

LITERATURE REVIEW

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AUTHENTICATION

We declare that this work was done under our supervision according to the procedures described herein and that the report represents a true and accurate record of the results obtained.

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GROWER SUMMARY

Headline

Two commercially available products, 'Phoslock' and 'ViroFilter', have been identified for their suitability in phosphate removal from watercress production systems. Consideration of the practical issues surrounding their use has been evaluated and is published in the Experimental Report for this project.

Background and expected deliverables

This review was carried out to identify suitable candidate materials and/or abstraction methods for reducing phosphorus levels in outflow from production beds or settlement ponds in watercress production systems. Adequate phosphorus concentrations in the water supply to the root systems of watercress can only be achieved by the supply of highly soluble phosphate mineral salts added to the production systems as commercial fertiliser. Fertilisers are compound and N and K levels are also increased but to a lesser extent on a proportional basis compared with phosphorus to support biomass production and acceptable watercress product quality. As only a fraction of the phosphorus added is actually captured by the root system of the watercress crop, relatively high levels of soluble phosphorus flow out from the production beds and then on into the wider environment. Techniques therefore need to be in place to scavenge excess phosphorus at source in the water outflow, with the additional requirements of being environmental acceptable and cost effective.

Deliverable

- To identify at least two commercially viable products for phosphorus scavenging from watercress farm water outflows.

Summary of project and main conclusions

The known methods of phosphorus removal from water were reviewed. The most common and effective approach adopted was cation exchange and precipitation. Whilst phosphorus is a mineral element with a positive charge, it exists in available form either bound to soil or made available for uptake by biological organisms in 'salt' or phosphate forms. As the predominant element it combines with is oxygen, and this has a negative charge, then the overall electrical charge of a formed phosphate ion is negative (PO_4^-). Products that effectively scavenge phosphorus contain Ca^{2+} , Fe^{2+} and Al^{3+} which will act to precipitate phosphate (PO_4^-) ions out of solution and therefore significantly reduce the phosphorus concentration of outflow water from water cress farms. Two commercially available

products, Phoslock™ and ViroFilter™, which could be used in watercress production systems to strip phosphorus from water discharges were identified.

Financial benefits

The aim of the work is environmental compliance and reduction of phosphorus contamination in the environment from concentrated sources such as watercress farms. The aim of the work is to find the most effective solution for growers for phosphorus removal; the relative costs associated with product are reported elsewhere (FV 388),

Action points for growers

The practical approaches to phosphorus removal using Phoslock™ and ViroFilter™ have been reported in HDC report FV 388, December 2010.

SCIENCE SECTION

Introduction

Phosphorus compounds are an essential element of both plant and animal life. In addition they are widely used in agriculture and for industrial processes and products. Supplies of rock phosphate, a core mineral source of P, are finite and concerns about future levels of demand have caused recent spikes in fertiliser prices.

Man's activities do however lead to discharge of phosphate in various forms into the environment; major sources include run-off from fertilisers used on agricultural land, use of phosphate-containing detergents, fruit and vegetable processing, pulp and paper manufacture and human sewage.¹ A consequence of phosphate (and other nutrient) discharge into watercourses is the process of eutrophication, whereby the growth of algae is encouraged, which depletes oxygen levels in the water, with consequent adverse effects on the invertebrate and fish species present.

Commercial watercress production involves the addition of phosphatic fertilisers, as the waters used for cropping contain inadequate supplies of that element. Whilst some of this added fertiliser is taken up by the crop, and further fractions are absorbed into the bed base or are retained in settlement tanks or lagoons, a proportion is present in discharges made from watercress farms to streams and rivers. The total amount of phosphate released is small in relation to other sources of phosphate currently discharged to water, but are nevertheless of some concern, both because of the high water quality of the chalk streams in the areas of watercress production and the ability to meet increasingly stringent regulatory requirements.

This review follows two previous HDC-funded projects looking at the use of phosphate fertiliser in the watercress crop. In 2006, project FV 302 examined the use of phosphate fertiliser through a survey of growers. It identified a wide range of crop yields being recorded per kg of P fertiliser applied, with phosphate applications varying between farms by a factor of up to five, although this was often related to the type of production system being employed. Some potential farm practices were proposed which could be tried to limit peak levels of phosphate discharge from the production beds.

A subsequent HDC Project, supported by the Environment Agency, (FV 338) evaluated 3 phosphate fertiliser regimes and established that current commercial rates of applied

¹ Environment Agency business/topics/pollution/39111.aspx March 2010.

phosphate fertiliser (2,200 kg/ha P₂O₅ per year) were necessary to maintain acceptable commercial standards of quality and economic yield. Watercress crops respond to higher applications of P to produce faster growing crops and superior quality. Lower rates of applied P fertiliser produced stem purpling and delayed scheduling which would cause product rejection and fewer crops per year; nutrient addition is therefore necessary for profitable commercial watercress farming.

The use of higher commercial rates of applied P was associated with higher discharges of P concentrations at the watercress bed outflow. Discharge P concentrations were also markedly higher when a more soluble 19:14:14 fertiliser was used compared with the less soluble and commonly-used Fibrophos fertiliser. Unfortunately, there are occasions in the growing season when remedial applications of more soluble P are required to maintain crop quality. Consequently, while adherence to the Best Practice policy of minimising the use of high solubility sources of P is desirable, in practice this cannot be sustained throughout the year.

However, whilst the evidence broadly supports the use of rates of phosphate fertiliser currently in use, new EU limits on phosphate levels in discharge waters being returned to watercourses are being introduced, which should not exceed an annualised level of 40-60 µg P /litre. Whilst a variety of techniques has been introduced by or is available to the watercress industry to reduce phosphate discharge levels, such as the construction of settlement ponds and rotational fertilising and harvesting on farms, discharge levels can remain at an unacceptably high level (60 -100 µg P /litre).

As these measures alone may not be sufficient to meet future regulatory requirements, an alternative approach is to examine novel means of reducing phosphate in discharge waters. This review is a pre-cursor to *in-situ* experimental work and is designed to identify the most suitable products or technologies which could offer potential to achieve this reduction in phosphate levels in the context of commercial UK watercress production.

This approach is based on a demonstration of one such material with phosphate stripping potential carried out in November 2008 at a production site belonging to The Watercress Company, using materials supplied by Virotec Ltd. This suggested that the technique has considerable potential when utilised *in-situ* to remove phosphate from fast-flowing discharge water.

Scope of review

The review thus sought to identify a number of potential phosphate removal (“stripping”) materials/techniques, with their availability and suitability for use on watercress farms given particular consideration. The criteria used to evaluate the potential of a material included:

- Operate effectively in the settlement pond environment i.e. pH, alkalinity, organic matter, high water flow
- Ease of achieving correct dosing
- Duration of P stripping materials
- Disposal costs of materials
- Product safety data
- Environmental safety
- Running costs incl. initial cost, equipment required, labour and maintenance

As referred to at the outset, the assessment of product suitability needs to ensure that the materials would not themselves pose an environmental risk downstream of the watercress farm. At a Review meeting for Project FV 338 held in December 2008, the Environment Agency stressed the importance of fully considering, at the initial review stage, the environmental safety of any materials to be used in the discharge water. This was necessary to eliminate any possible risk of environmental contamination prior to trials being undertaken. A range of stripping materials is available, but for a variety of reasons, e.g. scale of application, cost of equipment required or environmental profile, these may not be appropriate to the watercress industry.

As a result of this process 3 products and associated equipment were short-listed, all being commercially available products which appeared to have the potential to provide consistent and reliable results when tested in appropriate situations on watercress farms. These were subject to further review and evaluation [see Section 4].

Methods of phosphate (P) removal

Initial scoping

An initial appraisal of the literature indicated that the requirement for phosphate removal has been greatest in sewage treatment works (STW) where phosphate is present in high concentrations; consequently many of the currently available processes and handling technologies have been developed primarily to operate in the municipal wastewater treatment environment. This has implications in terms of the capacities and types of equipment that have been developed with this particular market in mind, as well as related capital and running costs.

P removal started as early as the 1950s, when it was first recognised that there was a need to reduce levels of entering surface waters discharged after sewage treatment. Where high levels of P need to be removed, **chemical precipitation** has been the leading and most cost-effective method in this area, utilising iron, alum, or lime (Donnert and Salecker, 1999). In more recent times, **biological removal** has also become firmly established, along with **crystallisation technology**.

The need to manage phosphate run-off from agricultural livestock production units has been a more recent requirement, but one which is being more actively addressed in Europe and the U.S. through increased regulation of waste and water quality. Similar comments apply to the loss of phosphate by leaching from arable land whereby reduction is being sought through adoption of 'best practice' methodologies, adherence to official guidance (such as Defra's RB209 Fertiliser Recommendations) and introduction of land management practices designed to reduce soil erosion and leaching. All methods, including **P stripping** have a part to play in water achieving a 'good' quality status, as required by the Water Framework Directive.

Where phosphate run-off has led to eutrophication of lakes and watercourses, reducing the exchangeable P levels through **sediment capping** by the application of materials that bind to P, has been largely successful.

Compared with the situations described above, phosphorus discharges from watercress farms are very low indeed. However, whilst total phosphorus levels in discharge waters can be successfully reduced with the use of settlement ponds and, where space permits, integrated constructed farm wetlands, they have a little or doubtful impact on low levels of soluble phosphate². There has not been a known requirement to reduce levels of soluble phosphate in discharge waters in any country currently involved in watercress production, so consequently there have been no research studies directed at this subject or 'off the shelf' solutions available for study to the UK industry.

Primary techniques for phosphate removal

The most commonly used methods employed in wastewater and water purification to remove phosphorus are:

- a. Physical flocculation, filtration and chemical precipitation of P
- b. Chemical adsorption

² Source: Scottish Environmental Protection Agency Best Management Practice No 75

- c. Biological uptake
- d. Ion exchange, magnetism, crystallisation

Physical flocculation, chemical precipitation and filtration of P

Flocculation is a process of water clarification in which any sediment or colour is removed, leaving the water clear or colourless. Particles finer than 0.1 µm remain continuously in motion, due to electrostatic charges which cause them to repel each other. However, once their electrostatic charge is neutralised, for example by the use of a coagulant chemical, the finer particles start to collide and agglomerate. These larger and heavier particles are called flocs, which then precipitate out of suspension.

Water that is slightly alkaline (>pH 7) ensures that the coagulation and flocculation processes work more effectively than at lower pH. The coagulated precipitate may then be filtered through a coarse sand filter or granulated anthracite.

Materials used

Many flocculants are multivalent cations such as aluminium, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles/molecules, reducing the barriers to aggregation, resulting in an insoluble metal phosphate precipitate that is settled out by sedimentation.

Where iron and aluminium are used, they are usually added as chlorides or sulphates. Lime is another agent used, to precipitate calcium phosphate. Where high concentrations of P are present, the flocculation process can be carried out several times in series in the flow of the water through the handling system, adding to its effectiveness.

Long chain polymer flocculants, such as modified polyacrylamides are manufactured and sold by the flocculant producing business. These can be supplied in dry or liquid form. The most common liquid, polyacrylamide, is supplied as an emulsion with 10-40% actives, the remainder consisting of carrier fluid, surfactants and latex. Emulsion polymers require activation to invert the emulsion and allow the electrolyte groups to be exposed.

