that ammonium is still susceptible to microbial action, meaning that it is open to being converted to anionic and non-adsorbed nitrate. For this reason, the possible modification of bentonite by adding metal salts, as in Phoslock, is believed to be the most promising approach to the use of this material in lakes remediation.

Calcium carbonate (limestone)

Calcium-phosphorus precipitation is a common method of phosphorus removal, mainly because of low cost and ease of handling. Removal of P is achieved by direct precipitation of calcium phosphate (hydroxyapatite, $Ca_5(PO_4)_3OH$) . However, the carbonate ion competes with phosphate for calcium ions, thus inhibiting the precipitation of calcium phosphate. This is an example of ion-pair formation affecting a precipitation reaction. Somewhat paradoxically, limestone is frequently used for phosphorus removal.

For example, a number of $CaCO_3$ limestone products have been trialled for P immobilisation in a small urban lake in Melbourne, Australia [49]. It was determined that two fine-grained, precipitated forms of $CaCO_3$, SoCal and ESCal, were effective at reducing the phosphorus release from lake sediments. Finely ground natural limestone was ineffective. Contrary to widely-held opinion, both of the precipitated limestone products were effective at reducing the mobilisation of P under anaerobic conditions by a factor of at least 10. Further work is underway.

Apatitic phosphatic minerals, which contain a high proportion of calcium, are generally resistant to dissolution in anoxic conditions.

The multinational Omya has a limestone plant at Te Kuiti. They process Queensland limestone (which is very white and is used in the paper industry) and the local product – about 30 grades of limestone are produced there. It may be possible to load $CaCO_3$ onto zeolite to produce a composite. The higher the surface area of the limestone the better should be the performance. The finest grade produced at Te Kuiti has a maximum particle diameter of 8 microns and a surface area of 6.3 m^2/g.This would prove difficult to apply over a lake surface, particularly if aerial application was being considered. There is a coarser grade, OMYACAL 5, which has a maximum particle diameter of 48 microns and is currently being granulated for aerial application. This could be an ideal product if it is decided that calcium carbonate is worth evaluating -- certainly the economics would be promising. There has been some work done on the adsorption of

phosphate by Calcium carbonate which shows it to be pH-dependant (Reference not located). (Dave Martin, Terrane Minerals (pers. comm.).

Calcium peroxide, hydrogen peroxide

A report of research carried out in China discussed the use of calcium peroxide and hydrogen peroxide as agents for transporting oxygen to lake sediments, to inhibit the release of P from sediments during periods of anoxia [50]. As these two materials break down, oxygen is released. Both CaO_2 and H_2O_2 were shown to be effective at reducing phosphorus loss from the sediments of two lakes, with CaO_2 being more effective. The production, during the decomposition of CaO_2, of $Ca(OH)_2$ and its binding of phosphate was believed to account for the superior performance of CaO_2 over H_2O_2. Both materials were more effective than water column aeration at reducing P release. Calcium peroxide does not appear to be manufactured in New Zealand, however hydrogen peroxide is manufactured in Morrinsville by Degussa Peroxide Ltd.

In waters with high organics, high temperature and a low content of oxygen the solubility of gaseous oxygen can be very low. In this case the dosage of hydrogen peroxide is much more effective at introducing available oxygen. In waste water treatment plants in Europe hydrogen peroxide is used as a so-called "accompanying measure" if the oxygen content is very low and aeration with oxygen is not sufficient. (Dawn Kapp, Degussa Peroxide Ltd., pers. comm.) Both bench and field trials are recommended before considering the use of hydrogen peroxide for lake oxygenation – the success and viability is dependant on the nature of the water. The cost of H_2O_2 supply and application would be a major consideration.

Cellulose

Discussion on the use of wood wastes, such as sawdust, in treatment trenches, will be found elsewhere in this report. An interesting possible modification of woodwaste-filled treatment trenches is the incorporation of polymer mesh mats to deliver oxygen (for nitrification of ammonia) or a carbon source such as methanol (for denitrification) [51].

Charcoal

Charcoal may be defined as "the black porous residue obtained by the destructive distillation of animal or vegetable matter in a limited supply of air." The so-called "graphitising" carbons tend to be soft and non-porous, with relatively high densities, and can be readily transformed into crystalline graphite by heating at temperatures in the range 2200-3000 °C. In contrast, "non-graphitising" carbons are hard, low density materials which cannot be transformed into crystalline graphite even at temperatures of 3000 °C and above. The low density of non-graphitising carbons is a consequence of a micro-porous structure, which gives these materials an exceptionally high internal surface area. This high surface area can be enhanced further by activation, i.e. by mild oxidation with a gas or by chemical processing, and the resulting "activated carbons" are of great commercial importance, primarily as adsorbents.
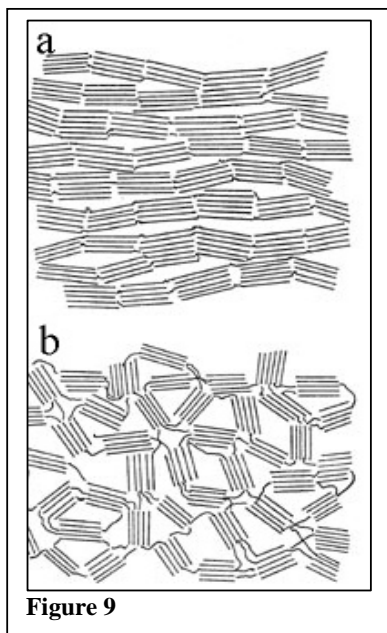
Figure 9

In the 1930s the crystalline nature of graphite was determined through the use of X-ray diffraction techniques. Non-crystalline carbon materials, such as soot, coke and char, were more difficult to examine. It was established that these carbons, like graphite, contained hexagonal carbon rings, but the way these were linked together remained unknown. Some workers suggested that char might have a three-dimensional network structure lying somewhere between those of graphite and diamond, but there was no direct evidence for this. The distinction between char and coke was also not understood. Rosalind Franklin is better known for her work on the structure of DNA than for her work on carbon. However in the late 1940s and early 1950s, before she moved into biology, she made a major contribution to the understanding of coals, carbons and graphite. She coined the terms *graphitising carbons* and *non-graphitising carbons* to describe the two classes of material she had identified, and proposed models for their microstructures, which are shown on the left (*Figure 9*). In these models, the basic units are small graphitic crystallites containing a few layer planes, which are joined together by cross-links. The structural units in a graphitising carbon are approximately parallel to each other and the links between adjacent units are assumed to be weak as shown in (a). The transformation of such a structure into crystalline graphite would be expected to be relatively easy.

In contrast, the structural units in non-graphitising carbons, are oriented randomly, as shown in (b), and the cross-links are sufficiently strong to impede movement of the layers into a more parallel arrangement. This is the type of structure which is found in charcoals.

Although these models do not represent a complete description of graphitising and non-graphitising carbons, since the precise nature of the cross-links is not specified, they provided for many years the best structural models available for these materials. The atomic structure of chars and the reasons for their resistance to graphitisation are still the subject of intense research, nearly 50 years after Franklin's work.

However there is a growing belief that the key to the problem may lie in the discovery of a new class of carbons known as fullerenes.

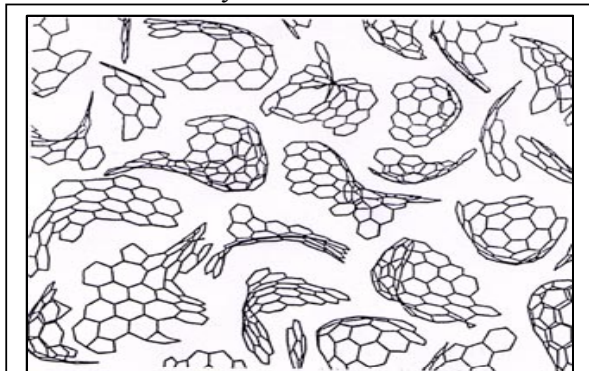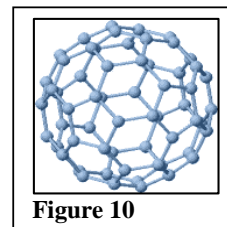**Figure 10**

Fullerenes are a group of closed-cage carbon particles of which the archetype is buckminsterfullerene, C_{60}, whose structure is shown on the right (*Figure 10*). There is growing evidence that microporous carbons

Figure 11

may contain fullerene-like elements. As a result of recent studies, many workers in the field now believe that charcoal has a structure made up of fragments of randomly curved carbon sheets, containing pentagonal and a heptagonal rings dispersed throughout a hexagonal network, as shown in Figure 11(*left above*). However, this idea is by no means universally accepted [52].

The use of charcoal as an adsorbent, like most of its other applications, has a very long history. Since the early 20th Century activated charcoal (also known as activated carbon) has been favoured, due to its superior adsorption properties. This is produced by subjecting charcoal to the action of an oxidizing gas such as steam or air at elevated temperatures. Chemical modification methods may also be used, such as heating in the presence of aqueous zinc chloride or phosphoric acid. This process enhances the adsorptive power of charcoal by developing an extensive network of fine pores in the material.

Several factors influence the effectiveness of activated charcoal. The pore size and distribution varies depending on the source of the carbon and the manufacturing process. Large organic molecules are absorbed better than smaller ones. Adsorption tends to increase as pH and temperature decrease. Contaminants are also removed more effectively if they are in contact with the activated charcoal for a longer time, so flow rate through the charcoal affects filtration.

Activated charcoal removed substances from water largely by physical interactions between the carbon surfaces and the molecules being removed. Organic molecules and non-polar molecules are most likely to be adsorped. However, there is a limited electrical interaction with some types of activated charcoal, so that a small degree of ion exchange may occur.

Activated carbon has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity. Commercial food grade products range between 300 and 2,000 m^2/g but some grades have surface areas as high as 5,000 m^2/g. The specific mode of action is extremely complex, and has been the subject of much study and debate. Activated carbon has both chemical and physical effects on substances where it is used as a treatment agent [53]. The modes of activity can be separated into four categories:

- **Adsorption**, which is the most studied of these properties in activated carbon. The majority of applications of activated carbon can be characterized by the adsorption that occurs when components of a liquid (the food or beverage) attaches to a solid (activated carbon). This can be either physical or chemical in nature, and frequently involves both. Physical adsorption involves the attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate.

Adsorption capacity depends on
   - a) physical and chemical characteristics of the adsorbent (carbon);
   - b) physical and chemical characteristics of the adsorbate i.e. the material to be adsorped;
   - c) concentration of the adsorbate in liquid solution;
   - d) characteristics of the liquid phase (e.g. pH, temperature)

e) amount of time the adsorbate is in contact with the adsorbent (residence time).

- **Mechanical filtration** involves the physical separation of suspended solids from a liquid passing through carbon arrayed as a porous media in a column or bed. Any finely divided solid—such as sand or cellulose—can accomplish this. While this accounts for some of the clarification properties of carbon, it is seldom the sole reason for the selection of carbon as a clarification medium. The effectiveness of filtration depends on particle size, bulk density, and hardness.

- **Ion exchange** may be defined as a reversible chemical reaction between a solid and an aqueous solution that allows the interchange of ions. Ion exchange involving charcoal can be enhanced by chemical activation. Carbon surfaces have both negative (anionic) or positive (cationic) charges to attract free ions in solution or suspension, depending on how they are treated. Treatment of carbon with a base increases the capacity of carbon to exchange anions; acidulation of the surface makes carbon a powerful cation exchanger.

- Surface oxidation involves the chemical adsorption of atmospheric oxygen to the carbon and the further reaction of the surface oxides that chemically react with other substances that are oxidized.

A reference in the analytical chemistry literature [54] refers to the pre-concentration of phosphate-phosphorus, before analysis, by passing the sample through a solid-phase extraction column prepared from activated carbon loaded with zirconium. The extractant material was prepared by mixing powdered activated carbon with zirconyl nitrate solution, filtering then drying. Presumably the zirconium was retained on the carbon particles by the limited amount of ion exchange activity displayed by activated carbon.

As may be seen in the preceding discussion, activated (in particular) charcoal is well suited for the adsorption of non-polar and organic compounds, but has limited ability to remove inorganic nutrients from solution, due to its relative lack of ion exchange capacity. In situations where organically-bound N or P are a major portion of the total nutrient loading, activated charcoal is a potentially useful material for nutrient removal, either by being incorporated in a reactive permeable barrier system or by being used in some type of retention system. However, activated carbon tends to be a high-value material, and this implies that small-scale applications are more viable.

It may also be commented that, despite limited ion exchange abilities (unless extensively modified) activated charcoal forms an excellent growth substrate for a wide variety of micro-organisms. This results in various side effects:
- It has been shown [55] that biological activity within an activated charcoal medium may result in higher adsorption ability than would otherwise be expected and this is due to the following factors:
   The biological ability of the colonising micro-organisms to themselves metabolise and remove contaminants.
   An apparent ability of many micro-organisms to regenerate the adsorption sites on the charcoal.

- Among the micro-organisms that may colonise charcoal are those which have the ability to remove nutrients by nitrifying and denitrifying activities.

The use of charcoal, particularly activated charcoal, in large scale removal of nutrients from the Rotorua lakes and their associated waterways may be regarded as meriting further investigation. Although activated charcoal is regarded as a high-value material, the combination of large volumes of locally available wood wastes (bark, sawdust, wood chips) and low-cost geothermal heat makes it of possible future potential.

Chitin

Chitin is a natural polymer, technically known as polyacetylglucosamine, characterised by the presence of a charged NH group and an acetyl group CH_3CO.

Chitin, a polysaccharide, is one of the main components in the cell walls of fungi, the exoskeletons of insects and other arthropods, and in some other invertebrate animals. It is made out of units of acetylglucosamine (more completely, N-acetyl-D-glucos-2-amine). These are linked together in β-1,4 fashion, the same as the glucose units that make up cellulose. So chitin may be thought of as cellulose, with one hydroxyl group on each monomer replaced by an acetylamino group. This allows for increased hydrogen bonding between adjacent polymers, giving the material increased strength. Approximately 16% of naturally-occurring chitin units are deacetylated. The strength and flexibility of chitin greatly assists in protecting and anchoring many invertebrates.

Chitin was first isolated in 1811 and along with cellulose and starch, it is one of the most abundant polysaccharides in nature. It is found naturally in the shells of crustaceans, molluscs, insect exoskeletons, fungal cell walls, microfauna and plankton. It is found in association with proteins and minerals such as calcium carbonate and it is estimated that approximately ten gigatonnes of chitin are synthesised and degraded each year in the biosphere. It is therefore very abundant.

Figure 15. Structure of chitin molecule.
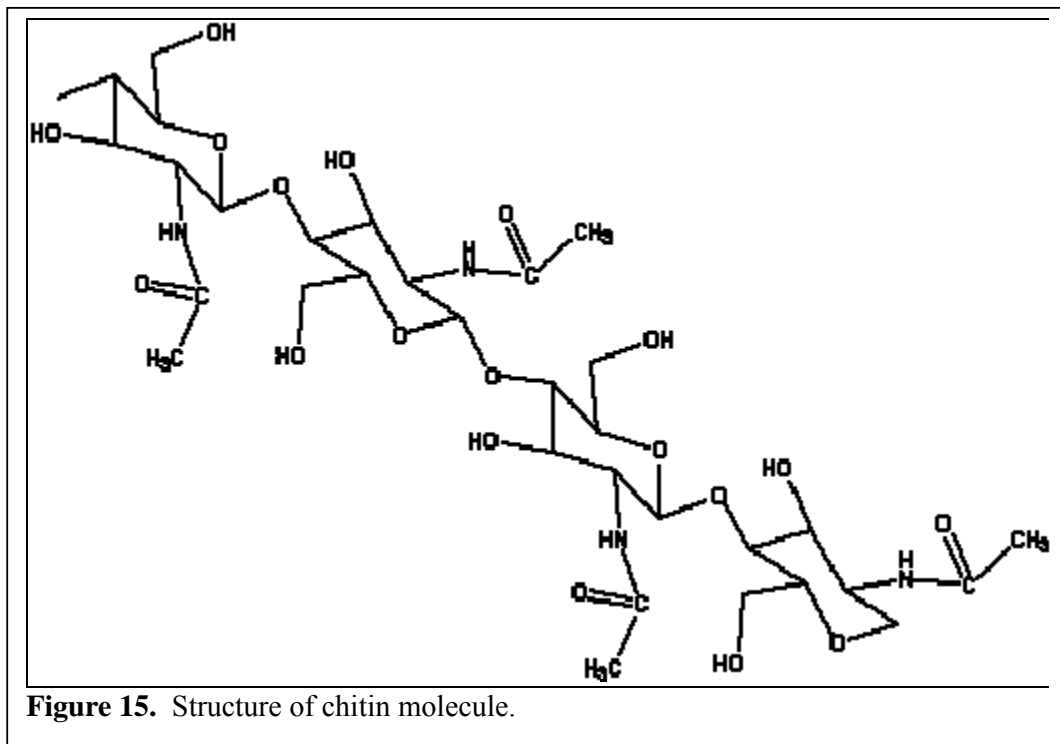
The various sources of chitin differ in their structure and chitin content. There are three polymorphic forms of chitin, α, β, and g. The most abundant form of chitin is α -chitin where the polymer bonds are tightly bonded in an anti-parallel arrangement that leads to a highly crystalline structure; hence α -chitin has poor solubility and reactivity [56]. B-chitin has a parallel arrangement of the polymer bonds, which makes it more susceptible to chemical modification and dissolution, due to weaker intermolecular hydrogen bonding.

Chitin is one of the most abundant organic materials, being exceeded only by cellulose in the amount produced annually by biological organisms. Chitin has a crystalline structure, and constitutes a network of organised fibres, which confers rigidity and resistance to organisms that contain it [57].

The principal derivative of chitin is chitosan, a family of copolymers with various fractions of acetylated units which are produced by alkaline deacetylation of chitin, under strongly alkaline conditions. Chitosan occurs naturally in some fungi, but is much less widespread in nature than is chitin. Chitosan has been shown to have a wide range of scientific, pharmaceutical and industrial uses. Chitin is distinguished from chitosan by being insoluble in 0.1 M acetic acid, whereas chitosan is soluble under these conditions. The degree of deacetylation is also a distinguishing factor, and it has been proposed that a degree of deacetylation exceeding 20% is characteristic of chitosan [58].

Chitin is readily available from by-products of the seafood processing industry, such as crustacean cuticles (from, for example, lobster and crayfish processing) and mollusc shells (from processing of oysters, mussels etc...) In New Zealand, much of the crustaceans that are processed are exported (or sold locally) in-shell, so the supply of chitinous material from this source is limited. However, such molluscan seafoods as oysters or green-lipped mussels are frequently sold without shells, so there is a significant supply of the shell material available. The 'pens' from squids, another mollusc, are also discarded after processing.

The nature of the molluscan shell has been well studied, and it is believed that calcified mineral crystalline layers are deposited on an organic matrix largely made up of proteins (about 50 to 80% of matrix dry weight), with a variable amount of chitin, up to about 40% of the matrix dry weight [59]. Calcium carbonate and various proteins are the other main constituents. The chitin in mollusc shells tends to be strongly incorporated into the overall structure, which has both advantages and disadvantages.

Extraction of chitin from crustacean carapaces or mollusc shells is a relatively difficult process, generally involving the use of strong acids and/or bases. However, certain enzymes, such as various chitinases and acetylglucosaminidases, are known to degrade chitins [60]. In addition, work being carried out at Otago University has shown that β-chitin, as found in squid pens, may be readily released by fermenting the pens with lactic acid bacteria. The presence of actinidin, an enzyme produced by kiwifruit (*Actinidia chinensis*) enhances the rate of chitin extraction from the pens [61]. The total allowable commercial catch of squid in New Zealand's economic zone is in excess of 100,000 tonnes per annum. Work is being carried out to find uses for the by-products (including pens) of processing this catch. The β-chitin that can be extracted from the

squid pens is more readily treated for chitosan production than are other forms of chitin [62].

Chitin and its derivative chitosan have been shown to be useful in removing a variety of materials from water. Chitosan has been recognised as an effective flocculating agent for several decades. This property is due to its cationic nature in acidic solution, which enables it to neutralise the negative charges present on suspended particles. Such flocculating agents have proved effective at reducing phosphorus levels in turbid stormwater, through their ability to remove turbidity and the adsorbed phosphorus. Both chitin and chitosan are moderately effective at removing a number of metal ions (Mg, Ca, Mn, Ni, Cu, Zn, Cd etc.) from solution, yet, paradoxically, they also have chelating properties. In this way, chitin still bound to a shell or carapace has the ability to remove metals from the surrounding solution..

There is considerable world-wide interest in the many potential uses of chitosan, ranging from water treatment through to pharmaceutical, medicinal and industrial uses. The various classes of chitosans have been shown to be susceptible to a wide range of chemical modifications, leading to a range of materials with wide-ranging and unusual properties. Full discussion of these materials is outside the scope of this report. However, some chitosan modifications of possible interest include:

- Chitosan Schiff bases (formed by reactions with aldehydes or ketones) – strongly swelling properties in water, yet hydrophobic
- Acetylated chitosans – useful as molecular sieves
- Glycoxylated chitosans – gelling agents
- Phosphorylated chitosans (and chitins) – effective at removing metals from solution
- Polyelectrolyte chitosans – effective flocculants, algal cell immobilising agents
- Film-forming chitins and chitosans – possible sediment capping agents

It may be commented that chitin is already being produced in our lakes due to the activities of molluscs such as the freshwater mussel *Hydridella menziesi,* crustaceans such as the koura (*Paranephrops planifrons*) and a wide variety of zooplankton. Chitin production by marine zooplanktonic copepods in the Bay of Calvi (Corsica) has been measured at up to 17 mg.m^{-2}.day^{-1} during the summer [63]. Such material settles to the lake bed upon the death of the organism, and slowly degrades. In marine sediments the enzyme chitinase is believed to be active in this process [64]. Chitin concentrations in marine sediments have been shown to reach up to 2800 μg/g of decalcified sediment. In freshwater sediments chitin has been shown to be decomposed aerobically or anaerobically, eventually producing carbon dioxide and methane, and generating an oxygen demand [65]. Work in a small tarn near Lake Windermere (U.K.) showed that the majority of anaerobic decomposition of chitin occurred in the 0-6cm horizon rather than in deeper horizons [65]. This decomposition may occur at a relatively rapid rate, with up to 90% of the chitin content of mollusc shells being degraded within 12 months, and up to 99% of the chitin content of crustacean carapaces being degraded within 4 months [66]. The chitin was shown to degrade more rapidly than the protein component of the shells and carapaces.

Partially degraded chitin has been shown to possess a strong ability to firmly bind a number of metallic elements, iron included [64]. Considering the known involvement of sediment iron in phosphorus binding and release, it appears that in-lake chitin may

already be a component of the phosphorus cycle in lakes. In theory, large-scale deposition of chitin waste derived from the seafood processing industry could be useful in potentially locking up iron (and therefore phosphorus). In addition, a reference in the analytical chemistry literature discusses the use of protonated chitin for the preconcentration of phosphorus from water samples before analysis, however it appears that the phosphorus is taken up as the 'phosphomolybdenum blue' complex. [67]. However, transport costs and the potential environmental impacts (oxygen demand, release of organic compounds) mean that more locally available mineral materials would seem to show more promise.

In any potential large scale endeavours towards improving lake water quality, chitin may be regarded as a relatively low cost raw material of intrinsically limited direct use for such endeavours, and chitosan as a potentially useful group of high-value materials with a variety of possible specialised applications. The limited literature available suggests a wide range of potential environmental applications but is very light on detail. In the event of large-scale production of chitosans commencing in New Zealand, possibly utilising squid pens as a raw material, it is recommended that further investigations be made into the potential uses of this group of materials for water quality improvement. At present, they may be regarded as promising materials in search of problems to solve. Cost and availability will be the controlling factors.

Kaolin

Kaolin (kaolinite) is another clay mineral, commonly found in deposits associated with hydrothermal activity. It is produced by the hydrothermal alteration of igneous rocks. It is frequent found in the central North Island, for example at Rotorua, Waiotapu and Wairakei. It often contains such impurities as allophane, residues from thermal waters, and iron compounds [68].

Trials on a modified form of kaolin were carried out in Australia. The material, known as MesoLite is made by caustic reaction of kaolin at temperature between 80-95°C. Although it has a moderate surface area (13 m^2/g), its cation exchange capacity is very high (CEC = 500 meq/100g) [69]. It was found that leaching of ammonium from a sandy soil modified by the addition of 0.4% Mesolite was reduced by 90% compared to unamended soil. Ammonium retention by the soil-MesoLite mixture was 11.5 times more effective than a similarly amended soil using natural zeolite as the amending agent. Glasshouse experiments in a separate study showed that NH_4^+ adsorbed by MesoLite was available to plants.

Pumice

Pumice is a light, porous volcanic rock that forms during explosive eruptions. It resembles a sponge because it consists of a network of gas bubbles frozen amidst fragile volcanic glass and minerals. All types of magma (basalt, andesite, dacite, and rhyolite) will form pumice, however it is most commonly formed from rhyolite. During an explosive eruption, volcanic gases dissolved in the liquid portion of magma also expand rapidly to create a foam or froth; in the case of pumice, the liquid part of the froth quickly solidifies to glass around the glass bubbles.   Pumice is considered a glass

because it has no crystal structure. Like many of the materials considered in this report it is an aluminosilicate. Some pumices have sufficiently low density that they will float in water. New Zealand possesses extensive pumice deposits.

Natural pumice possesses a porous structure, which contributes to its large specific surface area (often about 5 m^2 g^{-1}). The large proportion of free silica sites at the grain surface results in a negatively-charged surface.   However, the cation exchange capacity (CEC) is relatively low, typically 5-8 meq/100 g. The anion retention capacity is also relatively low, as might be expected.

Work with a Taupo pumice soil showed that adsorption of sulphate, a divalent anion was low, compared to an Egmont allophane soil, however sulphate adsorption in the allophane soil was largely due to paired adsorption of sulphate and calcium (a cation) [70]. In the Taupo pumice soil, the accompanying cation was not relevant to sulphate adsorption.

Work using pumice soil as a substrate for a planted wastewater treatment wetland showed that the pumice (derived from Mt Kilimanjaro, Tanzania) was effective at removing up to 71% of Total Phosphorus.   It was believed that sedimentation of particulate phosphorus and sorption of soluble phosphorus (onto the pumice) were responsible, and that the high concentrations of iron (18.2 %) , aluminium (13.7%), calcium (12.7%) and magnesium (7.3%) in the pumice were the source of this high sorption ability. It was calculated that 39% of dissolved phosphorus was removed by adsoption onto pumice, and 3% was removed by plant uptake. The adsoption of P was shown to be limited by mass transfer rates. Extensive biological activity was observed in the pumice, which was ground to a particle size of <420 μm. At this relatively small size, the bulk density increased substantially [71].

The farmed soils derived from yellow-brown pumice soils (as derived from the Taupo ash showers approximately 1800 years ago) have medium P retention and fairly low CEC. The undeveloped soils are very deficient in phosphorus [42].

Pumice has certain properties that make it undesirable as a material for immobilising nutrients in sediments. These include:
- Low ion exchange ability.
- Low density, therefore very slow to sink, and easily disturbed once in place.

Work by Forest Research, described elsewhere in this report, showed that pumice could be modified by the addition of aluminium. In this form, it showed the ability to adsorb phosphate-P from water. It was rather less efficient at this than was the treated zeolite, Z-2, probably due to substantially larger particle size. However, when suitable encased in a 'cage' to be placed in streams or in the water table, it would have potential for preventing phosphorus from entering lakes. This is considered elsewhere in this report.

Steel Slag

The ability of iron and particularly steel-making slags to remove certain elements from wastewater have been well understood for many years. Internationally, these materials have been used to clean up acid mine water, filter re-circulated water from fish farms

and remove phosphorus from treated sewage water, in the latter case often by filtering through constructed wetlands.

In NZ there are three main slags that come from the iron and steel industry:

- EAF (Electric Arc Furnace) slag from the scrap-based operation at Pacific Steel in Otahuhu.

- "Melter" or iron-making slag at NZ Steel's Glenbrook Works.

- KOBM or steel- making slag, also from NZ Steel.

Considerable research has been and is being carried out using melter slag from NZ Steel (Bill Bourke, SteelServ Ltd. *pers. comm.*) SteelServ Ltd is a 50/50 joint venture company between New Zealand Steel and the Multiserv Group based in London. SteelServ are responsible for processing and marketing most of the iron- and steel-making aggregates from the Glenbrook steel mill, as well as providing a range of services to NZ Steel under contract.