The following chemicals are used as flocculants to aid precipitation:

- alum
- aluminium chlorohydrate
- aluminium sulphate
- calcium oxide
- iron sulphate
- polyacrylamide
- polyDADMAC
- sodium aluminate

- calcium hydroxide
- iron chloride
- sodium silicate
- hydrous iron oxides (ochre)

Flocculating agents such as iron hydroxide and aluminium hydroxide may be added to the suspension to aid the process of filtration. Filtration using modified limestone combined with flocculants such as clay particles (< 2 µm) and surfactants such as polyhydroxy aluminium chloride (PAC) binds P to its surface, rendering it insoluble and consequently taking it out of solution. In this way, up to 95% of P can be adsorbed in 24 hours. Gypsum (calcium sulphate) can also be used as a source of calcium ions and magnesium for the precipitation of calcium phosphate.

Operational considerations

Within a given combination of flocculant chemical and water source, the degree and rate of flocculation will depend on the shape and water retention time of the various ponds in a settlement system. Typically, water being treated would leave a flocculation pond and then enter a sedimentation basin allowing floc to settle to the bottom. The distance between ponds is designed to prevent settlement or floc break up. The outflow is positioned opposite the inflow, typically over a weir to maximise retention time, which as a minimum is 4 hours. Deeper ponds will allow more floc to settle out than shallow, with large particles settling quickly, whilst smaller particles continuously aggregate becoming larger as they also settle to the bottom. Sludge layers forming at the bottom of the pond require regular removal and cleaning. Currently, settlement ponds used on watercress farms to remove organic matter are dredged approximately every two years, depending on their size and the speed at which sediment builds up.

Filtering is the final stage in the process to remove remaining suspended particles and unsettled floc. Rapid sand filters, often containing activated carbon or anthracite, allow water to run vertically through the sand while entrapping suspended particles down the sand profile. Clean water back flushing in the opposite direction is required to clean the sand and remove embedded particles. This system of sand filtration may be enclosed in a steel vessel and the water forced through it under pressure (pressure filter).

Slow sand filtration requires considerably more space, as removing the suspended particles from the water takes considerably longer due to the comparatively slow passage of water through the filter. This process relies on biological activity rather than physical filtration. A bacterial film, known as the zoogeleal layer or Schmutzdecke ('dirtcover') develops on the surface, acting as an effective nutrient filter, and requiring to be scraped off when the flow is obstructed by biological growth. The resulting filtered water has lower nutrient levels than

achievable from physical methods of filtering alone. It does not involve the use of chlorine, which some purification systems require.

A tertiary (i.e. final) form of water purification used for drinking water and sewage for reuse is membrane filtration. This process can remove virtually all particles $> 0.2 \mu\text{m}$, including the parasites *Giardia* and *Cryptosporidium*. It is particularly applicable for use where water is discharged into a river that is used again further downstream, or where high standards of water quality are required.

Physical filtration methods are however limited in their ability to remove dissolved substances in water including phosphorus, nitrates and heavy metals. The removal of P by the processes of flocculation and precipitation followed by subsequent sedimentation offers greatest potential when applied to the intake waters entering the sediment ponds.

Chemical adsorption

Adsorption is the accumulation of atoms or molecules onto the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It differs from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term 'sorption' encompasses both processes.

Adsorption processes are frequently referred to in cultivated wetland situations where the adsorption performance of different soils and substrates are compared for P removal characteristics. Adsorption characteristics are described by use of 'Langmuir adsorption isotherms' which relate the degree of adsorption with the concentration of the substance in the surrounding media. It is well known that soluble inorganic phosphate is readily immobilised in soils by adsorption and precipitation in reactions with aluminium, iron, calcium and clay minerals. Reactions with calcium occur mainly in alkaline conditions, those with iron and aluminium in acidic environments. Chemical adsorption of P ions onto the surfaces of hydrous oxides of Fe and Al is achieved through the displacement of water molecules and hydroxyl groups.

In constructed wetland studies, the sorption of P from a nutrient solution by *Trifolium repens* is influenced by both aluminium and iron due to physico-chemical sorption processes involving the root surface. Adsorbents are usually used in the form of spherical pellets, rods, mouldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapours.

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds – are typically hydrophilic and polar, including materials such as silica gel and zeolites
- Carbon-based compounds – are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds – are polar or non-polar functional groups in a porous polymer matrix.

Other adsorbents such as activated alumina and half-burned Dolomite, blast furnace slag, shale and bauxite have been shown to be effective at phosphorus removal. They have the advantage of being pH insensitive and produce no sludge in sewage treatment works (STW).

Biological uptake

Phosphates occur naturally in both organic and inorganic forms. The analytical measure of biologically available orthophosphates is referred to as soluble reactive phosphorus (SRP). Dissolved organic P and insoluble forms of both organic and inorganic P are generally not biologically available until transformed into soluble inorganic forms.

P in biological systems can be retained either by being:

- bound to organic matter as a result of being incorporated into living biomass
- precipitated as insoluble phosphates with iron, calcium and aluminium, as found in wetland soils.

In wetland systems, P retention results from the attraction between phosphate ion and those of aluminium, iron or calcium, resulting in the formation of various phosphates of these elements. However, the ability of the soil or water to oxidise or reduce chemical substances in uncontrolled situations may lead to a release of large quantities of bound phosphorus back into solution. Oxygen availability to the system over time is a major determinant of this occurrence.

Higher plants in wetland systems may be considered as transient storage compartments absorbing nutrients during the growing season and releasing large amounts at senescence. Aquatic vegetation may play an important role in phosphorus removal and if harvested, extend the life of a system by postponing phosphorus saturation of the sediments. Phosphorus removal of 60%, 28% and 46% were found for *Scirpus sp.*, *Phragmites sp.* and *Typha sp.* respectively. More recent work may prove these figures to be underestimates, as

artificial wetland plants may account for 67.3% of the inflowing P. Other work has attributed 80% of P removal to plant adsorption.

Only a small proportion (<20%) of P removal by constructed wetlands can be attributable to nutritional uptake by bacteria, fungi and algae; work by Richardson (1985) showed that initial removal of dissolved inorganic P from the water under natural loading levels is high, but quickly becomes saturated at which point the soil medium takes over as the major contributor to phosphate removal. Several studies have examined contributions of the substratum, macrophyte and biofilm components of a wetland site to P removal. Other studies have examined P uptake by the gravel substratum and its release back into the water when saturation of phosphorus binding sites were achieved. Close agreement was found between the P adsorption capacity of the gravel, as determined in the laboratory, and the adsorption capacity in the field. Quartz gravel substrate was examined but it was shown that plant uptake and subsequent harvesting removed more P than the gravel base.

There may be some potential for combining the benefits of adding gravel material and aquatic plants with good phosphorus adsorption capacity to the settlement pond on watercress farms, thereby exploiting all biological methods of removal. Removal of the sediment would depend on monitoring gravel and plant P uptake, with sediment removal required before P saturation point is reached, thus preventing release back into the water. This review and the subsequent experiments envisaged is unable to incorporate further consideration of the potential of biological systems for removal of P, due to limits on resources. There would however appear to be at least some potential for enhancing the biological systems operating in settlement ponds and thereby providing a more sustainable solution to P removal. The use of combined chemical and biological systems has been effective in lowering P levels in effluent waters where critical low levels are required. This complex system has the ability to remove nitrogen as well as phosphate.

In sewage treatment works, biological P removal is applicable where activated sludge is produced, such as in sewage works where chemical use is avoided. It is dependent on producing a chemical oxygen demand (COD), when in the absence of oxygen and nitrates, bacteria such as *Acinetobacter*³ initially release phosphorus into solution. However, during the later aerobic stage rapid uptake of phosphorus occurs, leading to 80-90% removal

³ The identification of the key bacteria responsible has been challenged, see:

A Review and update of the microbiology of enhanced biological phosphorus removal in wastewater plants Blackall LL, Crocetti GR, Saunders AM, Bond PL *Antonie van Leeuwenhoek* 2002 Aug 81 (1-4) 681-691.

rates. Due to inconsistencies which can occur, P removal rates can be variable so the technique often requires additional chemical precipitation.

Although there appears a considerable body of literature on enhanced biological phosphorus removal (EBPR) systems, the actual mechanisms operating are only beginning to be understood and it is known that failures do occur. It is contended therefore that this technology is unlikely to be at the stage where it is appropriate for watercress farms, whose need would be for a reliable system which was not resource-intensive.

Ion exchange, magnetism, crystallisation

Ion exchange is a process which takes place between two electrolytes or between an electrolyte solution and a complex. The term is generally used to denote the process of purification, separation and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral based 'ion exchangers'.

Ion exchange resins (functionalised porous or gel polymers) include zeolites, montmorillonites, clay and soil humus. Ion exchangers may be either:

- cation based, exchanging positively-charged cations
- anion based, exchanging negatively-charged anions
- amphoteric, capable of exchanging both cations and anions.

Performance is most efficient in mixed beds of cation and anion exchange resins or when treated solution is passed through several different ion exchange materials. Ion exchangers can be selective for certain ions depending on their chemical structure. This can be dependent on the size of the ions, their charge or their structure. Ion exchangers can attract:

- H^+ (proton) and OH^- (hydroxide)
- Single charged mono-atomic ions e.g. Na^+ , K^+ or Cl^-
- Double charged mono-atomic ions e.g. Ca^{2+} or Mg^{2+}
- Polyatomic inorganic ions e.g. SO_4^{2-} or PO_4^{3-}
- Organic bases, usually molecules containing the amino functional group $-NR_2H^+$
- Organic acids, usually molecules containing $-COO^-$ (carboxylic acid) functional groups
- Biomolecules which can be ionised: amino acids, peptides, proteins etc.

Ion exchange is a reversible process and the ion exchangers can be regenerated or loaded with desirable ions by washing with an excess of these ions. Applications include water purification and decontamination. In the ion exchange-precipitation process, a resin is used to remove the phosphate ions with struvite (magnesium ammonium phosphate) being produced. The addition of phosphate and magnesium salts regulates the reaction.

Crystallisation technology offers stringent P removal standards, as well as offering the benefits of a more marketable end-product where high recovery is possible as in STW. The process involves the crystallisation of calcium phosphate on a 'seeding grain', usually sand, within an enclosed fluidised reactor. The rate of calcium phosphate crystallisation is adjusted by adding either caustic soda or milk of lime. Rapid crystallisation allows for a short retention time and therefore a small reactor. A continuous process of grain replacement allows for uninterrupted operation and good fluidisation. The pellets of calcium phosphate and seed materials are the only by-products which can be recycled; there is no production of a sludge or additional sediment.

Other crystallisation technologies use different seeding agents. Phosphate rock is used as seed material when mixed in suitable conditions with calcium chloride and caustic soda to produce granular hydroxyapatite or struvite. Similarly, struvite will be produced from the addition of magnesium chloride and alkali. A fluidised bed may be used to remove phosphate by the crystallisation of calcium phosphate to improve removal efficiency.

Magnetic water treatment uses lime to precipitate calcium phosphate attached to magnetite and separated using an induced magnetic field. The magnetite is then separated from the calcium phosphate using shear forces in a drum separator.

Summary

This section has described the range of processes used to remove P in STW and wastewater applications such as constructed wetlands. The methods used commercially to remove P most efficiently often employ materials combining more than one of these processes.

While effective chemical dosing may appear to offer considerable potential as a robust low cost method, consideration needs to be given to their effectiveness when flow rates and pH vary significantly, which may require more sophisticated controls. Chemical dosing may also require strict health and safety control, with bunded areas for hazardous or dangerous goods.

Adapting existing methods and technologies for P removal which operate successfully in managed or cultivated wetlands, waste water treatment/purification works or by remedial dosing to reduce eutrophication in lakes, appear to offer growers the most promising

options if they can be successfully managed on watercress farms. While high levels of P in waste water from STW may require primary, secondary and tertiary treatment to ensure adequate reductions in P loading, treatment of discharges on watercress farms will require only tertiary methods that are used to reduce the P to <1 mg/kg, leaving a 'polished product'.