The iron and steel making processes at the New Zealand Steel site are unique in the world, chiefly because of the source material (titanomagnetite iron sand) and the processes required to convert it into iron and steel. The resulting chemistries of the iron- and steel-making slags are also different from the industry norm with unusual elements such as titanium being present in significant proportions [72]. It may be noted that titanium is a member of group IVB of the Periodic Table (CAS version), and therefore an element listed as being of potential in the development of modified clays for phosphorus immobilisation (US Patent for Phoslock). The slag also contains higher concentrations than the industry norm of magnesium oxide and alumina, and these components may also play a role in retaining phosphorus.

The following edited excerpts are from a report by Mr Bill Bourke, of SteelServ Ltd [72].

> In the early 1990s, New Zealand Steel's Environmental Engineering Department carried out a series of extensive leaching trials over a two year period, to check that the iron-making or "melter" slag was safe to use as a roading and drainage material. During these trials it was noticed that the slag had the ability to remove phosphorus and some heavy metals from water passing through the test rig.

> Subsequent field trials in a dairy farm wetland and in a commercial growing bed for water cress confirmed the laboratory findings. A series of trials comparing this aggregate and others were then initiated for the Franklin District Council. Supervised by Bruce Wallace Partners, the trials were designed to determine if the material was suitable as a final water polishing medium for the planned upgrade of the Waiuku Wastewater Treatment plant close to the steel mill.

> The trials were successful, which eventually led to melter slag aggregate being used in a wetland designed by Bruce Wallace Partners. Up to 80% of the phosphorus was removed by this system, although the performance started to drop off after about five years. Two further filter beds in the Ngatea and Paeroa

Wastewater Treatment Plants have since been installed, again from the design of Bruce Wallace Partners. At the time of writing, the Waiuku beds are still removing suspended solids and algae and have shown no evidence of clogging after ten years.

One possible solution to the gradually diminishing performance of slag-based filter beds, is to rejuvenate the material by drying it out. This was discovered by Dr Aleksandra Drizo and others working at the University of Montreal. The Canadian work indicated that with Electric Arc Furnace slags under test in the laboratory, rejuvenation levels of up to 75% were achievable. Following publication of these results, Massey University decided to further investigate this potential attribute.

Samples were taken from the Waiuku filter beds, and along with fresh melter slag were subjected to laboratory trial and microscopic examination. Rejuvenation of the samples from the Waiuku plant was achieved at varying levels and considerably lower than the Drizo studies. The University believes that the results may reflect the different nature of the input fluids – treated sewage water verses laboratory mixes. However, they are sufficiently encouraged to further pursue this attribute, as well as to examine why these materials work in the way they do. The University has obtained a grant to engage a PhD Graduate to undertake this study over the next two years. A paper discussing the work to date will be published later this year.

Concurrently (though independently of the Massey University work), AgResearch began examining various products for their potential to remove phosphorus from dairy farm run-off – particularly those where dairy effluent is being sprayed on pastures. Laboratory work by AgResearch in NZ and in the USA has confirmed melter slag's ability to remove phosphorus. AgResearch have since designed and patented a simple filter system for installation in farm drains.

Trials with this system are due to commence shortly on a dairy farm near to the steel mill. At the same time, AgResearch believe that these filters may be able to remove phosphorus from small creeks and rivers leading into lakes, simply by placing a series of the filters in creek beds.

Environment BOP has been approached regarding this concept and a trial is underway in the Mangakino Stream (Andrew Wharton, Environment BOP, pers. comm.). A research student from University of Waikato is trialling similar systems in geothermal inflows around Lake Rotoiti (Lisa Zheng, University of Waikato pers. comm.) in conjunction with Dr David Hamilton. Initial results from these various trials are expected shortly, with the study to be completed early in 2006. Other locally-derived steel slags will also be used in this work (Bill Bourke, SteelServ Ltd. pers. comm.).

SteelServ speculates that "Modified Gabion Baskets", or other custom-designed receptacles containing melter slag, may be able to be installed in tighter locations where there is insufficient room for a wetland. This may in the future (depending on the outcome of the Massey work), give the customer the opportunity to rejuvenate the material, by lifting out the basket and drying it out.

No work to date has been completed in NZ on this concept, although trials are underway. Key issues will be the volume of water to be treated, the amount of phosphorus in the water and the residual time required in the slag filters to remove the phosphorus (or heavy metals as the case may be).

Various trials being conducted in New Zealand are showing promising results in P removal. The AgResearch trials using 'socks' filled with slag and laid in a creek bed are giving promising results (Bill Bourke, SteelServ Ltd. pers. comm.).   Trials are being carried out using slag filter systems at several waste water treatment plants, to remove a variety of metals and other contaminants. The P-removal results for three of these plants are shown below in Table 3

Table 3
Phosphorus removal efficiency of NZ melter slag

Location of WWTP	Ngatea	Paeroa	Waipoua
Influent P mg/l	10.68	4.164	15.69
Effluent P mg/l	3.286	1.918	2.832
% P removed	69	54	82

It may reasonably be assumed that much of this phosphorus is organically bound, although this has yet to be determined (Jeremy Batchelor, Technical Services Manager, NZ Steel pers. comm.).   It is currently not clear what dissolved oxygen concentrations were in the water passing through these systems. Enquiries are being made on this.

Other elements of Group VA of the Periodic Table may also be adsorbed by melter slag. Trials on the ability of NZ melter slag to determine arsenic removal from wood waste leachate showed removal rates of up to 85% at a dissolved inorganic arsenic concentration of 10 mg/l. Further trials using the tannin-rich leachate also showed high removal rates [73]. Much of the arsenic in the leachate is assumed to be organically bound.

Further trials on phosphorus removal using iron slag (in this case described as 'an iron slag, of similar size, sourced from the electric arc furnace at the BHP steel mill in Waiuku') were conducted trialling the slag against a selected limestone from the Tararua area. Under laboratory conditions using a synthetic P solution (10 mg/l) the slag removed an average 27% of P compared to 64% removal by the limestone, at the same hydraulic residence times [74]. However, when tested on final pond effluent from a waste stabilisation pond system, the performance of the slag was markedly superior to that of the limestone (72 % P removal vs. 18% P removal respectively). It was concluded that algal activity in the stabilisation pond (possibly because of the consequent rise in pH) was responsible for the improved P-removal efficiency of slag and reduced efficiency of limestone. No consideration appears to have been given to the possibility that the presence of organic compounds in the pond effluent may also be a factor.

There are numerous other studies into the ability of steel-making slags to remove phosphorus from water. To quote but one such study, work in Canada tested a variety of different reactive mixture substrates, including silica sand, crushed limestone and various metal oxides as the three major components of the reactive mixture [75]. Iron/calcium oxides from steel-making activities and activated alumina outperformed

other oxides, typically removing 99% of phosphate from a 10 mg/l orthophosphate solution. Sand was added to provide a permeable matrix, but the presence of limestone significantly enhanced the ability of the metal oxides to remove P. Long-term removal of P was demonstrated (4 years).

Effects of pH
Only limited studies appear to have been carried out on this. Steel slags tend to possess high pH values, due to the nature of their composition. In a Japanese study, it was found that phosphate adsorbed onto granulated slag sourced from a blast furnace was most effectively adsorbed in the pH range 7 to 8. Below pH 6 and above pH 8 the adsorption decreased substantially. Adsorbed phosphate was strongly released below pH 5.5, with some minor release also occurring above pH 10 [76].

Supply situation
SteelServ currently has a stockpile of around 700,000 tonnes of steel slag and receives around 280,000 tonnes a year from NZ Steel "coming ready or not". NZ Steel are examining the expansion of their iron- and steel-making operation which if it goes ahead, would add another 140,000 tonnes of melter slag a year, commencing circa 2008. SteelServ will start getting close to reaching "equilibrium state" (selling as much as they receive) by the end of this calendar year. The use of these materials for roadmaking in major projects has the ability to significantly increase demand as each project requires up to100,000 tonnes or more. SteelServ have already have been specified for one such project and are working on another.

However it would be safe to say that SteelServ would have the ability to supply significant quantities in the foreseeable future, "significant quantities" being in the 20 – 100,000 tonne range. Orders of this size require generous lead times to enable them to get well ahead by manufacturing and stockpiling. For an order in the 20 - 50,000 tonne range they would ideally require 6 months notice. For smaller lots (<5000 tonnes) they can generally cope with a lead time of around 2 months. The upgrading of the plant mentioned below will give them considerably more flexibility to cope with larger orders of washed materials.

Cost
The forecast (2007) price for a washed 20/10 aggregate is $25.00/tonne ex yard. This forecast is based on current trends in aggregate use in Auckland, where quality aggregate is in short supply and various motorway projects are underway or shortly to commence. The chip-making and washing facilities at SteelServ Ltd. are to be upgraded to meet this demand. Very small aggregate sizes, from ~ 5mm down will need to be prepared off-site, and the anticipated cost is $150 to $200 per tonne. A recent quoted price for transport of slag aggregate to Rotorua is $24/tonne.   A reasonable estimate at present is $30/tonne. However, road transport costs are currently rising very sharply due to fuel price increases, and it is very difficult to obtain anything approaching a firm price for delivery except on a week-by-week basis (Bill Bourke, SteelServ Ltd. pers. comm.).

Rail delivery would be a possible option on orders exceeding approximately 20,000 tonnes, as the steel mill site is well served with rail access. This would, of course, be contingent on the railway line to Rotorua being reopened. Double handling would still be required at the Rotorua end.

Environmental effects

Slag is "tapped" or decanted off the iron-making process in electric melters at a temperature of around 1500° C and contains no organic matter. Most of the chemical elements are sealed or locked into the material – rather like glass. Slag is in fact a synthetic rock.

The leaching tests undertaken by NZ Steel and others, show that there can be a boron pulse released at the commencement of use. (The boron comes from the coal, used in the iron-making process).This drops off rapidly down to small fractions of parts per million. SteelServ can, on request, pre-wash filter aggregate that will be used in sensitive areas. If planted wetlands tare involved, it is recommended that the slag beds are flushed first, as some plant species are sensitive to boron. Subsequent trace amounts of boron in the wetlands appear to encourage plant growth. Full details of this work will be available in a forthcoming paper (Bill Bourke, SteelServ Ltd. pers. comm.).

Tests have shown that some iron and manganese will leach from the product if the water drops below a pH of 5.5 (i.e. becomes acidic). Constant water flows – such as in wetlands or filters in regular use – generally preclude this and there has not been a recorded issue to date. A filter bed at Waiuku, in use for 13 years shows no detectable levels of boron or the heavy metals Pb, Cd, Cr in the effluent from the bed (Bill Bourke, SteelServ Ltd. pers. comm.).

The reasons why the material removes phosphorus are not clearly understood. The material is quite vesicular (like scoria) which increases the surface area and provides plenty of residence space for suspended solids. It is also believed a chemical reaction is taking place, possibly with the lime or other elements that are present in the slag. Massey University will be examining this aspect more closely. Further discussion on potential removal mechanisms may be found earlier in this section.

Practical aspects of use of slag

Slag may be used in several ways to remove or immobilise phosphorus.

- In suitable retaining structures (gabion baskets, 'socks' etc..) placed in a stream and using water flow or head to drive water through slag of a suitable grade. Research work on this concept is being carried out by AgResearch. Field trials have recently commenced, by placing 168 socks, each containing 12 kg of a mixture of melter aggregate and Electric Arc Furnace (EAF) aggregates, in the bed of a small creek leading into Lake Rerewhakaaitu. Initial results indicate that about 20% of the P is being removed (Bill Bourke, SteelServ Ltd. pers. comm.). This relatively low removal rate may reflect the fact that the socks are arranged in such a way that trout passage will not be affected and, therefore, not all of the water may pass through the 'socks'. For smaller streams, where access allows the use of suitable machinery to place and retrieve these containers, this is a promising approach. For larger waterways, such as the Hamurana Stream, the economics and practicality may not be suitable.
- As a substrate in wetlands. These would be particularly suitable for treating seepage areas or small streams, where sufficient land area is available to construct a wetland.

- As a permeable barrier in a treatment trench. This would be a useful approach in areas near lakes where the soil has lower phosphorus retention capacity than is usual for the Rotorua district [7] or where the retention capacity has been exhausted and P breakthrough is occurring. The ability to obtain the material in grades that allow for high permeability would be an advantage, provided that a suitable hydraulic connection between soil and fill can be maintained.
- As a sediment capping material. More information is needed as to whether melter slag will retain P under anoxic conditions. If this proves to be the case, it would have some potential for sediment capping. A fine grade would be needed to reduce permeability, and cost may not be competitive with materials that can be located from the Rotorua district, such as allophane or zeolite.
- As a soil amending material, to improve nutrient retention. For large scale use, cost would be a major consideration. Certain local materials might be more competitive.

It is probable that the use of melter slag in containment structures placed in waterways, or as a wetland substrate, or as a permeable barrier in a treatment trench, show the most potential for this material. Its utility for in-lake remediation will depend on cost considerations and the material's ability to retain phosphorus under anoxic conditions will need to be fully investigated before such a use on a large scale could be contemplated. Such investigations are to be carried out under the supervision of Professor David Hamilton, Waikato University (Bill Bourke, SteelServ Ltd. pers. comm.). Initial in-stream results are not yet available but are expected to be available shortly (Prof. David Hamilton, University of Waikato, pers. comm.) Small-scale applications such as phosphorus removal in lakeside wastewater treatment plants [77] or stormwater nutrient removal installations would seem to be promising uses for steel slag.

The end use or disposal of material once it has become saturated with phosphorus or other contaminants must also be considered. Initial indications are that slag, once saturated with phosphorus, may be dried and the precipitated phosphorus physically removed. Work is being carried out at Massey University to investigate this possibility, with the results becoming available in 2006 (Bill Bourke, SteelServ Ltd. pers. comm.).

Zeolite

Zeolites are a group of aluminosilicates in which a permanent negative charge is distributed uniformly over crystal planes within the mineral lattice. This negative charge is regarded as permanent since it is not affected by the concentration and types of ions in the soil solution, unless the pH is so low as to induce decomposition of the crystalline lattice. This well defined lattice structure results in a crystalline solid with high porosity. The majority of zeolites found in New Zealand are bedded deposits formed by the deposition of minute particles of intermediate to acidic volcanic glass which settled in water (often but not always the sea) from volcanic ash showers. The zeolite deposits in the central North Island were formed by ash showers falling or being washed into lakes and forming clay sediment beds up to 80 metres deep, and by the subsequent transformation of these sediment beds by hot water being forced up through them by geothermal activity (the thermal alteration phase). During the thermal alteration phase amorphous material was washed out of the clays, leaving a 3-dimensional skeleton of alumina and silica oxides. These structures have a very high negative charge, resulting in a cation exchange capacity typically greater than 100

meq/100g. This results in a strong affinity for positively charged cations in solution. Also resulting from the unusual structure is a very large surface area (both internal and external) of up to 145 m^2/g.