Detailed considerations and analysis of P-removal methods

Much of the research into the methods and mechanisms of P removal have been directed at wastewaters with high or very high concentrations of dissolved phosphate (DP) (5-40 mg/l and up to 200 mg/l). These methods are essentially chemical (addition of metal salts) or biological (stimulation of microbial uptake) in nature and have been adopted in combination with physical removal (coagulation and flocculation) at sewage treatment works. The very high P concentrations present in wastewaters requires large amounts of chemicals, the final effluent P concentration is often not sufficiently low (>0.1 -0.5 mg/l) to improve aquatic ecology, and a P-rich sludge by-product has to be disposed of, or recycled. Further recent advances in P removal technology have included chemical (e.g. struvite) and biological (algae) recovery with the aim of recycling as a fertiliser or a biofuel. For recent reviews see Morse *et al.* (1998), DeBashan and Bashan (2004), and Barnard (2009).

Additional approaches to P removal at more rural locations include the strategic deployment of natural, or constructed, wetlands using materials that enhance the adsorption and precipitation of DP and particulate phosphate PP in a variety of influents with a much more variable range in P concentrations. These influents include those produced on livestock farms, fish farms and from septic tanks (Renman, 2008). The sedimentation ponds on watercress farms can be considered to be constructed wetlands (CWs) since they develop a range of microbial and aquatic plant communities that help to remove P in addition to the bottom substrate. Monitoring of settlement lagoons on a commercial watercress farm in Dorset by the Centre for Ecology and Hydrology (CEH) demonstrated an average removal of 62% of the P present, with a maximum of 94%, before discharge to a watercourse⁴.

Vymazal (2007) describes basically four types of CW: a CW with free-floating plants (FFP), a CW with free water surface and emergent macrophytes (FWS), a CW with horizontal sub-surface flow (HSSF) and a CW with vertical sub-surface flow (VSSF), (Figure 1).

Various hybrids of these basic four types may also be produced. The sedimentation ponds at watercress farms are a FWS type of wetland, where the main processes of P removal are

⁴ Privately commissioned report, CEH, 2007.

sorption onto the antecedent substrate material, accretion of new bed sediments (both inorganic and organic P inputs) derived from bed cleaning and biological uptake and storage in the biomass.

Phosphorus accumulates in the substrates (and plants) of CWs until they are saturated, which is typically 2-5 years (Kadlec and Knight, 1996). Once saturated, they become net exporters of P, especially in those systems where reducing conditions occur during summer (Richardson, 1985; Reddy *et al.*, 1999). The continued capacity of the CW to remove P is therefore finite, especially as any new bed sediments retained by the CW during spring (period of bed cleaning) are already rich in P (see previous HDC report) and the accumulated sediment requires regular removal. The degree of P retention depends very much on the type of CW and the substrate material used, but is generally in the range 40-60% for CWs which use natural soil substrates (Vymazal, 2007). Clearly higher P removal efficiencies occur in HSSF and VSSF types since there is a much greater contact surface area for adsorption of P to occur.

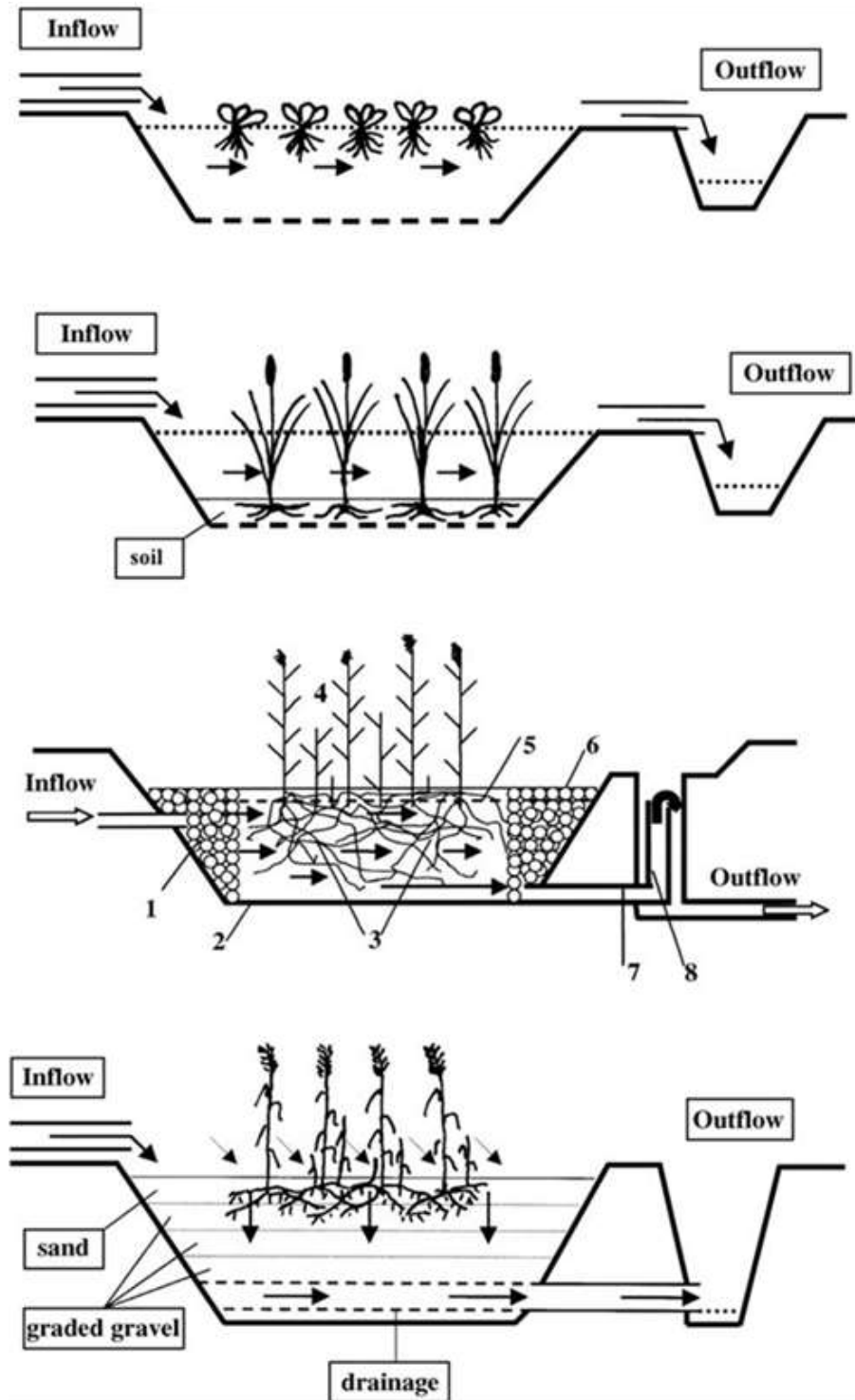


Fig 1. Constructed wetlands (CW) for wastewater treatment (from top to bottom): CW with free-floating plants (FFP), CW with free water surface and emergent macrophytes (FWS), CW with horizontal sub-surface flow (HSSF, HF), CW with vertical sub-surface flow (VSSF, VF) (Vymazal, 2007).

Approaches to maximise P removal within CWs to produce clean effluent include (a) incorporating a P-binding material as the substrate in the initial design, especially the HSSF and VSSF type of CW; (b) dosing of the CW or the inflow to the CW with a P-binding chemical that will remove P from the watercolumn and inhibit the release of P from bottom sediments, more suited to a FWS type of CW, (c) including a fixed bed filter unit containing a P-binding material to remove P in the influent water before entering the CW, or remove P from the CW effluent before discharge to the receiving stream, and (d) manipulating the type of biomass present in the CW. The latter is generally considered to have limited potential for removing P (although clearly effective at reducing BOD) because biological uptake is only short-term. Combinations of these approaches using P-binding materials may also be used (Park, 2009).

A large range of P-binding materials with variable suitability for enhanced P removal in CW designs have been evaluated and these are described below. Those in solid form have been termed 'adsorbents' and defined by Douglas *et al.* (2004) as:

'Materials of variable quality and source, often highly heterogeneous, which may be simultaneously involved in formation of insoluble precipitates and co-precipitation as well as adsorption, via surface complexation and/or interstitial ligand exchange. In addition the physic-chemical processes which produce P removal are often poorly characterized, and often do not display uptake and release equilibria that would be characteristic of true adsorption'.

The mechanisms of P removal are therefore predominantly adsorption, co-precipitation and precipitation and the main cations responsible are Fe, Al and Ca. Adsorption onto Fe and Al surfaces occurs due to the formation of inner and outer sphere complexes through ligand exchange, whereas adsorption onto Ca occurs directly at the surface through coulombic forces of attraction (Figure 2). At higher P concentrations, surface precipitates of P tend to occur at the surface giving an apparent increase in the materials P sorption capacity (Drizo *et al.*, 1999; Genz *et al.*, 2004). The surface charge on Fe and Al surfaces is highly pH dependent and at low pH, the amount of positive charge increases, thereby increasing the P sorption capacity. For example, Zeng *et al.* (2004) found that that the P adsorption capacity of iron oxide tailings was reduced by half (a difference of 5 mg P/g) at high (pH 9.5) compared to low pH (pH 3.2). When Al and Fe salts are added to water as liquid chemicals, they form flocs (sometimes called sweep flocs) which gradually settle through the water column to form bottom sediment. During transport they remove DP through adsorption and PP through entrainment.

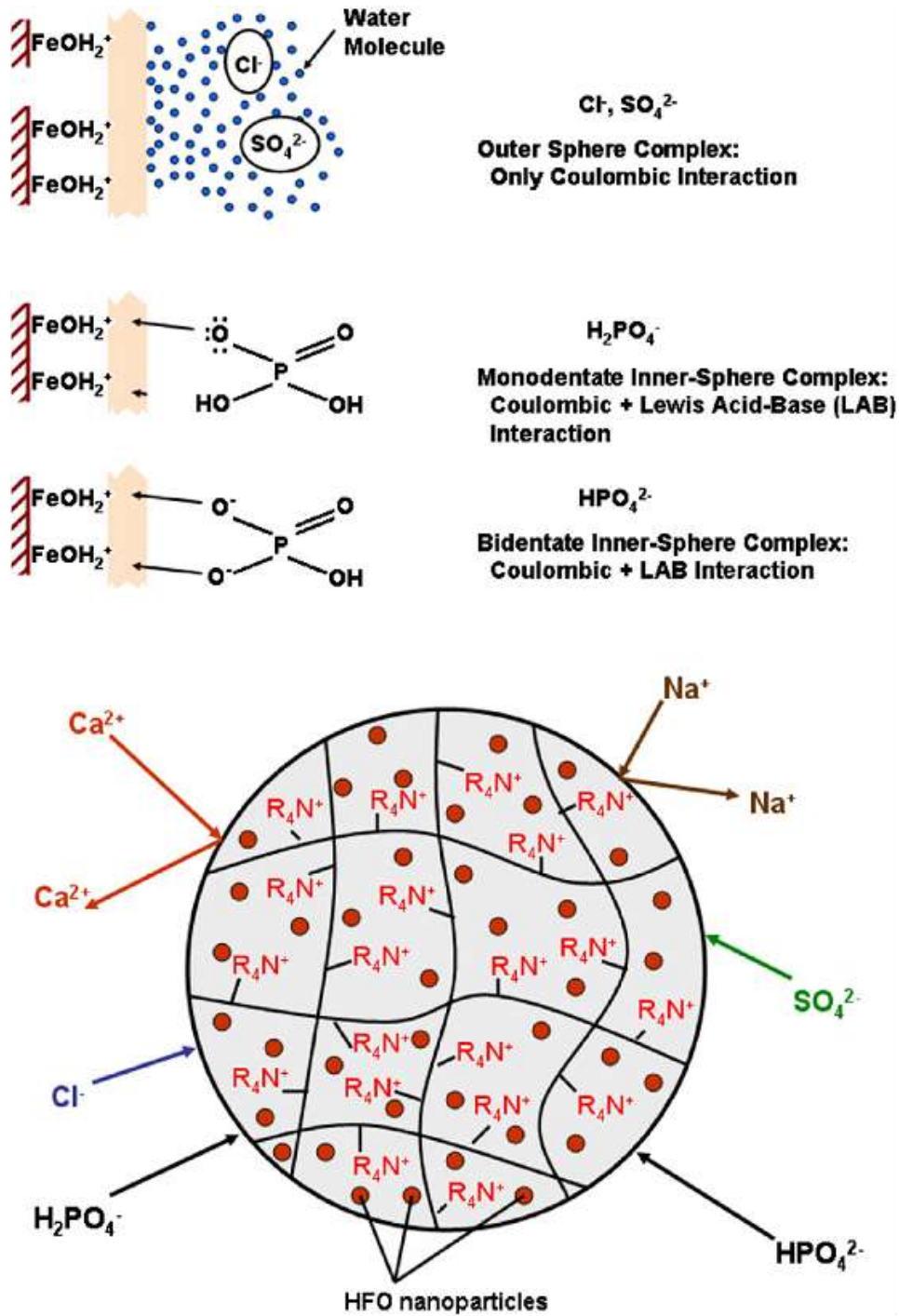


Fig 2. (a) Schematic illustrating the formation of mono- and bidentate inner sphere complexes between phosphate and HFO surface groups; competing sulfate and chloride anions form only outer sphere complexes and (b) Representation of an HAIX resin with quaternary ammonium functional groups (R₄N⁺) irreversibly dispersed with HFO nanoparticles.

Effectiveness of P-binding materials

Various studies have investigated the effectiveness of potential P binding materials, either singly or in combination, to remove DP and PP from influent water. These studies have been conducted in the laboratory, in indoor and outdoor mesocosms and/or in real-life field-scale installations. The purpose of these studies has varied from:

- an initial screening of the P sorption properties of potential materials to determine their maximum capacity (P sorption capacity, PSC) to retain P over different periods (e.g. Drizo *et al.*, 1997; Sakadevan and Bavor, 1998; Seo *et al.*, 2005; Xu *et al.*, 2006; Leader *et al.*, 2008). The methods used to characterise P-binding materials differ widely and it is generally accepted that such laboratory studies can only provide an initial indication of potentially suitable materials. For a discussion of this issue, the reasons and the ensuing problems of comparing and normalising laboratory data, see Johansson Westholm (2006).
- an assessment of the potential maximum efficiency of P removal by different materials by measuring the reduction in effluent P concentrations after passing influent vertically through columns, or horizontally through tanks, containing the material, for different periods of time and at different flow rates (hydraulic loading). Examples of studies adopting this approach are given in Renman (2008). In many cases, the effect of P-binding materials on the chemical composition of the outflow water other than P (i.e. pH, trace metals) has not been investigated, yet these are important determinands affecting the health of aquatic ecosystems.
- quantifying the effectiveness of actual constructed wetlands designed to treat wastewaters from various sources (Arias *et al.*, 2003; Shilton *et al.*, 2005).

The actual effectiveness of P-binding materials in full scale installations is often different to that obtained in laboratory or column/tank studies because the efficiency of P removal is influenced by a number of factors. Experiments often assume complete interaction between influent and substrate and over short residence times which is not always obtained at field scale, depending on CW type (Figure 1). The ionic strength and alkalinity of wetland water may be different to that used in the laboratory. The presence of organic matter in wetlands can block P sorption sites and biological activity can cause diurnal changes in pH and redox conditions which in turn affect P solubility and rates of precipitation/dissolution. For systems which employ pre or post filters, increased turbidity or precipitation of P onto the surfaces of the filter media can cause clogging. Drizo (2002) found that this clogging actually increased P retention because the hydraulic loading rate was increased, but in general clogging reduces the longevity of the filter media.

Mixtures of materials are more effective than their single materials on their own (Cui *et al.*, 2008). Many P-binding materials also reduce ammonium N.

Controlling factors

It is clear that the effectiveness of different P-binding materials in removing P will vary according to the type of material being tested/used, the degree of P reduction required (starting and desired final concentrations) and the general environmental conditions; including the chemical composition of the water (pH, ionic strength, turbidity), susceptibility to changes in reducing/oxidising conditions (redox), hydraulic loading rates and residence time in the CW.

Type of P-binding material

Key parameters of the P-binding material are its chemical composition and particle size. The chemical composition will dictate the type of P sorption process operating and type of precipitate; whether Fe, Al, Ca, or Mg or other binding cation is present. Particle size influences the surface area of the material available for P sorption; and in general the smaller the particle size the greater the P sorption capacity (Arias *et al.*, 2003). Filter media require a high degree of porosity so that the influent can pass through the media without clogging (Yamada *et al.*, 1986).

Target P concentrations in the effluent

Some studies have shown that the effectiveness of P removal is reduced at low initial P concentrations because generally high concentrations of DP are required for precipitation to occur (Brooks *et al.*, 2000; Hedstrom, 2006). For example, Brooks *et al.* (2000) found that maximum P removal efficiency (over 90%) by wollastonite was achieved only when the initial P concentration was over ca. 3 mg/l. Other studies have shown that substrates with a limited PSC work better at low concentrations, whilst materials which can adsorb large amounts of P and do not have to rely on surface precipitation to remove P, work well at both low and high P concentrations (Leader *et al.*, 2008). When initial P concentrations are high (20-40 mg/l), the P reduction achieved by some substrates is still not sufficiently low to meet water quality targets, even though a large proportion of the P has been removed. Target concentrations for DP in rivers in the UK have recently been revised (see Mainstone *et al.*, 2008).

Environmental conditions

The chemical composition of the water (pH, ionic strength, alkalinity) has a large impact on P sorption and precipitation processes because of their effects on P binding strength, the presence of competing anions (carbonate (CO₃), hydroxide (OH) and sulphate (SO₄) and P solubility. The order of P binding strength is Fe>Al>Mg>Ca such that P is bound very strongly and rapidly (in minutes) to Fe but the P bound to Ca is weak and takes much longer (hours) to form precipitates. Seeding (the introduction of a previously precipitated P compound) greatly reduces this reaction time by providing a focus for crystallisation (Brooks *et al.*, 2000; Jenkins *et al.*, 1971).

The optimum pH range for precipitation of Fe, Al and Ca-P compounds in water is pH 4.5-5.5, pH 5.0-6.5 and pH 7-9.5, respectively. Outside of these ranges, colloidal amorphous phases of intermediary compounds exist which tend to cause increased turbidity and poor P removal (Jenkins *et al.*, 1971). The greater the ionic strength, the higher the concentration of competing cations and anions and the less the opportunity there is for P sorption, at least initially. The affinity of sorbing surfaces for anions is usually CO₃>PO₄>OH>SO₄. Some P-binding materials (e.g. zeolites) adsorb both cations and anions depending on pH. Alkalinity (water hardness) greatly influences the concentrations of the Ca cation and the carbonate anion, both of which dictate the precipitation of Ca-P compounds (Song *et al.*, 2002).

Susceptibility to changing redox conditions also influences P removal by those substrates containing Fe because the development of anoxia in the bed sediments of CWs causes a shift in the ionic species of Fe present (from Fe³⁺ to Fe²⁺) which leads to a release of P into the overlying watercolumn (Reddy *et al.*, 1999). Anoxia develops due to the consumption of oxygen by microorganisms that breakdown organic matter (OM) in the wetland. It was found that the rate of water flow through shallow CWs (<1 m) was sufficient to prevent anoxia developing but deeper ponds/wetlands which receive inputs of OM are more susceptible. The release of P only generally occurs over the time period the system is anoxic and the released P becomes adsorbed again when oxic conditions return.

However, the period of anoxia may be sufficient to increase the outflow DP concentrations (Mitsch *et al.*, 1995). It is not known to what extent the sedimentation ponds at watercress farms, which tend to be 3 m deep, develop anoxia during summer. Flow rates through the ponds are high and therefore the ponds may remain aerated.

Residence time (time over which the water is in contact with the P-binding material) is also an important factor affecting P sorption and precipitation. Clearly the more time there is direct contact between influent and substrate the greater will be the P removal. In field-scale systems, the degree of P removal achievable will be largely dictated by the hydraulic

loading rates, especially for those CWs incorporating horizontal (HSSF) or vertical (VSSF) flows or using pre- or post-filter media. For example, Brooks *et al.* (2000) found that wollastonite needed 40 hrs of P contact to remove 96% of the P from a concentrated wastewater.

Availability of P-binding materials

Leader *et al.* (2008) suggested that P-binding materials should be 'free, non-toxic, industrial by-products, generated locally, widely available and potentially useful as soil amendments once saturated with P. Clearly the choice of material will depend on cost, availability, safety, sustainability, and potential for re-use.

Natural materials and their derivatives

Parent rocks (limestones, shales), soils (topsoils or subsoils) and soil constituents (sands, clays, minerals) have an inherent P adsorption capacity which makes them suitable as potential P-binding materials. They have most often been used as a P-binding substrate for use in CWs, where the P sorption capacity of the bottom substrate is considered to be the most important factor affecting their P retention efficiency (Cui *et al.*, 2008). The P retention capacity of natural P-binding materials is heavily influenced by their physical state (particle size and hence surface area) and chemical composition, both affecting overall exchange capacity and specificity for P. Some clays and minerals have a very high cation/anion exchange capacity but are not selective for P, and which ion is adsorbed is heavily pH dependent. Unamended natural materials have the advantage that they are chemically safe to use and re-use but they characteristically have very variable composition depending on source and may be difficult or hazardous to handle (dusty) when finely ground.

In many cases, local availability is a key factor in the choice of suitable materials; for example oyster shells from Korea (Seo *et al.*, 2005), volcanic materials from New Zealand (Ballantine and Tanner, 2010) and apoka from Scandinavia and Russia (Renman, 2008).

Parent rock materials

Suitable parent rock materials for P adsorption include sedimentary limestones (high pH, Ca/Mg rich) and shales (low pH, Fe rich). (Drizo *et al.*, 1999) compared a number of different P substrates in the laboratory for potential use in constructed wetlands and found shale to have both a high P binding energy (i.e. strongly bound) and a high P sorption capacity (PSC), (ca. 0.7 mg P/g). At high P concentrations (20-40 mg/l), precipitates of Ca-P were observed on the surface of shale plate-like particles. Calcitic limestone (composed of calcium and magnesium carbonates) had a similarly high PSC, but the P was bound

much less strongly. Guan *et al.* (2009) found a PSC of 2 mg P/g in the limestone they used. Removal of P by calcium carbonate is considered to be due to both initial surface adsorption of P and subsequent incorporation into the crystal structure, or precipitation of Ca-P compounds on the surface of particles, depending on the concentration of P present. However, addition of crushed limestone has had variable effects in field situations; Comeau *et al.* (2001) recorded 92% removal of P from trout farm effluent (mg/l), while elsewhere only 18% P removal was recorded when added to a pond system. Dolomitic limestones or dolomites (largely magnesium carbonates) have also been tested but tend to have lower PSC values of 0.2-0.3 mg P/g (Pant *et al.*, 2001; Prochaska and Zoubilis, 2006). The presence of Mg is known to interfere with CaCO₃-P co-precipitation (Diaz *et al.*, 1994) but tends to form a more stable and therefore longer-lasting precipitate. Opoka (calcium rich silicate rock) has variable Ca:Si ratios which make it potentially useful as a P adsorbent (Renman, 2008).