The main commercial source of locally produced zeolite is the Ngakuru area, near Rotorua. The Ngakuru zeolites are predominantly of the types known as mordenite and clinoptilolite. The deposits at Ngakuru occur in the Ngakuru formation, a 100-300 m thick sequence of siltstone, tuffite (which contains the zeolite), diatomite, sandstone, conglomerate and interbedded tuffs [78]. The individual zeolite deposits contain 30-80% zeolite over a thickness of up to 45 m. These zeolites possess low density (650 kg/m^3) , high cation exchange capacity (40-110 meq/100g) CHECK and a high liquid content (60% of dry weight). Both the mordenite and clinoptilolite are very fine-grained (1-10 μm).

  The Ngakuru zeolites are quarried at three sites by New Zealand Natural Zeolite. One of the quarries produces a zeolite with high cation exchange activity, which is marketed under the Zeotec label. The Zeotec form of zeolite (quarried at Ngakuru) is available in 40 kg bags and 700 kg bulk bags, and unbagged in larger quantities.

Zeolites have found a wide range of uses, ranging from ion exchange to catalysis and gas separation. In recent decades, synthetic zeolites have been widely developed, but the natural deposits are very heavily utilised.

Zeolites as a class show a number of characteristic properties:
  • High degree of hydration, easily dehydrated
  • Low density and large void volume when dehydrated
  • Stability of the crystal framework structure when dehydrated
  • Cation exchange properties
  • Uniform molecular-sized channels in the dehydrated crystals
  • Ability to adsorb gases and vapours
  • Catalytic properties with H+ exchanged forms
  • Special electrical properties
All zeolites are molecular 'sieves' which can selectively adsorb molecules on the basis of their size, shape or electrical charge [78].

The presence of large channels or cavities, with their associated extra-framework cations, facilitate cation exchange. Natural zeolites have cation exchange capacities between 200 to 400 meq/100g. making them superior to most other inorganic cation exchange materials.

Zeolites have been widely used for the removal of various ions from water. An example is the removal of ammonium from wastewater and other solutions, and considerable research has been carried out into this.

For example, one recent study examined the ammonium uptake of two zeolite materials quarried in New Zealand [79]. Both forms of zeolite were treated with sodium chloride solution to ensure that they were conditioned into the sodium form. During the work, the solution pH was maintained at <7.5, and it was thus assumed that all ammonia was present in the ionic form (in fact, in the pH range 7.0 to 7.5 a small proportion would be

present as dissolved ammonia, NH_3). Ammonium solutions over the concentration range 0–200 mg/l were used. It was found that both materials took up ammonium ion from solution but that clinoptilolite was slightly more efficient at removing ammonium at lower initial concentrations, whereas mordenite was more effective at removing ammonium at initial concentrations higher than 80 mg/l. The presence of other cations (potassium, calcium, magnesium) upon ammonium uptake was shown to be relatively small, with Ca having the largest effect, and Mg the least. Mordenite showed less reduction of ammonium uptake in the presence of other cations than did clinoptilolite. In all cases, the ammonium ion showed the highest uptake of the cations tested with both materials.

Another New Zealand study also examined the use of zeolites to remove ammonium from wastewaters [80]. Clinoptilolite and mordenite were evaluated for their ability to remove NH_4^+ from a range of wastewaters under both batch and flow-through conditions. Two zeolite particle size ranges (0.25-0.5 mm and 2.0-2.83 mm) were tested. In the batch trials both zeolites, regardless of their particle size, were equally effective at removing ammonium from domestic wastewaters or synthetic solutions containing NH_4^+ concentrations up to 150g. m^{-3}. Mordenite was more effective than clinoptilolite at removing NH_4^+ from dairy and piggery wastewaters and for synthetic solutions containing high NH_4^+ concentrations. The removal of NH_4^+ by both zeolites was significantly reduced by the presence of competing Na^+ cations. In slow flow-through trials NH_4^+ breakthrough did not occur even at high NH_4^+ loadings. However, at faster loading rates breakthrough occurred almost immediately (at one bed volume) for coarse particle sizes, and after 22 bed volumes for the fine zeolite particles. The fine zeolites were more effective than coarse zeolites at removing wastewater NH_4^+, even after receiving 64 bed volumes of wastewater (95% and 55% removal, respectively).

Other (overseas) work investigated the use of zeolite to enhance nitrification in a biofilter used to treat wastewater [81]. Both zeolite (source and type not specified) and activated carbon were used as media in laboratory-scale biofilters, over an operational period of 4 months. Zeolite was found to be very much more effective ($K = 0.5117$) than was activated carbon ($K = 0.0006$) at removing ammonium ion from solution. The ability of activated carbon to remove ammonium was described as 'negligible'. The biofilter with natural zeolite was initially less effective at removing COD than was the filter using activated carbon, but over the course of the trial the zeolite filter showed greater ability to remove COD at high concentrations. As biofilms developed on both filter media, ammonium removal due to nitrification was similar with both media, however the zeolite media was less effected by high ammonium loading rates, due to higher nitrification rates in the biofilm supported by the zeolite medium. The biofilm supported on zeolite displayed much higher counts of *Nitrobacter* than did the carbon media biofilm. *Nitrosomonas* counts were similar for both media. It was concluded that the ability of zeolite to remove ammonia provided a favourable environment for *Nitrobacter*, which is susceptible to ammonia toxicity. The biofilms were approximately 100 μm in thickness, and extended throughout the zeolite matrix, but it was suggested that thicker films would improve the treatment efficiency

It is clear that when using such materials as zeolite in a capacity as a treatment medium, they are likely to become colonised by biofilms which will introduce a variety of reactions and processes other than those carried out by the treatment medium alone. In

the use of zeolite for ammonium removal, the fact that much of the ammonium is being nitrified to nitrate may be expected to prolong the ion exchange activity of the zeolite, thus significantly reducing costs, both for replacement media and for regenerating chemicals (such as NaCl) and treatment.

Because of the chemistry, structure and ion exchange ability of zeolites, they are susceptible to deliberate modification to achieve specific functions.
Recently, trials have been carried out at Forest Research (now Scion) by a research student in conjunction with Forest Research staff [82] on the utilisation of modified zeolite (and other materials) for nutrient removal. A nutrient-stripping media based on the chemical modification of two abundant New Zealand natural minerals, zeolite and pumice, was developed in this study. Modified zeolite and pumice were investigated for their ability to adsorb phosphorus and /or nitrogen from aqueous solutions. Batch incubation studies with nutrients were performed at laboratory scale with artificial and natural lake waters. Modified zeolite and pumice samples with different treatment processes and conditions were employed to understand the effect of various factors on phosphorus-removal capacity. The Zeolite was supplied by New Zealand Natural Zeolite Ltd. and presumably originated from Ngakuru. The pumice was supplied by Works Filter Systems Ltd. and was presumably of Central North Island origin.

Results showed that modified zeolite and pumice exhibited substantially higher phosphorus-removal capability than that of natural zeolite and pumice. Trials were conducted to compare modified media and two imported commercial remediation products: *Phoslock*[TM] and *Baraclear*[TM]. Modified zeolite and *Baraclear*[TM] showed the best performance for nutrient reduction in water, though all media have the ability to achieve greater than 95% phosphate removal if sufficient dose is applied. The binding of phosphate appears to be largely irreversible under natural pH and temperature conditions for all media tested. Unexpectedly, all media tested also had the ability to remove more than half of the nitrate present.

Three different processes were used to modify raw zeolite and pumice. The zeolite products were referred to as Z1, Z2, Z2; the pumice products were PM1, PM2, PM3.
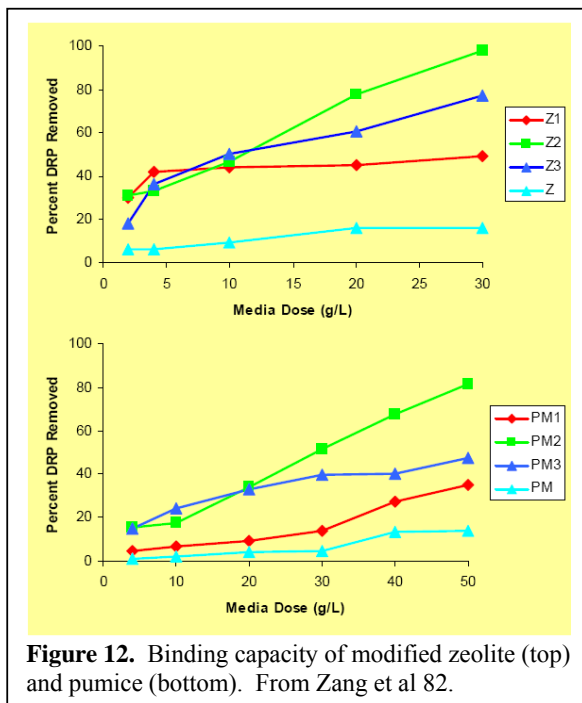

The details of these processes have not been made available to date, due to issues of commercial confidentiality. It is known that the raw materials were acid-washed with 0.1M HCl, in order to remove extractable materials and thus enhance the adsorption capacity. The initial laboratory trials of these various materials were carried out using concentrated nutrient solutions. Typically, 100 mg/l of phosphate was used in the test solutions, at least 100 times the levels found in most natural waters.

It is noticeable that at lower phosphate concentrations, the P removal efficiency was markedly lower (see Figure 12, *left*). This is to

Figure 12. Binding capacity of modified zeolite (top) and pumice (bottom). From Zang et al 82.

some extent in conflict with further findings showing little effect of initial starting phosphate concentration (Figure 13, *below left*).

Since modified zeolite gave superior results compared to modified pumice (possibly due to increased surface area per unit weight of zeolite, which has significantly smaller particle size) the majority of the further work was carried out with modified zeolite, in the Z2 formulation which showed the most promising initial results. The Z2 material was shown to possess slightly higher P binding efficiency, compared with Phoslock, over the pH range of 5 to 9.7. Significant re-release of P did not occur with Z2 or Phoslock. To date, no trials appeared to have been conducted to determine the release rates of P from Z-2 in anoxic conditions. Aluminium-phosphorus complexes are usually stable in anoxia, but this may vary according to the nature of the complexes, which are determined by water and sediment chemistries.
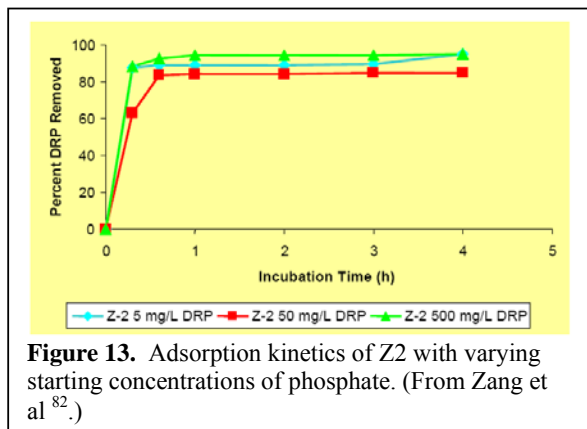
Interestingly, the Z-2 modified zeolite was found to be effective at binding nitrate ions, with removal efficiencies ranging from 87% to 98%, with the lowest efficiencies at low nitrate concentrations, Zeolites generally do not possess significant anion exchange capacities, so this effect may be due to the modification treatment that was imposed upon the zeolite. For example, it is known that pre-treating zeolite surfaces with cationic surfactants will confer anion exchange capacity to zeolites [83]. This matter is discussed further, below.
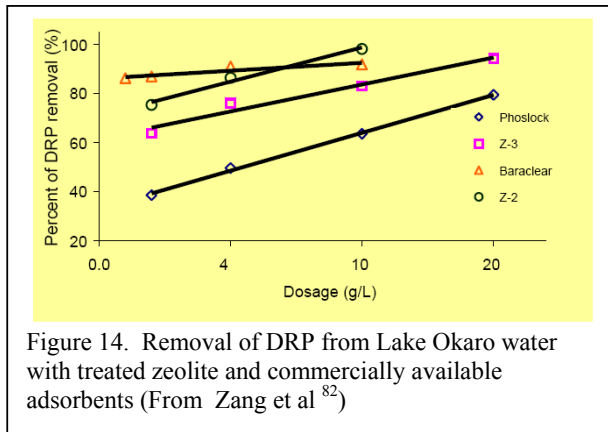
Trials were also carried out to determine the removal efficiency of nutrients from water samples collected from Lake Okaro. Lake Okaro has the lowest water quality of the larger Rotorua lakes. The Trophic Level Index in 2003 was reported to be 5.61 and the average total phosphorus and nitrogen were 0.122 mg/L and 1.25 mg/L, respectively [84].

In this part of the study, a sample was taken from the inflow creek to the north-west of Lake Okaro, draining farmland. This sample had initial DRP and NO_x-N concentration of 0.185 mg/L and 1.520 mg/L, respectively. Modified zeolite Z-2, Z-3 and two commercial products, *Phoslock* and *Baraclear,* were selected as the adsorbents. All adsorbents were tested at media concentration of 1, 4, 10 and 20 g/l.

It was found that both *Phoslock* and *Baraclear*(which are clay-based pellets) disperse very quickly in water to form a suspension. Treated zeolite also forms a suspension upon agitation, but this suspension settles within minutes as opposed to hours for the clay-based particles. For major lake treatments in which sediment capping is the main priority, this would be an advantage. It is interesting that the modified zeolite settled out rapidly in water, as the raw material possesses a density below that of water [78].

The Z-2 treated zeolite and *Baraclear* demonstrated the highest efficiency for DRP

Figure 13. Adsorption kinetics of Z2 with varying starting concentrations of phosphate. (From Zang et al [82].)

Figure 14. Removal of DRP from Lake Okaro water with treated zeolite and commercially available adsorbents (From Zang et al [82])

removal from Lake Okaro water as both were able to exceed 90% removal efficiency (Figure 14 *left*). This was followed by Z-3 treated zeolite then *Phoslock*. From the relationships obtained, *Phoslock* would require much higher doses to achieve the same removal efficiency as *Baraclear* and Z-2. The use of Lake Okaro water resulted in a reduction of phosphate removal efficiency as compared to that seen with lab water samples spiked with phosphate (which were presumably Milli-Q deionised water spiked with A.R. grade reagents, although this is not clarified in the report) and the reasons for this loss of efficiency are unknown. Possible explanations are:

- There are interfering substances in the lake water (other ions, organic compounds etc.)
- Not all of the 'DRP' was in purely ionic forms, such as orthophosphate, which could be readily taken up by the zeolite and other materials.