Some rock minerals have also been tested; for example serpentinite (magnesium rich silicate mineral) and wollastonite (calcium-rich silicate mineral with Fe). Wollastonite has a high PSC (0.85 mg P/g) but is not very efficient at low P concentrations (<4 mg/l) and needs a long retention time (40 hrs), (Hedstrom, 2006; Brooks *et al.*, 2000). Drizo *et al.* (2006) found that the efficiency of P removal by serpentinite was very high (90-100%) for only a month, after which it fell drastically.

Soils and soil constituents

Soils and soil constituents (sands, clays, alumino-silicate minerals) have an innate affinity for P due to the wide range in P adsorbing surfaces present including clay surfaces, Fe/Al oxides and hydroxides surface coatings, CaCO₃ and organic matter (OM). Soils are however expensive to remove and transport. Sakadevan and Bavor (1998) measured PSC values of up to 5 mg P/g in soil substrates collected from constructed wetlands. Liikanen *et al.* (2004) found subsoil was a very effective substrate for removing P in a constructed wetland on previously arable land.

Sands have a naturally low particle size coefficient (PSC), but when naturally or artificially enriched in Ca or Fe/Al, the P retention capacity is increased (0.3-0.4 mg P/g) sufficiently to aid removal of P in domestic effluents; for example for treating septic tank effluent in Scandinavia (Hylander *et al.*, 2006). Sands are inherently attractive as filters because they can have a good infiltration capacity, although when P-retentive sands are used to treat high-P effluents, precipitates of Ca-P or Fe-P form on the surface of sand particles and start to clog the filter (Arias *et al.*, 2001). Jenssen and Krogstad (1988) suggested this clogging might actually enhance P removal. Quartz sand, masonry and concrete sands have not

been shown to be effective (Leader *et al.*, 2008) but calcareous shell sands successfully removed a proportion of the P in a constructed wetland to treat septic tank effluent (Søvik and Kløve, 2005).

Clays have variable but naturally high ion exchange capacities and adsorb both cations and anions depending on their swelling properties and degree of pH-dependent surface charge. They have low hydraulic conductivity but have been used to form the base of constructed wetlands. Example of clay materials that have been tested include bentonite and allophone (e.g. Yuan and Wu, 2007). Hanly *et al.* (2008) tested a volcanic ash material (tephra) in New Zealand and found it to be very effective (96% retention) at low P influent concentrations (0.25 mg/l), but only 51% when treating an effluent with 12 mg P/l.

Zeolites are a group of aluminosilicates naturally found in soils that not only have very high ion exchange capacities but are also porous. New Zealand experience with zeolites is summarized by Ballantine and Tanner (2010); they appear variably effective (30-90%) depending on particle size. Sakadevan and Bavor (1998) measured a PSC of 2 g P/g for one particular zeolite as compared to up to 5 g P/g for topsoils and subsoils.

Other

Various other natural materials including maerl; calcified seaweed, (Gray *et al.*, 2000); peat (Renman, 2008); turf (Cui *et al.*, 2008); tree bark (Bolan *et al.*, 2004) and woodchips have been tested and used to remove P, often on the basis that they are locally available. However their composition can be very variable and concerns over rapid depletion and scarcity of non-renewable resources suggest most of these materials are best not widely used. Bark and woodchip materials are more abundant and are now used to control emissions of N and P from excreta deposited by livestock.

Industrial by-products

A number of industries produce by-products as a result of their manufacturing processes which can potentially be re-used as P binding materials, usually after some physical and/or chemical modification of their state/composition. There are numerous examples of such by-products including: slag, industrial Fe/Al oxides/hydroxides, bauxite (red mud), fly ash, wastewater treatment residuals (WTRs) and gypsum. The advantage of these products is that they are available in large quantities and therefore relatively cheap. Their composition is variable depending on the particular industrial process operating and all three of the main P-binding cations (Fe, Al and Ca) are usually present. The effectiveness of these materials and the main P-removal process will depend on which of the three cations is in most abundance in the by-product. A number of workers have shown that the presence of more

than one cation increases the P removal efficiency beyond that calculated for the sum of the individual cations (Sibrell *et al.*, 2009).

(a) Slag

Slag is a by-product of the iron and steel industries and contains variably high concentrations of Ca, Si and Al which are capable of dealing with high influent P concentrations. However, different processes of manufacture produce different types of slag including basic slag from an oxygen steel furnace, electric arc slag produced from scrap metal, blast furnace and melter slag from steel produced from iron sands. These slags have been widely tested in both laboratory (Oguz, 2004; Kostura *et al.*, 2005) and field studies (Drizo *et al.*, 2006; Shilton *et al.*, 2006; McDowell *et al.*, 2008). Calcium is usually present as CaO and the pH is naturally (pH10), (Johansson, 1999). Adsorption of DP is dependant on the amount of Ca present at the surface and subsequent surface precipitation of Ca-P is thought to occur as hydroxyapatite (Yamada *et al.*, 1986; Johansson and Gustafsson, 2000; Kostura *et al.*, 2005). Kostura *et al.* (2005) report PSC values in the range 0.6-44 mg/g. Shilton *et al.* (2006) found 77% P removal efficiency in the first 5 years. Drizo *et al.* (2006, 2008), found electric arc furnace slag to be more effective (75-90% removal) than blast furnace or iron melter slag when treating dairy effluents.

Johansson (1999) measured P removal of >95% for crystalline and amorphous blast furnace slags treating pure solutions of 10 mg/l but the pH of the effluent increased from pH7 up to pH11, although effluent pH did decline during the 2 month column experiment.

However, slags contain heavy metals in varying proportions and their suitability for waterways is in doubt (McDowell *et al.*, 2008).

(b) Industrial Fe/Al oxides

Various types of industrial by-products are concentrated in Fe and/or Al. Materials containing a high proportion of Fe oxides exhibit rapid P adsorption with low reversibility; for example Zeng *et al.* (2004) measured 12-14% de-sorbability of P in water removed by dried iron oxide tailings from the mineral industry with 30% Fe oxides.

Iron ochre is an alkaline by-product of the acid mine waste industry which after drying and pelletising becomes a potential P-binding material due to its high content of Fe oxides (Heal *et al.*, 2005; Dobbie *et al.*, 2009). It is abundantly available in the UK, but the red and dusty nature of the material making it unpleasant to handle. Laboratory studies have shown the material has a high PSC (ca. 20 mg P/g). Dobbie *et al.* (2009) tested its use as a filter medium in two full-scale wastewater systems but flow rates had to be reduced considerably

to enable P removal efficiencies of over 50%. Maximum retention of ca. 80% was observed initially for P influent concentrations of up to 6 mg/l but this declined rapidly as the filter clogged up with biofilm and organic matter. It appears that large quantities of the material are needed to ensure sufficient residence time for effective P removal and therefore is perhaps best suited to small scale situations where flow rates are low.

Sibrell *et al.* (2009) dried neutralized acid mine drainage spoil to form 'Ferroxysorb' containing a mixture of Fe and Al hydroxides and PSC values ranging from 2-24 mg P/g. They measured P removal efficiencies of 60-90% in 5 minutes for influent concentrations of 0.13 mg/l, but the column experiments were conducted with clean water. Metal contamination of the effluent after treatment with acid mine spoil waste by-products was not detected in the above experiments (Dobbie *et al.*, 2009; Sibrell *et al.*, 2009).

Genz *et al.* (2004) similarly found that granulated ferric hydroxide (GFH) and activated aluminium oxide (AA) were effective commercial adsorbents for effluents low in P and SS concentrations. GFH showed a higher maximum capacity for phosphate (8-12 mg P/g) and a higher affinity at low P concentrations compared with AA (5-8 mg P/g), but both reduced effluent P concentrations from 300 µg/l down to 50 µg/l. Competition by inorganic ions (CO₃, SO₄ and DOM) was negligible for both adsorbents at pH 8.2.

Blaney *et al.* (2007) describe the dispersion of Fe oxides within an anion exchange resin; a process which increases both the durability of the material during operation and the specificity for P against competing cations. This combined material (called a hybrid anion exchanger, HAIX) removed >90% of P at influent concentrations of 0.3 mg/l and pH 7.5. This technology is now commercially available under the tradename Solmetex™, but it is very expensive. As with other adsorbents, the P can be recovered from the material when P is saturated by NaOH.

(c) Bauxite residues (red mud and Bauxsol™)

The by-products from the Bauxite mining industry have a high Fe/Al content that makes them potentially useful as a P adsorbent. The fresh residue is highly caustic but when neutralised by addition of gypsum (red mud) or seawater (Bauxsol™) and converted to granular form, the materials are safe to handle but still have a high pH and Na content. To some extent the pH and fineness of the material can be modified to suit particular conditions. These two by-product materials have been widely tested in a range of media and environmental conditions (Lopez *et al.*, 1998; Li *et al.*, 2006). They are very effective at removing P from wastewater streams but may increase the pH and alkalinity of the effluent. The high P removal efficiency of Bauxsol is probably related to the presence of hydrotalcites formed during the neutralization process. Hydrotalcites are layered double hydroxides of

Mg, Fe and Al which have an internal crystal structure that carries considerable positive charge and PSC values of up to 25-30 mg/g (Douglas *et al.*, 2004). Hydrotalcites are not P selective and will adsorb the carbonate ion CO_3 in preference to PO_4 .

(d) Fly ash

Fly ashes are the Al/Fe-rich by-products produced from the combustion of coal in thermal power plants. However, their pH can be very high (e.g. pH >12) and, as with slags, they may contain significant amounts of potentially toxic trace elements (McDowell *et al.*, 2008).

(e) Waste water treatment residuals (WTRs)

WTRs are the residues left after treating water supplies with Al/Fe/Ca salts to remove turbidity and colour and make them potable. In the UK, these residuals are often referred to as 'clean water sludges' (30% moisture content) and currently largely disposed to landfill because they are classed as a 'waste'. In the USA, their potential use in reducing P losses during manure application and in land runoff is increasingly being recognised (Elliot *et al.*, 2005; Agyin-Birkorang *et al.*, 2007; Leader *et al.*, 2008). They are more usually richer in Al than Fe or Ca. Leader *et al.* (2008) report PSC values of close to 1 g P/g for Fe and Ca-WTRs. Zhao *et al.* (2008) found that addition of Al-WTR to a reed-bed system increased P retention by 42%. According to Ballantine and Tanner (2010), there are concerns over Al toxicity build-up in soils from repeated application and over the risk of transfer of faecal pathogens (*Cryptosporidium* and *Giardia* sp.) present in the water. However, these risks have not been investigated.

(f) Gypsum

Gypsum (calcium sulphate) is well known for its potential to absorb phosphate and studies using the material in by-product form have been undertaken to ascertain its effect as a soil amendment on soils which have had high P levels, leading to eutrophication in nearby water bodies. In a study by Callahan *et al.* (2002) water-extractable phosphate was reduced when gypsum was incubated with 3 acidic and 1 neutral soil, with little difference in effectiveness between 21 and 120 days, indicating the material was quick-acting and stable in effect. This study did not however examine efficacy under alkaline conditions.

(g) Oyster shells

Seashells from the shellfish industry have a high Ca content making them suitable as P adsorbents. Park and Polprasert (2008) report that oyster shells have a PSC of ca. 25 mg P/g which is very much greater than many natural materials and found >95% P removal

efficiency over one year. This contradicts with data from Arias *et al.* (2003) who found variably low P retention suggesting they may have very variable P composition.