Nitrate/nitrite nitrogen (N_{OX}-N) was also taken up from Lake Okaro water by all of the materials tested, with Phoslock being the most efficient at the lowest dosage rates (4g/l) and Baraclear the most effective at the highest dosage rate of 20 g/L. However, all materials tested (Z-2, Z-3, Phoslock and Baraclear) showed N_{OX}-N removal efficiencies of around 50% at the low dosage rate. Raising the dosage rate five-fold to 20 mg/l produced, at the most (with Baraclear) a 10% increase in the N_{OX}-N removal rate, suggesting that such a large increase in the dosage rate would be uneconomic in terms of the additional N_{OX}-N that would be removed. It is not known, as yet, whether the binding of this N_{OX}-N was reversible or not.

It should be pointed out that the water samples on which these tests were carried out was not, strictly speaking, 'Lake Okaro water', being taken from the inflow creek to the north-west of Lake Okaro, draining farmland. It is possible that water collected from the lake itself, where biological activity would have been at work for a much longer period and under different environmental conditions, might have shown somewhat different results.

However, these results, using modified zeolite, show that the material, particularly the Z-2 formulation, displays distinct promise for removing nutrients from water and possibly for immobilizing nutrients in sediments although, as the authors of the study comment "sediment capping would be expected to be more permeable as compared to *Phoslock*" This is presumably due to the significantly larger particle size (in water) of the zeolite samples that were used, compared to the bentonite-based Phoslock. Testing of the latter ability has yet to be commenced, but sediment/water column trials have been proposed, and it would be very desirable for them to be carried out.

SUMMARY AND RECOMMENDATIONS

This report examines a number of locally sourced (i.e. within New Zealand) inorganic and organic materials with a view to determining their actual or potential usefulness for reducing or removing nutrients from lakes, streams or groundwater in the Rotorua District. The major properties and nutrient removal potential of the various materials are examined, and an attempt is made to rank them in terms of potential utility.

A tentative ranking, in order of potential usefulness, is
6. Allophane
7. Zeolite
8. Bentonite
9. Steel slag
10. Limestone

Where two materials show similar promise, the material that may be obtained more cheaply is given preference. Considering the current rapid increase in fuel prices, proximity to the Rotorua Lakes is considered to equate to 'cheapness' to a substantial degree. Not all of the materials studied have been included in this order of preference, which includes only those materials considered likely to be appropriate for large-scale use. The fact that a material does not appear does not, however, mean that it would not find use in small-scale applications.

A number of recommendations and cautions arise from the material reviewed in this report. They include the following:

- Before aluminium is released on a large scale into any of the Rotorua lakes, it would be very desirable to reliably determine the hypolimnetic pH during the period of anoxia.

- As flocculated material sinks the equilibrium conditions change as it passes through various physically and chemically distinct water strata before arriving at the lake bed. Therefore the results of bench tests may not necessarily reflect the reality in-lake.

- It is suggested that 'cost-effectiveness' should not be the prime characteristic used to choose a flocculating agent.

- Lakes that experience significant internal loading of phosphorus (P) or nitrogen (N) to their water columns may be the rule rather than the exception. In this type of lake, additional in-lake steps may be necessary, following diversion, in order to prevent a prolonged eutrophic state.

- In trying to manage the nutrient status of waterbodies it would be beneficial to know which of various abiotic and biotic processes has the potential to dominate the P release from sediments and, under what conditions.

- It should be emphasized that, in order to carry out successful phosphorus inactivation in any of the Rotorua Lakes, the chemical and physical nature of the sediments and the overlying water column will need thorough investigation.

- It is recommended that a biomonitoring procedure, using aquatic flora, be adopted should field trials with Phoslock™ or similar materials be carried out in the Rotorua Lakes (see Appendix 2).

- It has been shown that significant adsorption of lanthanum, as the free ion La^{3+} and also as an EDTA-La complex, occurred to membrane filters and to glass vessels. This finding should be kept in mind when conducting or assessing *in vitro* trials on toxicity or bioavailability of lanthanides.   In addition, much of the lanthanide data obtained from laboratory studies is regarded by some authors as being of poor quality, probably due to analytical difficulties and insufficient attention to questions of solubility.

Appendix 1 summarises the aquatic chemistry of aluminium (an element central to a number of lakes remediation strategies). Appendix 2 briefly examines several overseas-derived modified mineral materials that have been used in lake remediation. Appendix 3, included for reader convenience, is a Periodic Table of the Elements. An Addendum proposes some less well-known methodologies or processes to remove nutrients from water or sediments.

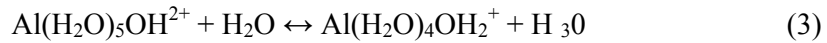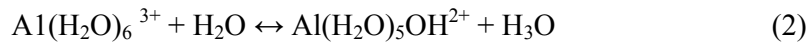## APPENDIX 1: AQUATIC CHEMISTRY OF ALUMINIUM, AND USE IN LAKE RESTORATION

The following section on the chemistry of aluminium in the freshwater aquatic environment is reproduced from Cooke et al (1993)[18] , who describe the various processes very clearly.

"The chemistry of aluminium is complex and still incompletely understood (Dentel and Gossett, 1988 [85]; Bertsch, 1989 [86]). It has been reviewed by Burrows (1977 [87]), Driscoll and Letterman (1988 [88]), and Driscoll and Schecher (1990 [89]), among others. The following is drawn from these reports, and from the first detailed lake and laboratory studies on aluminium salts for P inactivation (Browman et al., 1977 [90]; Eisenreich et al., 1977 [91]).

"When aluminium sulphate, or another aluminium salt, is added to water it dissociates, forming aluminium ions. These are immediately hydrated:
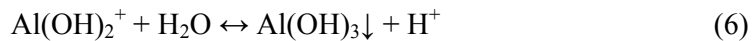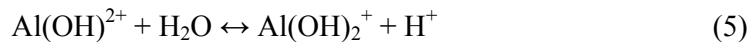
$$Al^{3+} + 6\ H_2O \leftrightarrow Al\ (H_2O)_6{}^{3+} \tag{1}$$
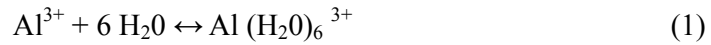
"A progressive series of hydrolysis (the liberation of hydrogen ions) reactions occurs leading to the formation of aluminium hydroxide, $Al(OH)_3$, a colloidal, amorphous floc with high coagulation and P adsorption properties:

$$Al(H_2O)_6{}^{3+} + H_2O \leftrightarrow Al(H_2O)_5OH^{2+} + H_3O \tag{2}$$

$$Al(H_2O)_5OH^{2+} + H_2O \leftrightarrow Al(H_2O)_4OH_2{}^+ + H_3O \tag{3}$$

"etc...

Omitting coordinating water molecules from the equations, the following occurs:

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \tag{4}$$

$$Al(OH)^{2+} + H_2O \leftrightarrow Al(OH)_2{}^+ + H^+ \tag{5}$$

$$Al(OH)_2{}^+ + H_2O \leftrightarrow Al(OH)_3\downarrow + H^+ \tag{6}$$

In equation 6, $Al(OH)_3$ is precipitated as a solid.

"$Al(OH)_3$ is a visible precipitate or floc which settles through the lake's water column to the sediments. A surface application produces a milky solution which quickly forms large, visible particles. The floc grows in size and weight as settling occurs, and within hours, water transparency increases dramatically.

The pH of the solution is the primary determinant of which aluminium hydrolysis products dominate and what their solubilities will be, as illustrated in Figure 8-1 (*below*). At the pH of most lake waters (pH 6 to 8), insoluble polymeric $Al(OH)_3$ dominates and P sorption and inactivation proceeds. At pH 4 to 6,

various soluble intermediate forms occur, and at a pH less than 4, hydrated and soluble Al^{3+}, dominate.

When alum is added to poorly buffered waters, the acid neutralizing capacity (ANC) is exhausted, pH falls, and soluble aluminium species dominate. At higher pH levels (>8.0), the amphoteric nature (having both acidic and basic properties) of aluminium hydroxide results in the formation of the aluminate ion:

$$Al(OH)_3 \leftrightarrow Al(OH)_4^- + H^+ \tag{7}$$

"At increasing pH levels above 8, as would occur during intense photosynthesis for example, solubility again increases which could lead to a release of P sorbed to an aluminium salt.
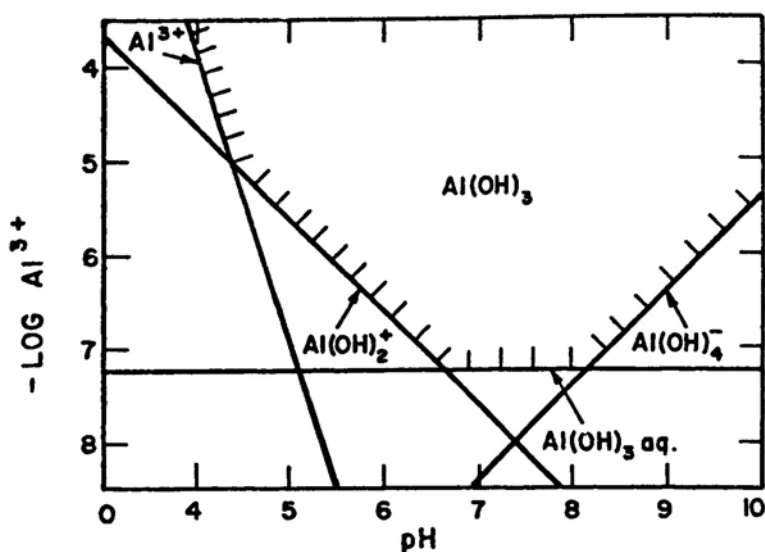

Figure 8-1. Solubility of amorphous aluminium hydroxide (From Eisenreich S. J., D. E. Armstrong, and R. F. Harris. Tech. Rep. 77-02, Water Resources Center, University of Wisconsin, Madison (1977). With permission.)

"Aluminium salts in water have a time-dependent component to their chemistry (Burrows, 1977 [87]). The concentration of monomeric forms (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$) stabilizes within 24 h. But crystallization takes over a year to complete as larger and larger units of polymeric $Al(OH)_3$ are formed. In lakes, this continued reaction occurs in the sediments, though its consequences to the control of P release are poorly understood. Burrows points out that toxicity studies carried out with a freshly prepared solution of buffered aluminium, present a different array of potentially toxic aluminium, species than an aged solution with a lower concentration of monomeric species and intermediate polymers. **This also may be the reason why continuous exposure to the early hydrolysis products of alum, as would occur in a treatment of flowing waters, appears to be far more deleterious to biota than the single lake treatment (Barbiero et al., 1988 [92]).**

"Properties of $Al(OH)_3$ which are of greatest interest to lake managers are its apparent low or zero toxicity to lake biota *(see later section)*, its ability to adsorb

large amounts of inorganic P, and the binding of P to the floc. Low or zero dissolved oxygen conditions in lake sediments do not solubilise the floc and allow P release, in contrast to iron, though P release may occur following an increase in pH.

"$Al(OH)_3$ is less effective in removing or sorbing dissolved organic P complexes. Browman et al. (1977 [90]) found that naturally occurring (Snake Lake, W1) dissolved organic molecules were not removed by $Al(OH)_3$. Franko and Heath (1981 [93]) reported similar results for the West Twin, OH, treatment. Kennedy and Cooke (1982 [94]) obtained dissolved organic P removal of 1 to 36% in laboratory studies, and 65% in the alum treatment of Dollar Lake, OH. This problem could be of significance to the longevity of the treatment because P can be released from organic molecules, although Heath (1986 [95]) has shown that the rate of release of inorganic P from dissolved organic P compounds accounts for < 1 % of P demand by phytoplankton.

"Particulate organic P (cells, detritus) is removed to some extent from the water column by coagulation and entrapment in the $AI(OH)_3$ floc. The settling of the floc through the water column clarifies the water in this manner.

"Because $AI(OH)_3$ is so sorptive of inorganic P, the ideal time that is often suggested for treatment is just after ice-out, or in early spring in warmer climates, before the spring bloom of algal cells and corresponding uptake of P occurs. Driscoll and Letterman (1988 [88]) report that temperature alters the rate and extent of reactions of aluminium salts in water. At low temperatures, coagulation and deposition are significantly reduced and high quantities of species such as $AI(OH)_2^+$ which are toxic to some organisms, might occur. This suggests that aluminium solubility is temperature dependent as well as pH dependent. There are other reasons why early spring is less than an ideal treatment time, even though inorganic P may be the dominant form. These reasons include:
 (1) sediment P release, not water column P content is the primary target of P inactivation,
 (2) early spring months are windy, making application difficult,
 (3) wind mixing may distribute the floc to one area of the lake, or scour it from the sediments before the floc consolidates into those sediments, and
 (4) silicon content, a major means of complexing soluble and possibly toxic aluminium species, may be low if there has been a spring diatom bloom. Thus, summer, before blue-green algal blooms appear, or early fall months, are more appropriate periods for application.

"Because hydrogen ions are liberated when an aluminium salt is added to water, pH falls at a rate dictated by alkalinity. In lakes with low or moderate alkalinity (<30 to 50 mg $CaCO_3$/1), treatment produces a significant decline in pH at a low or moderate alum dose, leading to increasing concentrations of toxic, soluble aluminium forms, including $Al(OH)_2^+$ and $A1^{3+}$. This limits the amount which can be added. This problem has been addressed by adding buffers to the lake or to the alum slurry as it is applied. The work of Dominie (1980 [96]) for Lake Annabessacook, ME and Smeltzer (1990 [97]) for Lake Morey, VT, are examples. Buffering compounds were tested, including sodium hydroxide, calcium hydroxide, and sodium carbonate. The buffer chosen was sodium aluminate ($Na_2Al_2O_4$. n H_2O), a high alkalinity compound with

the added benefit of having a high aluminium content. According to Smeltzer (1990 [97]), much of this compound's alkalinity comes from the NaOH used in its production.

"In summary, the primary objective of an in-lake alum treatment is to form an $Al(OH)_3$ "blanket" over the sediments. P, which otherwise would diffuse into the water column, is sorbed, thereby reducing internal loading. The formation of $Al(OH)_3$ also removes particulate organic and inorganic matter with P from the water column, a secondary objective. The formation of large amounts of $AI(OH)_3$ and negligible amounts of other hydrolysis products depends upon maintaining water column pH between 6 and 8. Because lakes differ in alkalinity, the dose to a lake is lake specific. In some cases a buffer must be added."