Processed (man-made) materials

Processed materials maybe defined as natural materials that have been modified, or chemically synthesized, to enhance their P removal capacity (Johansson Westholm, 2006). Some examples of trademark products on the market are given below:

(a) Alum (Aluminium sulphate)

Alum ($\text{Al}_2(\text{SO}_4)_3$) has been widely used to remove P from the watercolumn in lake systems suffering from eutrophication. The use of Alum provides a means of reducing in-lake TP concentrations to very low levels ($< 10 \mu\text{g/l}$) that will inhibit the growth of algae. Aluminium is not redox sensitive and forms stable precipitates over the pH range 5-10 making it a suitable material to remove P at low concentrations and help prevent re-release of DP from bottom sediments (Welch and Cooke, 1999; Paul *et al.*, 2008). Pilgrim and Brezonik (2005a) describe experiments testing Alum application to the inflows of lakes rather than treating the whole lake area itself. When Alum is added to water, it forms flocs of $\text{Al}(\text{OH})_3$ which bind with DP and trap PP as they slowly settle to the bottom of the lake. Application is either in liquid form (large areas) or applied dry (small areas).

For whole lake treatments, Alum reduces TP concentrations by over 80% for up to 8 years provided external P loading rates are not high (Welch and Cooke, 1999). Pilgrim and Brezonik (2005a) found Alum applied to lake inflow water reduced TP concentrations (up to 0.5 mg/l) by 60-85% provided there was sufficient turbulence to promote floc formation. They recommend applications of ca. 6 mg Al/l , a mixing distance of between 30 and 150 m and a 6 hr retention time in a pond for the flocs to settle. Lower P applications (1 mg Al/l) were effective for removing DP. Alum is also widely used within the poultry industry to reduce ammonia losses from litter in houses and shown to very effective in reducing the water solubility of P in poultry manure on application to soils and subsequent field runoff (Moore and Edwards, 2007). Smith *et al.* (2001) found alum to be effective in reducing P concentrations in field runoff (84% lower) after application of pig slurry.

The main environmental concern over using Alum is the toxicity of Al to aquatic biota and the link between Al and dementia in humans. Aluminium is only soluble at extremes of pH (<5 and >10) and various studies suggest that only when applied to softwater lakes is there a risk of toxicity. In hardwater lakes, the alkalinity is sufficient to buffer any declines in pH; a minimum pH of 6.0 is suggested by Pilgrim and Brezonik (2005b). Loss of benthic invertebrates may occur in streams and settlement ponds due to the smothering effects of

the Al-flocs (Barbiero *et al.*, 1988). Toxicity is inactivated when Al becomes bound to mineral and organic matter and the available P in many agricultural soils (pH 5-8) is regulated by Al-oxide surfaces (Hartikainen *et al.*, 2010).

(b) Phoslock™

Phoslock™ is bentonite clay coated with the rare earth Lanthanum (La). The combination of the high exchange capacity of the clay and high specificity for P by the La has been shown to be highly effective at removing various forms of P (polyphosphates as well as ortho-P) from water over the wide pH range 6-10 (Douglas *et al.*, 2004). The PSC is typically over 10 mg P/g and the mixing with clay removes any risk of direct La toxicity to aquatic organisms. Over a range of applications, it is said not alter the basic chemical properties of the water (pH). The solubility product of the La-P precipitate (called rhabdophane) is also extremely low due to a high stoichiometric reaction rate (molar ratio of La:P is 1:1) and therefore extremely stable, being also resistant to microbial attack in bottom sediments. As such they have also been used as a sediment capping agent to prevent the release of sediment-bound P that occurs under reducing conditions in ponds and wetlands (Robb *et al.*, 2003). Further details of this material are given in Appendix 1. Yuan and Wu (2007) tested Phoslock™ and found it had a lower PSC than allophone (a non-crystalline mineral). Work by Ross *et al.* (2008) confirmed the stability of La-P in the environment, even under a wide range of pH or anoxic conditions. Ballantine and Tanner (2010) report some work suggesting there is a small release of La but details are not presented.

(c) Baraclear™

Baraclear™ is manufactured from a mixture of bentonite, alum and a buffering agent to prevent pH change. It is marketed as a material to prevent P release from bottom sediments and is suitable for small scale application.

(d) Polonite™

Polonite™ is manufactured from the cretaceous rock opoka found in Scandinavia and Russia. The product is formed by heating opoka and has a very high pH (11-12). As a consequence, although it was shown to be very effective at removing P from septic tank effluent containing 4 mg/l (>95% removal), it also increased the pH of the outflow water considerably from pH 8 to pH10, although this pH rise became less over the experimental period (Renman, 2008). However, pH monitoring did not prove to be a successful tool for assessing when the efficacy of Polonite was eroded (Renman and Renman, 2010).

(e) Materials coated with Fe/Al

Typical materials that have been tested include calcareous shell sands (Søvik and Kløve, 2005) and sands artificially coated in Fe/Al (Ayoub *et al.*, 2001, Arias *et al.*, 2006). Ayoub *et al.* (2001) measured over 90% P removal from relatively pure solutions containing <0.5 mg P/l when filtered through sand or olivine (a MgFe silicate mineral) coated with Fe and Al chloride. The final effluent concentration was ca. 50 µg/l. Lower P removal (70-80%) was achieved when the solution ionic strength was increased due to competition from other anions (SO₄). Industrial experience with high P concentration waters suggest that Fe-coated filters soon get clogged with precipitate, but for low concentration, sediment free water, these materials are effective.

(f) Modified or synthetic zeolites

Adding cations (Fe/Al/NH₄) to natural zeolites is a method of increasing their anion (i.e. P) exchange capacity (Jacobs and Forstner, 1999). Ballantine and Tanner (2010) provide details of New Zealand work which showed such materials were as effective as Baraclear™ and Phoslock™ with the best zeolite and Baraclear™ removing >90% of P from lake water. Interestingly much larger quantities of Phoslock™ were needed to produce the same P removal efficiency as the zeolite or Baraclear™.

(g) Expanded clay materials (Filtralite™, LECA™)

Expanded clay materials are widely used in Scandinavia to reduce P concentrations in the effluents discharging from small wastewater treatment plants and septic tanks. Expansion of the clay lattice structure is achieved by firing the granules at a very high temperature in a rotary kiln and results in a greater surface area for adsorption.

Filtralite™ is an expanded illite clay with a high Ca/Mg content and high pH. Experiments showed P removal efficiencies of 73-99% in laboratory and field studies, although this varied with pH. Arias *et al.* (2003) suggested that the most promising results for P removal (by binding or precipitation) were from media rich in Ca or Fe. They proposing wetlands constructed of artificial media or the establishment of an external P-binding filter.

Similarly LECA™ (lightweight expanded clay aggregate) is a highly porous, Ca/Mg rich expanded clay product which is pH neutral and amongst its uses are purification of waste- and drinking waters, as well as treatment of industrial wastewaters and for fish farms. Zhu *et al.* (2003) found that 50% of the total phosphate it absorbed was removed in the first 4-8 hours. Temperature did not substantially affect the absorption capability of the 0-2 mm grade material.

(h) Filtra-P™

Filtra-P™ is produced after heating a mixture of limestone, gypsum and Fe oxides and contain a significant proportion of CaO or Ca(OH)₂. Materials containing calcium oxide (CaO) rather than CaCO₃ are more reactive and therefore more P-retentive but tend to have a very high pH (Hylander *et al.*, 2006). As with Polonite, Renman (2008) found that Filtra-P was very effective at treating septic tank effluent but also raised the pH of the outflow significantly.

SWOT analysis

In prioritizing suitable substrate and filter materials for improving P retention from farm drainage wetlands in New Zealand, Ballantine and Tanner (2008) applied a scoring system (low, medium and high) to key desirable factors: effectiveness; availability, cost, and re-use potential. Natural materials scored highly both as substrate and filter-type because they are locally available, safe to use and have relatively low cost. Aluminium-based products, fly ash and steel slags also scored reasonably well.

Summary

A large range of P-binding materials, either singly or in combination, are available to remove P from natural and waste waters. Their suitability, practicality and cost-effectiveness is largely site specific and depends on a number of environmental factors. Choice of material is likely to be an iterative process requiring some preliminary evaluation in the laboratory and/or in mesocosm studies before full field-scale implementation (Douglas *et al.*, 2004). This is especially important where materials contain potentially toxic elements and/or where discharge waters enter ecologically sensitive waters.

Waters discharging from watercress beds generally have high pH and alkalinity, low but variable levels of DP (up to mg/l on present evidence) and large discharge volumes (1-20 million L/day). The presence of sedimentation ponds greatly reduces discharges of sediment during bed clearing out and also helps to reduce DP and PP levels entering streams. Diurnal changes in pond pH due to biological respiration and photosynthesis will also help to remove P from the system due to co-precipitation with calcite. The residence times of the ponds is usually limited and the minimum target TRP concentration is 0.05 mg/l. These site features enable the following options to be considered:

1. Chemical dosing of the sedimentation ponds, or the inlet to the sedimentation ponds, during crop growth cycles when fertilisers are regularly applied. Potential P-binding materials for dosing include alum, Baraclear and Phoslock. The literature suggests

that these materials will remove P effectively at pH 7.5-8.0 and will not increase the pH of the effluent water. At this ambient pH, concentrations of Al or La should not be increased but this requires testing to ensure there is no risk of any adverse effects on the aquatic community.

2. Filtering out P from the pond discharge waters using a porous fixed bed filter, or a combination of filters, containing a P binding material in granular or pelletized form. Potential P-binding materials that could be used in a filter bed include those containing Fe, Al and/or Ca. Materials containing high proportions of Ca (especially as CaO or Ca(OH)₂) have very high pH and are likely to increase the pH of the effluent, and as such are less suitable (e.g. Polonite, Filtralite, LECO, Bauxsol). In some cases, (e.g. Bauxsol), the pH of the industrial by-product can be altered so that this pH rise is largely absent. A variety of industrial by-product materials containing mixtures of Fe/Al oxides and Ca/Mg have been shown to be very effective without raising pH of the effluent (e.g. industrial Fe/Al oxides and tailings). The critical factor influencing P removal at the flow rates operating within watercress beds is the residence time.
3. A third option involves altering the design of the sedimentation ponds such that they become either a horizontal, or vertical, constructed wetland where the inflow water is directed through a bed containing a suitable P-binding substrate. A range of natural and industrial by-products have been successfully used to remove P in these two types of constructed wetland but further investigation as to the required scale would be needed for the quantities and water flow rates encountered in many watercress farms. In addition, site limitations may mean that there is simply not space for this type of installation.

Environmental context

Chalk streams

Chalk streams are highly-valued ecosystems which have developed unique but fragile food webs based on a base rich but P-limited nutrient supply. As such they are highly sensitive to inputs resulting from human activity. They have a naturally wide biodiversity, including vulnerable species such as water crowfoot (*Ranunculus* spp.), Atlantic salmon (*Salmo salar*), Bullhead (*Ictalurus*), Sea Lamprey (*Petromyzon*), the Desmoulin's whorl snail (*Vertigo moulinsiana*), white-clawed crayfish (*Austropotamobius pallipes*) and southern damselfly (*Coenagrion mercuriale*), (Berrie, 1992; Wheeldon, 2003; The Vitacress

Conservation Trust, 2008). In recent years, chalk streams have been variably suffering from siltation, eutrophication and general 'chalk stream malaise' which has upset the natural balance of aquatic ecology, with a loss of key aquatic plants and declines in salmonid and coarse fish species and invertebrates (Acornley and Sear, 1999; Environment Agency, 2002). A number of potential contributory causes have been identified including point source effluent discharges, diffuse inputs from agriculture (phosphates and pesticides) in the headwaters, water abstraction and riparian (adjacent) land use. Influx of P leads to the symptoms of eutrophication, including growth of benthic algae (those living at the bottom/sediment layers of the stream), reduced diversity of invertebrates, loss of submerged aquatic plants and proliferation of undesirable weeds (Hilton *et al.*, 2006).

Under the EU Water Framework Directive (WFD) and Habitats Directive (HD), targets of dissolved P to achieve good ecological status in chalk streams have been set at a low level: 40-60 µg/l (Mainstone *et al.*, 2008). Their sensitivity and vulnerability to the effects of human activity strongly suggests that any P stripping technology applied to the outflow discharge from watercress farms must not increase the concentrations of other potentially harmful substances.

Chalk stream chemistry

Watercress production in southern England relies on clean groundwater extracted from underlying chalk aquifers. This groundwater has a fairly consistent chemical signature: it has a naturally alkaline pH (pH 7.8) and high background concentrations of Ca (ca. 120 mg/l), reflecting the calcareous nature of the chalk parent material. Concentrations of nitrate N (NO₃-N) also tend to be high (e.g. 6 mg/l at Maxwells Farm), reflecting historically high usage of N fertilisers on soils in chalk catchment areas. Streams within chalk catchments have a similar chemical signature due to the large contribution that groundwaters make to river flow during the year (Jarvie *et al.*, 2006). For example the baseflow index (proportion of flow contributed by groundwater) for the River Test in Hampshire is 0.95 (National Environment Research Council, 1998).

Whilst extracted groundwater might have a background dissolved P concentration of only 20-25 µg/l, draining streams will have elevated P levels depending on the amounts of 'man-made' inputs (domestic wastewater, industry and agriculture) and the extent to which these inputs of P are naturally retained within stream and river networks. The natural physical, chemical and biological processes of P retention operating within flowing and standing waters (including wetlands) have been regularly reviewed (Reddy *et al.*, 1999; Withers and Jarvie, 2009) and include:

- Uptake by aquatic flora and fauna (aquatic or marginal plants, organisms living attached to underwater surfaces, microorganisms and succession food webs)
- Sorption and exchange between bottom sediments and the overlying watercolumn⁵
- Chemical precipitation and dissolution within the watercolumn
- Sedimentation to, and re-suspension of, bottom sediments during storm events

Of particular relevance to chalk streams is the co-precipitation of P with calcium carbonate (calcite) within the watercolumn, when pH and Ca concentrations are high (Neal *et al.*, 2002). For example, Diaz *et al.* (1994) found that dissolved P was rapidly precipitated from the watercolumn when pH exceeded 8.0 and Ca concentrations exceeded 100 mg/l. This apparent 'self-cleansing' mechanism occurs particularly at low P concentrations and adjacent algal biofilms (Hartley *et al.*, 1997). The mechanism of P removal is considered to be initial adsorption of P onto calcite crystals followed by formation of Ca-P compounds at the calcite surface. At higher P concentrations, calcite crystal formation is inhibited; precipitation is more rapid and the precipitate more stable (Jenkins *et al.*, 1971). Higher stream temperatures will also accelerate precipitation. Diaz *et al.* (1994) found that at Ca. pH 9 and Ca of 100 mg/l, 90% of the precipitated P was released back into the watercolumn when the pH dropped to 7.

Fluctuations in streamwater pH during each 24 hour period due to biological activity therefore have a significant impact on the concentration of dissolved P in chalkland streams and linked constructed wetlands. During the day, photosynthetic activity will reduce the partial pressure of carbon dioxide (CO₂) in the watercolumn and the pH will rise. At night, CO₂ saturation increases and stream pH will drop. Examples of this diurnal variation are given by Neal *et al.* (2002). In streams or wetlands which are more impacted by human activity and which therefore support a higher level of photosynthetic activity, the day/night variation might be expected to be wider. Interestingly Diaz *et al.* (1994) found that the presence of magnesium tended to render the precipitates formed at high pH more stable, with around 50% released back into the watercolumn when the pH dropped. At the high Ca levels recorded in groundwater at watercress farms on chalk, precipitation of P in the watercolumn will be more sensitive to both pH (photosynthetic activity) and temperature fluctuations.

⁵ Watercolumn = a conceptual column of water from the surface to the bottom sediments.

Aspects of watercress production

Flow rates

Watercress production relies on a continuous flow of groundwater through each bed. Flow rates of discharge waters from an entire watercress farm are therefore large but with much variation both between watercress growers and over the growing season. For example, at Maxwells Farm, flow rates of 5-6 million l/day have been measured in early June during active growth because of the transpiration draw of the crop whilst Bowes *et al.* (2006) recorded flows of 20 million l/day from a farm effluent channel in Dorset possibly because of higher background water flow rates, crop developmental stage or prevailing environmental conditions. Any mechanism to remove P from discharge outflows will therefore have to take into account these spatial and temporal variable rates of water flows on watercress farms.

Phosphorus retention

Single or multiple sedimentation ponds (essentially a constructed wetland since the ponds develop their own macrophyte and epiphyte populations) are widely installed to remove sediment and organic plant debris from the outflow channels of watercress farms discharging to rivers. The sedimentation ponds are typically 300-500 m² in area and 3 m deep, and the accumulated sediment/debris is removed at regular intervals (1 - 4 years) to ensure their optimum functioning. Limited data collected on one watercress holding by Bowes *et al.* (2006) found that 94% of inflow total phosphate was retained by a sedimentation pond, but that inflow concentrations of dissolved P (40-60 µg l⁻¹) were similar to those in the outflow. Clearly such ponds are effective at removing sediment-associated P but not dissolved P.

These ponds could therefore provide a focus for removal of dissolved P prior to discharge via the pond outfall, in addition to the P attached to any sediment retained by the pond. Since reducing conditions may develop at the bottom of these ponds (due to increased biological oxygen demand (BOD) of deposited organic debris), any P stored in bottom sediments may be re-released as dissolved P to the overlying water-column. This release of P is well documented in constructed wetlands (Reddy *et al.*, 1999), especially where the sediments are high in iron, which is redox sensitive. Sedimentation ponds also develop their own natural vegetation canopy which further adds to the organic debris in bottom sediments when dieback occurs during winter.

Water P concentrations

Inflow concentrations of soluble P to sedimentation ponds are likely to vary quite considerably both between farms and during the growing season. Previous continuous

monitoring at Maxwell's Farm showed that very high concentrations of dissolved P (up to 37 mg/l) can be discharged from individual watercress beds directly after fertilization, but levels will depend on the type of fertilizer applied and the length of time between sampling and fertiliser application. For example, Bowes *et al.* (2006) recorded a peak concentration of 0.7 mg/l after application of slow-release fertiliser, which is similar to that observed at Maxwells Farm after Fibrophos application (1.1 mg/l). Typically, soluble P concentrations reduce to background levels after 24 hrs. However, some limited analysis of the outflow from watercress farms by the EA suggest discharge concentrations to the river are considerably lower with maximum peak concentrations of only ca. 2-3 mg/l and more usually well below <0.5 mg/l. Averaged over the year, outflow concentrations at some locations may already meet the current EA target of 0.06 mg/l, so the focus of water quality contamination is particularly related to the few occasions when peak concentrations are greater than this threshold target.

Significant retention of dissolved P during transport (possibly by the sedimentation pond), and / or dilution by low-P groundwater, accounts for the large difference between outflow concentrations from individual beds and outflow from the farm as a whole. Watercress farms use various combinations of slow-release and highly water-soluble fertilisers and apply them in different combinations at different times of the year. The critical period for peak P concentrations in discharge water is likely to be during spring and early summer when fertiliser application rates and frequency of application are higher due to the increased crop demand during periods of rapid growth. Higher dissolved P concentrations also accompany bed harvesting and/or cleaning (Bowes *et al.*, 2006).

Phosphorus stripping materials: use in watercress settlement ponds

Selected phosphorus-removal product assessment

Three commercially available stripping materials, **Phoslock**, **ViroFilter** and **Baraclear**, with potential to remove phosphates from water are reviewed, with emphasis placed on studies with relevance to their performance and environmental impact and describing the environment required for optimum operation.

Other technologies mentioned earlier in Section 3 are not included in this part of the review as they relate to processes or technologies that are considered to be too complex or otherwise inappropriate for use on watercress farms.

Substantial research has been conducted on removal of phosphate (P) from the sediment of shallow lakes, where it is leading to eutrophication; and removal from wastewater in sewage

treatment plants, whilst other reports cover laboratory experiments that have examined removal of the FRP/SRP⁶ as the material moves down the water column in suspension.

On watercress farms, settlement ponds tend to remove the TP while the dissolved SRP in the discharge water needs intercepting and precipitating to the bottom. These are commonly 3 metres deep, similar in depth to many of the lakes referred to in the studies mentioned in this review.

Anoxic (deficient in oxygen) conditions are considered unlikely in watercress settlement ponds, due to the amount of water entering and leaving on a daily basis, so the impact of this condition on the efficacy of treatments is not considered.

Phoslock™

Phoslock™ is sold throughout the world for restoring recreational bathing lakes and large open waterways where P concentrations have led to eutrophication. Phoslock™ functions as a sediment cap to minimise the exchange of P from the sediment base into the soluble form in the presence and absence (anoxic) of oxygen.

Numerous studies have been conducted on its efficacy and environmental profile. The product is easy to handle and dosing accuracy not critical. Where low P concentrations are to be lowered further, release of lanthanum is possible but dependant on pH and alkalinity.

Physical and chemical properties

Lanthanum is a rare earth element (REE) that is relatively abundant in the earth's crust compared to other REEs.

Early research found that lanthanum was effective at removing P from water but could be toxic depending on its concentrations and application rate (Douglas *et al.*, 2004). In 1990's, lanthanum was stabilised by being incorporated into the structure of bentonite, a high exchange capacity mineral, by taking advantage of the cation exchange capacity of clay minerals. This exchange capacity is a result of a charge imbalance on the surface of the clay platelets, which is balanced by surface adsorbed cations. These cations are exchangeable in aqueous solutions.

During the preparation of Phoslock™, lanthanum ions are exchanged with these surface adsorbed exchangeable cations. As the rare earth element locked into the clay structure, it can either react with the phosphate anion in the water body or stay within the clay structure

⁶ For description of phosphate forms, see main Report Glossary.

under a wide range of physiochemical conditions (Douglas *et al.*, 2000). Rare earth-anion products are stable, due to their low solubility (Firsching, 1992). Phoslock forms a highly stable mineral known as rhabdophane in the presence of oxyanions such as orthophosphates (Douglas *et al.*, 2000). The stability of rare earth complexes is noted by their low solubility product (Douglas *et al.*, 2004).

Rhabdophane lends its name to a small group of phosphates. All members of the Rhabdophane Group are hexagonal or pseudo-hexagonal and have a general formula of $(X)PO_4 \cdot 1-2H_2O$. The X can be calcium, cerium, lead, lanthanum, neodymium, thorium, iron or uranium. Some sulphate ions, (SO_4) , can replace a portion of the phosphate ions, (PO_4) .

Phoslock™ was initially prepared as a slurry, as the lanthanum exchange process must be carried out in solution. However, a number of disadvantages were encountered with the production and the application of this form of Phoslock™. These included the transportation of excess residual lanthanum ions from the manufacturing process. These issues were resolved with the advent of the granular form of Phoslock™ with the properties that are summarized in Table 1. By manufacturing granular Phoslock™, the transportation and the application of Phoslock™ have become significantly more economical and convenient. In addition, the low dust level and the acceptable degree of packaging stability of the Phoslock™ granules make the transportation and the application of the product convenient and minimize any possible health risk associated with dust levels to the personnel involved in these processes.