The use of aluminium salts to inactivate nutrients in sediments
Aluminium salts have been used for at least three decades in attempts to restore eutrophic lakes [98]. Depending on the method of application, the end results may include both P precipitation from the water column, and P inactivation. As discussed above, phosphorus precipitation by aluminium removes phosphorus by different mechanisms, depending on the pH.

In one recent study, water samples from two southern California lakes (moderately deep and mesotrophic Big Bear Lake and shallow, eutrophic, alkaline and sodic Lake Elsinore) adversely affected by internal nutrient loading, were treated with a 20 mg/L dose of Al^{3+} in laboratory studies to examine Al solubility and solid-phase speciation over time [99]. Alum (aluminium sulphate 18-hydrate) applications to water samples from the two lakes resulted in a rapid initial decrease in pH and alkalinity followed by a gradual recovery in pH over several weeks. Dissolved Al concentrations increased following treatment, reaching a maximum of 2.54 mg/L after 17 days in Lake Elsinore water and 0.91 mg/l after 48 days in Big Bear Lake water; concentrations in both waters then decreased to <0.25 mg/L after 150 days.

The solid phase was periodically collected and analysed by a variety of techniques to investigate the nature of the reaction products and crystalline development over time. Poorly ordered, X-ray amorphous solid phases transformed over time to relatively well-ordered gibbsite ($Al_2O_3.3H_2O$). X-ray diffraction also indicated the formation of a second (possibly aluminosilicate) crystalline phase after 150 days in Lake Elsinore water. Surface areas also decreased over time as crystals reordered to form gibbsite/microcrystalline gibbsite species. Analytical results suggested that the initially formed amorphous $Al(OH)_3$ underwent transformation to >45% gibbsite. These findings indicate that $Al(OH)_3$ formed after alum treatment undergoes significant chemical and mineralogical changes that may alter its effectiveness as a reactive barrier to phosphorus release from lake sediments and, in particular, that the solid-phase transformations and loss of surface area upon aging of the alum floc may lead to decreased P sorption capacity and reduced effectiveness as a reactive barrier to P release from the sediments relative to freshly formed amorphous phases.   This type of change in the floc occurred more rapidly and to a greater extent in water from the more alkaline, sodic and eutrophic Lake Elsinore, nonetheless these results deserve close study. It was also found that silica was removed from the water by adsorption to $Al(OH)3$, and this could have implications for algal population balances.

Overseas case study 1

There have been numerous overseas studies on the short-term results of aluminium treatment of (mostly) small lakes, but one of particular interest was a study of the long-term effects of treating Lake Süsser See in north-eastern Germany [98]. This polymictic lake is larger than most that have been treated, with an area of 2.68 km^2. It is relatively shallow, with a mean depth of 4.3 m and a maximum depth of 8.2 m. The hydraulic residence time is 1.2 years. The lake was treated with alum on an annual or biannual basis from 1997 to 1992. Treatment was carried out in the spring, using 500 to 700 tonnes of alum, giving a dosage rate of 2 mg Al l^{-1}. A total of 7000 tonnes of alum were applied over the period, equating to a total dose of 100 g Al. m^{-2} of lake surface. The effectiveness of these treatments was less than expected, both in P-removal and duration of effect. Possible reasons for this reduced effectiveness were given as:

- High P loads in the inflows
- Resuspension of precipitated Al resulting in the formation of mobile aluminate at high pH
- Insufficient quantities of added Al
- 'Technically inhomogeneous applications'

The study was carried out between 1999 (approximately two years after the final treatment) and 2002. Sediment cores from the lake bed were collected, sliced into narrow layers, and analysed for a variety of analytes, including a number of different phosphorus fractions. 'Peepers' (Dialysis samplers) were also used to determine ionic concentrations at the sediment-water interface. Three sediment layers were defined:

- Sediments settled after Al treatment had ceased (fresh sediment)
- Sediment settled during the period of Al treatment (Al-P layer)
- Sediment settled before Al treatment started (old sediment)

The total added aluminium was equivalent to about one order of magnitude less than the estimated background levels of Al in the sediments, and the added Al did not form a recognizable pattern in the Al distribution in the sediments. The Al-P layer contained higher concentrations of Total Phosphorus and NaOH-extractable phosphorus (i.e. strongly-bound P) than did other layers. It was shown that the ability of the Al-P layer to sorb P was much greater than the other layers, and that fluxes of P into this layer occurred from above and below, indicating that the Al-P layer was still sorbing P. The molar ratio of added Al to additionally bound P was determined at approximately 2.1:1 – a more favourable ratio than found in other studies.. It was concluded that different chemical compositions of water and sediment would result in different reaction mechanisms, resulting in different reaction products and different molar ratios. The high calcium concentrations in Süsser See water (140 mg.L^{-1}) were thought to be a possible cause for the favourable Al:P ratio.

Following the re-unification of Germany in 1989, catchment changes lead to a sharp decrease in SRP concentrations in the lake water over the period 1989 - 1992. These changes included:

- Introduction of phosphate-free detergents
- Collapse of fruit-growing
- Industry closures
- Improved wastewater treatment.

Over the same period, the nett sedimentation rate in the lake also decreased.

Figure 1. Porewater concentration profiles of SRP, Süsser See. From Lewandowski et al [98].
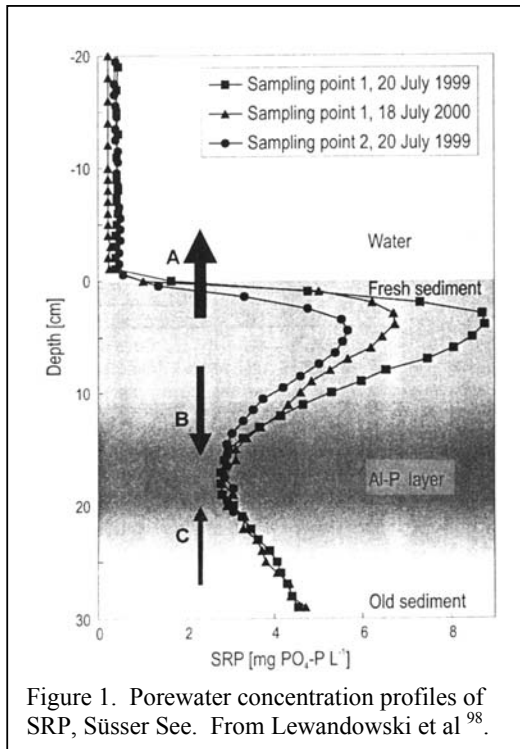
Figure 1 (*left*) shows the P diffusion fluxes out of the fresh sediment, with the upwards flux (A) representing the P release rate. If the layer of fresh sediment is thin, the flux downwards (B) decreases the pore water P concentrations in the fresh sediment, and thus the flux upwards decreases, due to a smaller concentration gradient. If the thickness of the fresh sediment layer increases, eventually the upwards flux from the fresh sediment layer increases. Therefore the thickness of the fresh sediment layer determines the effectiveness of the Al-P layer, and the gradual burial of this layer under fresh sediment causes a decrease in P-retention. Even thin layers of fresh sediment were shown to result in higher P-release rates from the sediment, whereas further thickening of the fresh sediment layer caused only a slight increase in P-release rates. The authors commented that the model they used was also valid for other types of P sink layers and that bioturbation (see below) might enhance the effect of the P sink layer by mixing freshly settled sediments into it. During the period of Al application, no significant improvement in the trophic state of the lake was recorded because the amount of added Al was far too small compared to the external P load. Once effective external measures were applied, following re-unification, the SRP concentrations fell rapidly, leading to an improvement in the trophic state. It was concluded that, as far as possible, external measures should be conducted prior to internal measures.

Lessons to be learned from the Süsser See.
The implementation of external measures is being done in the case of Lakes Rotorua and Rotoiti, with such strategies as land use changes, diversion of the Ohau Channel inflow (to Rotoiti) and sewerage of lakeside settlements being carried out as a first priority. Once these initial measures are taken, if aluminium treatment is then carried out all possible efforts should be made to reduce the rate of in-lake sedimentation. Hopefully the initial reduction of P flux from the sediments (assuming that sufficient aluminium was applied for the treatment to be effective) would result in reduced sedimentation from dying algal or cyanobacterial blooms, but in order to increase the effective life of aluminium treatment the control of sediment inputs from other sources would need attention. Such sources would include:
- Subdivision activities
- Forest clearance
- Runoff from pastoral (and other) lands during severe rainstorm events.
- Landslips

Overseas case study 2
The Barleber See near Magdeburg, Germany, was treated with aluminium sulphate solution in 1986. The resulting aluminium hydroxide/aluminium phosphate sediment cap has ensured that the previously experienced cyanobacterial blooms had not returned by 2003. Before this treatment, each time the small hypolimnion in this lake became oxygen depleted, P was redissolved from the sediments. The lake still experiences anoxia but phosphorus is not liberated [100].

Local case study – Lake Okaro
Lake Okaro has recurrent blue-green algal blooms and is considered to have the poorest water quality amongst the lakes of the Rotorua region. It is classified as hyper-trophic. With declines in water quality of several Rotorua lakes, Environment Bay of Plenty trialled flocculation with aluminium sulphate at a dose rate of $5g/m^3$ ($0.45g/m^3$ aluminium) based on the epilimnion volume of the lake. The principal aim of this trial was to reduce phosphorus in the epilimnion through adsorption by aluminium hydroxide, produced by a series of reactions following aluminium sulphate application. As heterocyst-bearing blue-green algae such as *Anabaena* sp. are capable of fixing atmospheric nitrogen, reducing phosphorus concentrations to the point where phosphorus limits growth has the potential to reduce problematic *Anabaena* blooms.

The lake was stratified throughout the sampling period (2 December, 2003 to 13 January, 2004) and dissolved reactive phosphorus concentrations were high in the presence of an anoxic hypolimnion. Surface pH exceeded 8 throughout the sampling period, including the time of alum application.

A bloom dominated by *Anaebaena spiroides* was present at the time of the application, and dosage of the aluminium sulphate was low compared with applications elsewhere in the world. From 12 to 22 December, 2003, the TN:TP mass ratio in the epilimnion increased from 12:1 to 34:1, but this resulted mostly from an increase in ammonium concentrations rather than a reduction in phosphorus *per se*. There was no immediate impact of the aluminium sulphate application on the density or biomass of *Anabaena spiroides*; *Staurastrum* sp. was the dominant species in the presence of low phytoplankton biomass while *Anabaena* sp. dominated when biomass was higher [101]. Further discussion of the work on Lake Okaro may be found in the main body of this report.

In general, aluminium salts are favoured over iron salts for sediment capping, due to the ability of aluminium/phosphorus compounds to resist dissolution under anoxic conditions, and due to the fact that aluminium salts are easier to handle than the corrosive iron salts that have sometimes been used.

APPENDIX 2: BRIEF SURVEY OF SOME IMPORTED SEDIMENT CAPPING MATERIALS.

Phoslock™ and its potential environmental impacts

Phoslock™, a material developed in Australia and currently manufactured in China, is based on a bentonite clay that has been modified by the addition of lanthanum. It has been shown to be effective at removing phosphorus from solution, and at reducing the loss of phosphorus from aquatic sediments into the overlying water column. The demonstrated performance of the material relies on the very low solubility products of lanthanum-phosphate complexes [102]. As an imported material, a lengthy discussion of Phoslock™ lies outside the scope of this report. The production process is briefly described below, followed by a consideration of the potential environmental implications of its use.

In the process of manufacturing Phoslock, bentonite is modified under the following processes (the US Patent is rather ambiguous as to the precise processes used, so a degree of conjecture is involved in describing them):

- Treatment with a concentrated acid such as HCl or H_2SO_4, in order to remove a large proportion of the interlayer structure (see description of the bentonite structure above) and /or structural cations (such as Na^+, Ca^{2+}, Mg^{2+}).
- Dehydration, by means of heating, to control the degree of retention of lanthanum or other complexing elements.
- Addition of an organic or inorganic ligand material.
- Mechanical mixing with 0.1 M lanthanum chloride ($LaCl_3$) solution over a 24 hour period.
- Centrifuging to remove the supernatant liquid, followed by a second lanthanum chloride treatment, washing with clean water, centrifuging then repeating this treatment process a third time.
- Drying, followed by grinding or pelletisation, where appropriate, using a variety of binding agents.

A number of possible modifications to this process are described in the patent, including:

- The use of other mineral materials as the carrier.
- Addition of other divalent or trivalent cations, such as Ca^{2+}, to the product to form a liquid that will deliver the material to the sediments and inhibit resuspension.
- Containment of the material within geotextile mats.
- Use of other elements than lanthanum (such as zirconium) as the complexing element or elements.

Phoslock is currently being manufactured under licence in Mainland China. A granular form has recently been introduced which is claimed to be easier to transport and apply, and to reduce the amount of dissolved lanthanum potentially available for release into the environment.

The following comments may be made on the general concept of discharging a rare earth element, such as lanthanum, into waterways.

The rare earth elements (REEs) include the 15 homologous metals known as the lanthanides (of which lanthanum is a member) plus scandium and yttrium, both of which occupy a lower place in the periodic table than do the lanthanides, but which have rather similar chemical behaviour (a copy of the Periodic Table is included as Appendix 3 to this document). Despite the name, the REEs are not particularly rare in nature, and lanthanides may be found in many soils and sediments in concentrations similar to those of lead and cadmium. In recent decades REEs, such as lanthanum, have become widely used in industry and agriculture. The widespread use of REEs as additives to fertilizers, especially in China, inherently leads to their residues in the environment entering the food chain and accumulating in organisms[103]. Lanthanum, for example, forms complexes with a variety of organic compounds, and these complexes are of varying stabilities – some are stable enough to survive a chromatographic separation at pH 5.0 [103].

Lanthanum is the lightest of the lanthanides. Its Atomic Number is 57 and its Atomic Weight is 138.91. There are another 14 lanthanide elements, with the heaviest being lutetium (No. 71) with an atomic mass of 174.97. In the original concept of the Periodic Table, as proposed by Mendeleev there was no place for the lanthanides, because they did not follow the general rule of adding electrons to outer shells with increasing electric charge. Instead, electrons are added to an inner (4f) shell. Because these electrons are well shielded, they are little involved in chemical bonding. This, coupled with the fact that all lanthanides favour the (III) oxidation state, results in great similarity between these elements, to the point where they were very difficult to separate, both in isolation and analysis, until quite recently. In most representations of the Periodic Table, lanthanides, together with actinides, are generally shown as removed from all the other elements, for the reasons detailed above. (See Periodic Table, Appendix 3 to this report).

The environmental behaviour of the REEs is strongly influenced by solution chemistry. Due to the complexation of REEs by a variety of ligands, only a small fraction of each REE in circumneutral waters is typically in the form of free hydrated REE ions (M^{3+}).[104] The soluble concentrations of REEs in the aquatic environment are strongly limited by the low solubility products of lanthanides with carbonate and phosphate [105].

Relatively little is known about the environmental effects of rare earth elements (REE) in either terrestrial or aquatic ecosystems. Results of Chinese research suggest that supplying these elements may have beneficial effects on plant growth. By 1993 some 3.73 ha of land in China was reported to have been treated with REE, with claimed productivity increases typically in the order of 5 to 15% [106]. Unfortunately, the majority of the available literature is in Chinese. In addition, most of the published literature was difficult to evaluate critically due to lack of detail concerning experimental methods and the absence of statistical treatment of the data[106]. The limited number of studies in the Western literature have not greatly clarified the effects of REE on plant growth.

However, more recent studies [106] suggest that relatively low concentrations of REE may be toxic to some plants, with lanthanum being shown to inhibit root elongation of mungbean (*Vigna radiata*) by 50% at a concentration of 3.1 μM. Another REE, Cerium, was more toxic than lanthanum (50% inhibition of root elongation at 0.9 μM). Corn (*Zea mays*) was much less sensitive to REE than mungbean. Interestingly, at pH 4.5 concentrations of La up to 10 μM remained in solution in the presence of phosphate-

P concentrations up to 5 μM , but at pH 5.5, substantial losses of La and P from solution occurred. Additional work by the same authors[107] showed that low concentrations of lanthanum (0.63 μM) increased the root growth of corn by 36%, and La at 0.19 μM increased the root growth of mungbean by 21%, relative to controls. However, no beneficial effects of La on the total dry matter yield of either species was demonstrated, with the dry matter yield of corn being unaffected, whereas the dry matter yield of mungbean was reduced by over 30% by La concentrations greater than 0.19 μM. Roots of both plant species accumulated 20 to 150 times higher concentrations of La than did the shoots. The highest La concentrations in corn roots were 1775 mg/kg and in mungbean roots the highest La concentrations were 2955 mg/kg.

Only limited work appears to have been carried out into the impacts of REE on aquatic systems, until recently. One Chinese study indicated that concentrations of water soluble species of REE (including lanthanum) in freshwater lake sediments correlated well with concentrations of bioaccumulated REE in the green alga *Chlorella vulgaris.* Concentrations of acid-extractable and organic sulphide-bound species of REE did not correlate well with the bioaccumulated REE. Factors such as pH, redox conditions and the presence of chelating agents were shown to be very important in determining the bioavailability of REE.

A study carried out in the Netherlands indicated that dissolved lanthanides are complexed mainly to carbonates and dissolved organic matter [108]. The biota sediment accumulation factors (BSAFs) in the amphipod *Corophium volutator* was highest for lanthanum, of the REE series, and did not depend on salinity or pH. Alkalinity correlated negatively with lanthanide uptake, suggesting that increased complexation reduced bioavailability under the prevailing estuarine conditions. Field BSAFs were significantly lower than laboratory values for the same sediments, which was explained by adaptation of the organisms to the presence of lanthanides.

The Netherlands appears to be a centre of research into the environmental effects of REEs. One extensive study recently carried out there investigated the bioavailability of lanthanides in freshwater, paying particular attention to the solution chemistry of these elements [105]. It was determined that significant adsorption of lanthanum, as the free ion La^{3+} and also as an EDTA-La complex, occurred to membrane filters and to glass vessels. This finding should be kept in mind when conducting or assessing *in vitro* trials on toxicity or bioavailability of lanthanides. As a part of this study, bioaccumulation measurements were carried out using the floating aquatic macrophyte duckweed (*Lemna minor*) as a subject. It was found that bioconcentration factors (BCF) of lanthanides were high in duckweed, with heavier lanthanides tending to have lower BCFs than lighter lanthanides (such as lanthanum). Duckweed was taking up lanthanum as La^{3+} and/or a La/EDTA complex. Neither stimulating or toxic effects of lanthanum at 10 nM were observed, however the rate of uptake was such that a longer term exposure to lanthanum may have shown effects. In similar tests, the rooted aquatic macrophyte *Potamogeton pectinatus* showed variations of up to two orders of magnitude in lanthanide concentrations in its tissues.

Further testing showed that lanthanides were toxic to the bioluminescent bacterium *Vibrio fischerii* (used in the commonly applied Microtox® toxicity assay procedure) with the heaviest lanthanide (lutetium) being most toxic, and the lightest (lanthanum) being the least toxic. The toxicity range of the lanthanides coincided with that for Cd,

Cu, Pb and Zn. Lanthanum had similar toxicity to Cd or Zn. The EC_{50} of lanthanum was determined as 0.22mM for a 7.5 minute exposure period, and the toxic effects increased with longer exposure times.   Speciation calculations were used to ascertain the true concentrations of lanthanides in the test media. Work with active isotopes suggested that the lanthanide species responsible for toxicity are the free-ion forms, however a contribution from -hydroxide, -nitrate and -carbonate complexes could not be ruled out. It was commented that the presence of organic matter may be expected to increase the solubility, and therefore the geochemical mobility and bioavailability, of lanthanides, and that the majority of soluble lanthanides in freshwaters are associated with dissolved organic carbon (DOC).

It was also observed, that based on the extensive literature search carried out as part of this study, much of the lanthanide data obtained from laboratory studies was of poor quality, probably due to analytical difficulties and insufficient attention to questions of solubility. The advent of ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) techniques in the last 2 decades has greatly assisted in the collection of reliable data. It was suggested that, due to their high BCFs, aquatic plants should be used as monitors for the presence of available lanthanides in the aquatic environment.

It is recommended that this biomonitoring procedure, using aquatic flora, be adopted should field trials with Phoslock™ or similar materials be carried out in the Rotorua Lakes.

NIWA (National Institute of Water and Atmospheric Research Ltd.) recently conducted acute toxicity trials on Phoslock™ [109]. The test organisms used were algae (*Pseudokirchneriella subcapitata*), crustacea (*Daphnia magna*) and fish fry (rainbow trout, *Oncorhynchus mykiss*). These organisms were exposed to a filtered 50 g.l^{-1} elutriate of Phoslock™. The new granular formulation, which is claimed to release less dissolved lanthanum into the water column, was used. The following were among the findings:

- Fish were the most sensitive species (with a LC_{50} of 4350 mg Phoslock™.l^{-1}), 11.5 and 3.4 times more sensitive than the crustacea and algae respectively.
- Based on the most sensitive species (fish) the acute LC50 of Phoslock™ was markedly (44x) higher (i.e. less toxic) than the ERMA (2001) acute ecotoxic threshold of 100 mg/l.
- The granular 'Eureka 1' formulation of Phoslock™ that was tested did not trigger HSNA (2001) ecotoxic thresholds and was therefore considered non-toxic for the purposes of the Hazardous Substances and New Organisms (HSNO) Act 1996.
- As might be expected, addition of phosphorus as phosphate to Phoslock™ elutriate resulted in significantly reduced mortality to fish.
- A risk-based assessment showed that for a normal phosphorus-related application (200 parts of Phoslock™: 1 part of phosphorus) and a high concentration of phosphorus likely to be found in New Zealand receiving waters, a low risk of adverse effects for aquatic biota exists. For an aerial dosing sediment capping scenario (200 g.m^{-2} application rate) there is a greater risk, but there remains at least a 20 times factor of safety against adverse effects.
- The results of this study indicated that additional chronic toxicity testing would not trigger the ERMA (2001) ecotoxic thresholds and not require amendment of

the "Not Classified' HSNA classification derived from the acute toxicity test results.

It is unclear whether chronic toxicity testing is to be carried out. EDTA or other complexing agents were not used in the test media. Time did not permit the detailed assessment of these results in the light of the major Dutch study referred to above, but it is recommended that this be carried out, with a view to determining whether chronic toxicity testing of Phoslock™ should be carried out or not. The effects of organic complexing agents should be considered in such an assessment.

Recent work comparing the use of Phoslock and Bauxsol (*below*) in laboratory mesocosms showed that the use of Phoslock may lead to increased levels of dissolved iron in the water column [110]. Iron concentrations in the water column above Phoslock-treated sediment cores in the anoxic mesocosms rose steadily to a concentration several times the concentration specified for the protection of aquatic ecosystems in the ANZECC Guidelines (1992). This effect was attributed to the ability of lanthanum to desorb P ions sorbed to iron oxyhydroxide surfaces, thus permitting the co-release of ferrous (Fe^{2+}) iron into the water column. A higher dose of lanthanum than was recommended was used in this work. Interestingly, redox potentials in the (anoxic) mesocosm water column 150 mm above a Phoslock-treated sediment fell much less than was the case in the water column above untreated or Bauxsol-treated sediments.

Baraclear
Baraclear is an Australian-developed product based on aluminium-modified smectite. According to the US patent for the material (US 2003/0213753 A1) the material consists of a smectite (which may include the minerals bentonite – the preferred choice, attapulgite, saponite, hectorite, sepiolite and fullers' earth) to which alum (aluminium sulphate) has been added. A pH buffering agent is frequently added, and an algaecide may also be added. The material may be coated with a variety of materials in order to control the rate of dissolution in water. The material may be applied as pellets, briquettes, tablets etc... The patent suggests that the product is designed to deliver alum to the target area (usually the water/sediment interface) but it does not appear to suggest that the alum is permanently or long-term bound to the mineral substrate.

Bauxsol™
Bauxsol is a chemically and physically modified waste product from the aluminium smelting industry.
Bauxsol™ reagents are proprietary environmental improvement products prepared from the red mud residue resulting from the caustic soda leaching of bauxite during the production of alumina. Bauxsol™ reagents have a pH of <10.5.
Red mud may be classified as hazardous due to the presence of caustic soda and sodium carbonate at unspecified and uncontrolled concentrations and a resultant pH that usually exceeds 11.5.
Bauxsol™ reagents are prepared by:
- Converting caustic soda and sodium carbonate into low solubility hydroxide, carbonate and hydroxycarbonate minerals. This essentially converts soluble basicity to soluble alkalinity.
- Buffering to pH 8-pH 10.5.
- Adding minor amounts of additional mineral reagents to enhance particular properties of the raw material.

- Drying, size grading, pelletising, or otherwise physically modifying the raw material or the blend to suit particular applications.

Bauxsol™ reagents are used for the treatment of acid mine drainage, sulphidic waste rock, tailings and sediments, acid sulphate soils, acidic metal containing industrial effluents and municipal sewage. The iron and alumina components are largely responsible for the binding of phosphorus, with the P-binding largely regulated by adsorption and co-precipitation reactions on iron oxides and hydroxides. Bauxsol materials are mostly used for the immobilization of heavy metal contaminants, and they resist re-releasing these contaminants under anoxic conditions. The composition of Bauxsol products varies somewhat from blend to blend [110].

The typical composition of virgin Bauxsol™ reagent is as follows:

	% WASHED MEAN
Iron oxides & oxyhydroxides	33. 2%
Hydrated alumina	18. 1%
Sodalite	17. 8%
Quartz	7. 0%
Cancrinite	6. 5%
Titanium oxides	5. 0%
Ca(Al) hydroxides & hydroxycarbonates	4. 6%
Mg(Al) hydroxides & hydroxycarbonates	3. 9%
Calcium carbonates	2. 2%
Other)	1. 7%

Australia is a major producer of alumina, from very large natural deposits of bauxite. There are consequently large quantities of 'red mud' available, and looking for uses. Although New Zealand has an aluminium smelter, at Aramoana, this relies on imported supplies of alumina, and therefore bauxite by-products such as Bauxsol are not readily available. A comparison of Phoslock and Bauxsol indicated that Bauxsol was not effective at retaining and immobilising P under anoxic conditions [110], thus rendering the material unsatisfactory for use in major Rotorua Lakes.

AlgalBLOCK
AlgalBLOCK is a specialised form of surface-activated precipitated calcium carbonate (PCC) capable of significantly reducing phosphorus concentrations.

During dosing, soluble phosphorus binds onto the surface of the AlgalBLOCK as it settles through the water column. Once it falls to the bottom, AlgalBLOCK forms a reactive barrier or blanket which prevents further seasonal release of phosphorus from the basal sediments. This provides sustained protection against algal blooms. AlgalBLOCK forms an essentially insoluble natural mineral (hydroxy-apatite) on reaction with phosphorus in standing water and sediments.

Independent research by the Water Studies Centre at Monash University concluded that the phosphate-binding capacity of AlgalBLOCK is in the order of 5 grams phosphorus per 100 grams of AlgalBLOCK. AlgalBLOCK can be supplied to site as a powdered reagent. Specialised dosing equipment is used to dispense AlgalBLOCK evenly over the surface of the affected water body as a slurry. Fine suspended

particles of AlgalBLOCK then settle through the water column, removing phosphorus on the way, to form a reactive barrier or blanket over the bottom sediments.

APPENDIX 3: PERIODIC TABLE OF THE ELEMENTS

Despite its success and usefulness, the Periodic Table suffers from inconsistent column labels. At present, there are 3 versions of the Periodic Table widely used, each with its own unique column headings. The 3 formats are the Chemical Abstract Service (CAS) table, the old International Union of Pure and Applied Chemistry (IUPAC) table, and the new IUPAC table. The CAS version is the one used in this report and is reproduced below. It is used here due to its use in US Patents to which reference is made in the report.

CAS Version

ADDENDUM :OTHER POSSIBLE OPTIONS MERITING CONSIDERATION.

This addendum, slightly modified from another document in preparation, has been included in order to bring some more speculative options for water quality improvement forward for examination.

Removal of phosphorus as volatile forms.

There are a number of inorganic compounds of phosphorus in which phosphorus occurs in lower oxidation states. Strangely, these compounds have been virtually overlooked in limnological and environmental research until very recently. This is all the more curious in that the importance of similar compounds of other important elements which occur in natural waters is well understood (the importance of denitrification, for example, is well recognised.) A glance at the Periodic Table (*previous page*) will emphasise this. Series VA of the table includes (among others) the elements Nitrogen, N, Phosphorus, P, and Arsenic, As, arranged contiguously in increasing order as elements 7, 15 and 33 respectively. Elements sharing the same series in the table are generally considered to display similar chemical behaviours. Both nitrogen and arsenic are well known to possess volatile, chemically-reduced forms and also volatile, biologically- transformed methylated forms. In the case of nitrogen, there is the nitrogen trihydride form, generally known as ammonia. In the case of arsenic, arsenic trihydride is generally known as arsine. Both are gases at STP. Methylamines (for N) and methylarsines (for As) are also volatile. The fact that this is also the case with phosphorus appears to have been largely overlooked in the limnological world.

Recent work on microbial hypophosphite and phosphite oxidation support the hypothesis of a full phosphorus redox cycle and suggest that the phosphine evolution detected in anaerobic habitats is due to microbial processes [111], [112]. Further discussion on environmental phosphine occurs later in this document. The various simpler inorganic compounds (involving hydrogen or oxygen) of these three elements, that are likely to occur in natural waters, are shown below in Table 1.

Some reduced forms of inorganic P

Phosphite
This ionic form of P with three oxygen atoms (as opposed to phosphate, which has four) is also known as phosphonate, but phosphite appears to be the more commonly used term. Both are acceptable in terms of IUPAC nomenclature. As with phosphate, phosphite occurs in different species according to pH [113].

The author of this report, when carrying out anion ion chromatography on pore waters from Lake Rotoiti sediments, has several times observed an unidentified peak which co-elutes with the phosphite ion. A phosphorus-specific detector would be required to confirm whether this unidentified peak is, as suspected, phosphite.

Phosphine
Limnological research on phosphorus in the aquatic environment generally focuses around the role of 'phosphate' and 'total phosphorus' in both water and sediments. Little attention is given to phosphorus trihydride, better known as phosphine (PH_3). This is a malodorous, colourless, poisonous gas (used as a fumigant), with a boiling point of $-87^{\circ}C$. This, of course, means that at normal environmental temperatures it is

volatile. It is soluble in water, with a solubility of 260 ml.l^{-1} at 17°C, although in practice its solubility is dependant on its partial pressure [114].

Table 1
Some simple inorganic compounds of nitrogen, phosphorus and arsenic[115]

Element Oxidation state of nutrient element	Nitrogen	Phosphorus	Arsenic
-3 **Reduced**	Ammonia NH$_3$	Phosphine PH$_3$	Arsine AsH$_3$
-2		Hydrogen diphosphide P$_2$H$_4$	
+1	Nitrous oxide N$_2$O	Hypophosphite H$_2$PO$_2^-$	
+2	Nitric oxide NO		
+3	Nitrite NO$_2^-$	Phosphite HPO$_3^{2-}$	Arsenite H$_2$AsO$_3^-$
+4		Hypophosphate P$_2$O$_6^{4-}$	
+5 **Oxidised**	Nitrate NO$_3^-$	Phosphate	Arsenate HAsO$_4^{2-}$

It has been recognised for some decades that certain micro organisms may be able to reduce phosphate to phosphine under appropriate environmental conditions. The natural phenomenon known as *ignis fatuus* or will-o'-the-wisp has been ascribed to the spontaneous ignition of phosphine evolved under wetland conditions [116]. Various claims have been made concerning the isolation of soil bacteria that reduce phosphate, under anaerobic conditions, to phosphine, but these claims have been disputed by other workers. Problems in reliably and sensitively detecting phosphine at low concentrations have not helped this situation. More recently, sensitive gas chromatographic techniques have been developed, but initially failed to show significant production of phosphine in waterlogged soils, however the authors of this work concluded that this failure may have been due to the demonstrated ability of soils to sorb phosphine in amounts larger than were likely to be produced during the period of the experiments [117].

Coupling gas chromatography with mass spectrometry has lead to improved analytical techniques for phosphine. The use of this hyphenated technique has lead to some interesting studies on phosphine evolution and a reappraisal of its potential importance in nutrient budgets [114]. One study examined phosphine release from sediments in a planted treatment tank in an open air wastewater treatment plant, and an experimental lake, average depth approximately 1 m, planted with submerged and emergent macrophytes, both located in Hungary. The following results were obtained (see Table 2).

Table 2
Phosphorus budget at wastewater treatment plant and artificial lake in Hungary.
(from Devai *et al* 1988).

	Parameter	Total phosphorus content (kg.yr^{-1})	
		Wastewater treatment plant	Artificial lake
A	Total P in influent	2,522	85.5
B	Loss through seepage	1	18.2
C	In submerged macrophytes (October)	0	5.9
D	In emergent macrophytes (October)	20	16.4
E	Loss by chironomid emergence	5	0.3
F	Accumulated in the sediment	113	(-36.7)
G	Loss through effluent	1,705	6.8
H	Phosphorus deficit H = A- (B+C+D+E+G)	678	37.9
	Average estimated phosphine production (based on measurements)	175	16.85
	% of P deficit in phosphine	26	44.5
	% of influent P lost as phosphine	7	20

These results are of interest as they suggest that, under some circumstances, phosphine
may play a significant role in the phosphorus cycle. In the case of the shallow planted
artificial lake (= pond), nearly half of the apparent phosphorus deficit may be attributed
to phosphine evolution, and phosphorus lost as phosphine amounts to 20% of the total
influent P.

In the wastewater treatment plant basin, release of phosphine (along with other gases
such as methane) occurred more or less continuously, whereas in the pond, gas release
was intermittent and controlled by factors such as a sudden drop in barometric pressure.
These workers also demonstrated a significant degree of *in vitro* production of
phosphine, by growing anaerobic bacteria in a medium rich in organic compounds.
Such a culture lost 42% of its original phosphorus in 56 days. The authors speculate
that other volatile phosphorus compounds, such as diphosphine and organic P
compounds, may also be produced in reducing conditions. This research has been
described as 'controversial', for reasons which have not been apparent.

If phosphine is released along with other reduced gaseous compounds, such as
suggested above [114], then it may behave in a similar way when being lost from the
sediments or water column. Gases may be lost from sediments by ebullition of bubbles
or by molecular diffusion. Various workers have also demonstrated that certain
emergent aquatic macrophytes provide a significant conduit for such gases to be

transferred from the sediments to the atmosphere. For example, work at Bool Lagoon, South Australia, showed that both *Baumea arthrophylla* (black rush) and *Triglochin procerum* (water ribbon) provided a significant pathway for loss of methane to the atmosphere [118]. Interestingly, substantial methanogenesis was occurring in the sediments, despite their apparently becoming a non-reducing environment during the day.
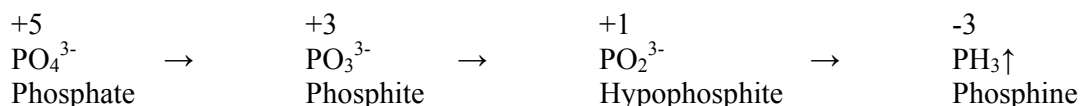
It is interesting to speculate whether similar mechanisms may operate in the case of phosphine and/or other volatile phosphorus compounds. Recent work suggests that it may, with quantifiable phosphine emissions being reported from brackish and salt marshes in Louisiana [119]. This study resulted in field measurements showing phosphine emissions of 0.91 ng PH_3/m^2/day for a Louisiana salt marsh and 0.42 ng PH_3/m^2/day for a Louisiana brackish marsh (both undisturbed). Disturbance of the experimental sites by treading resulted in an increase in phosphine emission rates to 6.52 ng PH_3/m^2/day and 3.03 ng PH_3/m^2/day respectively. Laboratory trials using freshwater marsh soils (Florida Everglades) and Louisiana salt marsh soils showed higher phosphine emission rates from the freshwater marsh soil (15.7 pg PH_3/g wet soil/day and 1.64 pg PH_3/g wet soil/day respectively).

One estimate, extrapolating from this work, suggests an annual global phosphine production from wetlands of 30,000 to 500,000 tonnes per year [120]. This compares with an estimated anthropogenic production of 2000 tonnes per year. The authors of this study admit that this estimate is imprecise, being based on a small number of measurements and a vague estimate of global wetland areas.

One study found a summer maximum peak of soluble phosphorus in Colorado rain water and the authors speculated that it was the oxidation product of an atmospheric gaseous carrier of phosphorus [121]. A later study detected phosphine in the lower troposphere from widespread locations including Germany, Argentina, Israel, Namibia, Tunisia and the Seychelles [122]. The average phosphine concentrations (at 1 m above ground) ranged from 157,000 (urban Germany) to 40 (rural Namibia) pg.m^{-3}. The authors of this study calculated that 310 g of phosphine was released per km^3 of atmosphere (lower troposphere) per year. They comment "This small contribution of atmospheric phosphine to the phosphorus cycle could not be insignificant for areas where P limits the biomass stock." A further finding of this study was that atmospheric phosphine concentrations vary widely between day and night. A series of samplings carried out in Leipzig showed that the average night-time phosphine concentration was 850 pg/m^3, whereas the average day-time concentration was 120 pg/m^3. The concentration began to decrease about 4 hours after sunrise, and it is believed that phosphine, although not auto-oxidised, is broken down ($PH_3 \rightarrow H\bullet + \bullet PH_2$) by hydroxyl radicals induced by ultraviolet light from the sun, and is subsequently oxidised.

The chemical pathway from phosphate to the atmosphere and possible implications

Phosphate may be reduced through a chain of reactions as follows:

+5		+3		+1		-3
PO_4^{3-}	$\rightarrow$	PO_3^{3-}	$\rightarrow$	PO_2^{3-}	$\rightarrow$	$PH_3\uparrow$
Phosphate		Phosphite		Hypophosphite		Phosphine

It is interesting to speculate to what extent this pathway is occurring in the wetland areas and benthic sediments of lakes in New Zealand. The possible presence of phosphite in Lake Rotoiti sediments has been mentioned earlier in this discussion. A study of the literature pertaining to phosphite in plants (the phosphite ion is widely used in horticulture as an agent to combat *Phytophthora* root rots in, for example, avocados) suggests that phosphite is surprisingly long lived in both soils and plants, being largely oxidised to phosphate by 90 days after application [123]. In my opinion the whole field of low-oxidation-state forms of phosphorus is one which merits more attention from the limnological community. It could hardly receive less.

Electronic simulation and stimulation of nutrient removal

Nutrient removal processes such as denitrification fundamentally rely on electron transfer. Normally this occurs through the intervention of living organisms, such as bacteria. However, electrons can be manipulated by other means, such as the application of electric potentials or electric currents, under the appropriate conditions. Such nutrient transformations may be accomplished either electro-chemically or by electronic enhancement of microbial processes. Such technology is in its infancy, but aquarists may already purchase electronic denitrification units. This field of endeavour is one that merits scrutiny.

A variety of investigations have been carried out on such processes, generally in the field of wastewater treatment. Space does not permit a discussion of such work here, however a few titles, with references are given.

'Electrochemical oxidation of leachate pretreated in an upflow sludge blanket reactor.[124]

'Selective reduction of nitrate to nitrogen gas in a biofilm-electrode reactor.[125]

'Electrolytic stimulation of denitrification in sand columns.[126]

'An evaluation of two cathode materials and the impact of copper on bioelectrochemical denitrification.[127]

'Electrochemical removal of nitrite and ammonia for aquaculture.[128]

In-situ enhancement of groundwater denitrification

A major route of nitrogen inputs into the Rotorua Lakes is via groundwater flows. The following work is therefore of interest, as it suggests a possible approach to addressing the problem of long-term nitrogen enrichment in the aquifers supplying Lake Rotorua (in particular).

Groundwater studies in various aquifers have established that denitrification can be an important mechanism for removing nitrate from aquifers. Denitrification is a natural process where nitrate is converted to N_2 gas. The process requires an anaerobic environment, denitrifying bacteria and sufficient electron-donating species such as dissolved organic carbon (DOC), ferrous or sulphide ions. Work carried out on the Burdekin catchment (Australia) [129] included an analysis of existing nitrate and iron data for the Lower Burdekin which showed a negative correlation between the

two. Further investigation was carried out into this, sampling and analysing 57 single and nested groundwater monitoring bores during September to October 2003 and in January 2004.

Although the nitrate concentrations in the majority of the bores were below the ANZECC Guideline levels, values as high as 15 mg of NO_3-N/l were measured in this area. Nine of the 50 single bores exceeded the ANZECC nitrate-N guidelines and these mostly occurred at shallow depths (<30 m), which had low ferrous levels (<2 mg/l). The data also showed that nitrate-N concentrations above 5 mg/l tended to occur where ferrous levels are less than 4 mg/l. As shown in Figure 3, the negative correlation of nitrate with iron indicates that the nitrate is being consumed via denitrification processes. Nitrate concentrations were also undetectable in the nested bores along the coast where high ferrous concentrations were common.

These results suggest that nitrate could be attenuated in the groundwater along the flow path before reaching the GBRL (Great Barrier Reef Lagoon). . Geochemical conditions such as pH, dissolved oxygen and redox potential prevailing in the lower Burdekin aquifer support the presence of ferrous iron in abundance and the availability of a reduced environment. Also, low nitrate-N concentrations are coincident with high ammonium, suggesting the possible occurrence of dissimilatory nitrate reduction.

These initial results suggest that denitrification is an important mechanism that reduces the amount of nitrate in groundwater with time, and that the shallow groundwater systems have greater potential for denitrification than the deeper groundwater systems. This has implications to coastal agriculture and its impacts in terms of the nitrogen load it may contribute to the GBRL and is the subject of ongoing studies in this region.

Work on *in situ* denitrification is also being carried out in New Zealand by Lincoln Environmental Research, which involves the use of reactive well testing methods to measure the rates of denitrification and other natural attenuation processes that occur in groundwater. Other work carried out by this organisation suggests that some commonly used agricultural nutrient models do not adequately allow for in-ground denitrification processes. Further details of this work may be viewed on their website [130].

Electrolytic dispersal of phosphorus-flocculating metals

In the early 1970s, investigations commenced on ways to get around the problems involved in dosing treatment chemicals to wastewater and water treatment plants. One approach that was adopted in some plants was to dispense these materials by electrochemical means, whereby an electrode which has the ability to produce the necessary ions is placed in the water to be treated and an electric current is passed through it [131]. By this means, a stream could be dosed with, for example, aluminium by immersing aluminium electrodes in the stream and applying an electric current at a carefully regulated low voltage (typically 1-2 volts). As the aluminium was gradually dissolved by electrolysis, aluminium ions (Al^{3+}) would enter the water, remaining in solution by interacting with counter ions already present in the water. This has the advantage of adding the necessary aluminium, without also adding the companion ions such as sulphate, with their consequent impacts on water chemistry.

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