Table 1. Summary of properties of Phoslock™ granules

Physical/chemical property	Description
Phoslock content	> 90%
Dispersing agent	Precipitated silica 5%
Water content	5%
Appearance	Brown free flowing granules
Packaging stability	No deterioration of the packaging or physical appearance of the product
Size of granules	2-4 mm x 1-3 mm
Bulk density	910-960 kg m ⁻³
pH	6.8 – 7.5
Dust content	< 1% weight 50 µm

Case studies of P removal

Phoslock™ has been extensively researched for its ability to remove phosphate both under laboratory conditions (Haghseresht, 2004; Ross *et al.*, 2007; Haghseresht & Schoeman, 2006), to reduce the FRP and SRP content of freshwater and recreational lakes Baerensee, GDR; Het Groene Eiland, GDR. by Institut Dr Nowak and reduce the discharge levels from STW (Fyshwick STP, Australia). The performance of Phoslock™ has been compared with alum (Haghseresht, 2004)

In addition, research on reservoir water quality for Pretoria, SA (Ross *et al.*, 2006) after Phoslock™ tracks P and pH changes over a number of weeks while Waikato peat lake sediments nutrient removal study (Faithfull *et al.*, 2005) provides a most detailed investigation of Phoslock and alternative materials for P removal.

Lanthanum compounds have been used in an extensive number of water treatment processes, as they are considered cheaper than those derived from other rare earth elements and the point of zero charge of lanthanum oxides is higher than that of other well known adsorbents (Wasay *et al.*, 1996a,b; Tokunaga, 1999).

Environment for optimum adsorption capacity and properties

- *pH*

The reduction of FRP (similar to SRP) by using clay modified with lanthanum ions is provided by the attachment of the phosphate anion. This reaction is stable as the lanthanum ions are either locked in place within the clay particles or reacts with the phosphate anions. Some lanthanum does leach out of the lattice into solution.

In laboratory studies, the kinetics of FRP uptake (Haghseresht, 2004) by application of clay modified with lanthanum (Phoslock) as it descended in a 1 m water columns at pH 7.5 containing FRP concentrations 0.5 – 2 ppm, the study indicated that the maximum adsorption capacity of the clay was less than 60 minutes with adsorption rate highest at 0.5 ppm P.

The P concentration reduced to 0.01 ppm after 24 hours. Organic matter levels were low at 8.6 ppm total organic carbon. This laboratory study also included toxic release discussed later.

In another study, pH has little influence on adsorption rate between pH 6 and 7 (Ross, G., Haghseresht, F., Cloete, T., 2008) but is reduced above pH 7. The equilibrium adsorption capacity (q_e) of Phoslock decreased from 4.38 to 3.19 mg /g as the initial pH of the solution increased from 5 to 9. However, the adsorption capacity of Phoslock remained similar within the range of pH 5 -7.

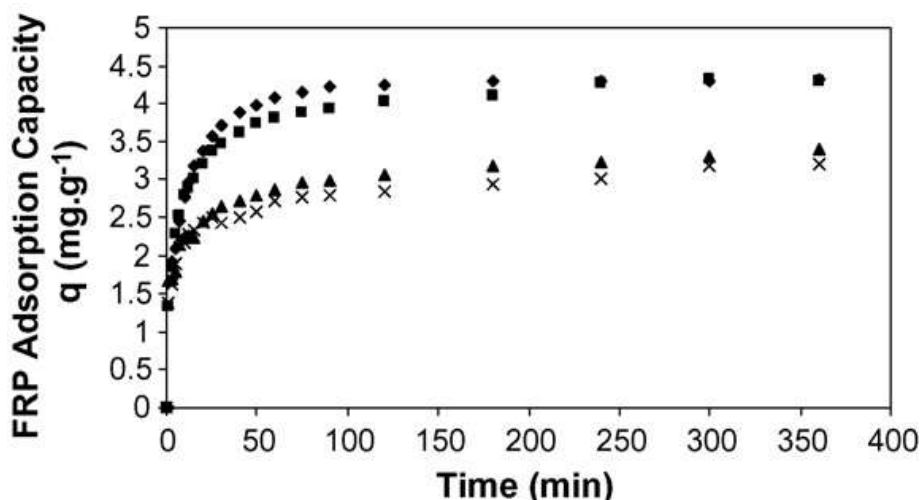


Fig 1. FRP adsorption capacity of Phoslock vs. time at various initial pH values (■) pH 5 (▲) pH 7 (◆) pH 8 (x) pH 9.

At pH 9, only 40% SRP is removed after the first hour but after 24 hours 60% is removed (not shown). The observed decline is due to the formation of the hydroxyl species of the lanthanum ions decreasing the number of phosphorus binding sites on the Phoslock surface (Douglas *et al.*, 1998) then estimated that if the observed rate of P uptake at pH 9 were to continue, 99% of the phosphorus load could be removed in less than 4 days.

Other researchers (Dibtseva *et al.*, 2001), found lanthanum hydroxides begin to precipitate at pH 8.35 so a rapid decrease in adsorption capacity is therefore expected above this pH. The solution turbidity following the Phoslock application decreased at a faster rate when the initial solution pH was 9, when compared to the pH 5 solution. This is supported by the particle size data. The particles were bigger in the pH 9 column, and settled out at a faster rate, as a result of the aggregation of the smaller particles at this pH. The faster settling time at high pH values may contribute to the reduced performance of Phoslock due to a shorter contact time with the solution.

It was also concluded that apart from the loss of lanthanum sites to hydroxylation, another reason for the observed decrease in the adsorption capacity could also be due to the unavailability of the lanthanum sites, caused by aggregation of the small particles. Aggregation of the smaller particles reduced the available surface area; hence less lanthanum ions per unit surface become available for reaction with the phosphate anions.

The addition of the modified clay over the time period appeared to lower the pH of the column to between 6.8 and 7.3. This neutralising effect may not be desirable if the pH of the water on the watercress farms is lowered below its normal level.

In gravel recreation lake studies, Bentophos (trade name for Phoslock in Switzerland) was applied to Lake Baerensee in 2007 (Institut dr Nowak) a six hectare, highly eutrophic water in the Federal German State of Hessen, with a sediment containing 700 mg P/kg dry weight with an application of 11.5 tonnes Bentophos.

The study calculated that this dosage was the sum of the 1.5 tonnes of Bentophos[®] required to remove a concentration of 96 µg/l of P from the water column and 8.5 tonnes of Bentophos[®] required to bind a total of 100 kg of measured bioavailable phosphorus in the sediment (anoxic). Samples of water were taken at 3 and 6 metre depth and from the sediment prior to and 7 days after application. As it settled, Bentophos[®] adsorbed the available phosphate in the water column before settling on the lake sediments. Due to the time of year (June) most of P had settled to the bottom of the lake and the impact of the Bentophos was to attract TP in the sediment rather than the ortho-phosphate which is more likely to be in solution earlier in the season in April. The reduction in the orthophosphate as it exchanged with TP in the sediment was slow and measured over a year but a 70% reduction 83 – 25 µg P/l was achieved. This study gave no indication of the pH of the lake before and after application.

In a second German lake study, Lake Silbersee near Stuhr, 7 hectares in size, contained sediment that measured approximately 1,000 mg P/kg DW prior to treatment in 2006. About 40% of this was bio-available P. Prior to treatment, de-stratification of the water and sediment occurred due to high winds providing an ideal opportunity to measure the removal of P in the water column with a depth of 7 m in aerobic conditions at a pH 7.6. Upon applying Bentophos, it was considered possible to achieve the maximum phosphate binding efficiency during the slow settling phase through the water column.

Prior to application of the Bentophos, the P concentration was 0.1 mg P/l in the water column. Twelve days after application, it was claimed that the orthophosphate in the water column had fallen to 0.02 mg/l. Total phosphorus concentrations in the lake's water were also reduced by 80%.

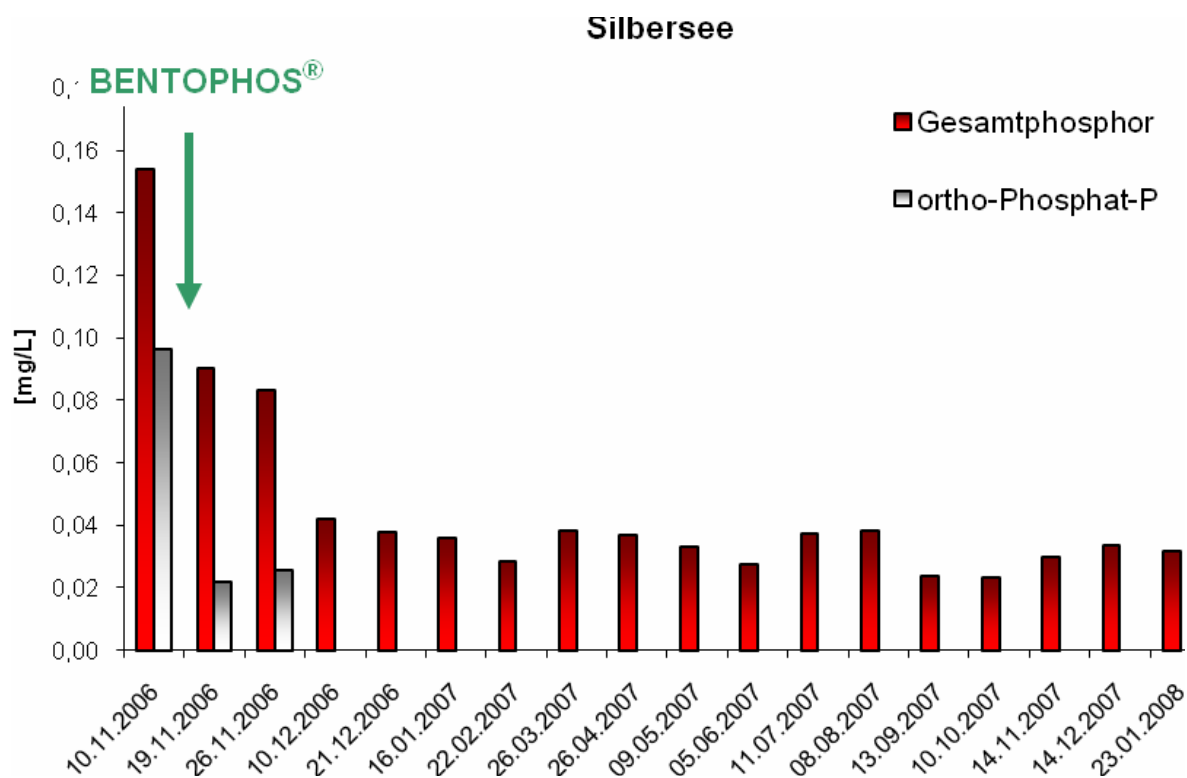


Fig 2: Trends in the concentrations of Total Phosphorus (Gesamtphosphor) and Orthophosphate ($\text{PO}_4\text{-P}$) in the Silbersee lake water.

Sediment testing following the application indicates a very stable situation in relation to phosphorus.

In a STP Phoslock Trial at Fyshwick STP Lagoon (Flapper, 2003) assessed the applicability of the product to remove algal blooms.

Figure 3 compares the concentration of OP in the treated and untreated lagoons before and after application. It can be seen that OP levels drop dramatically after application on 12 February, and then progressively rise over the two months following application. This demonstrates the successful removal of OP using Phoslock, with the application volume sufficient for a two month period only. This study further illustrates that at pH 7.75 Phoslock remains active, albeit at a reduced rate.

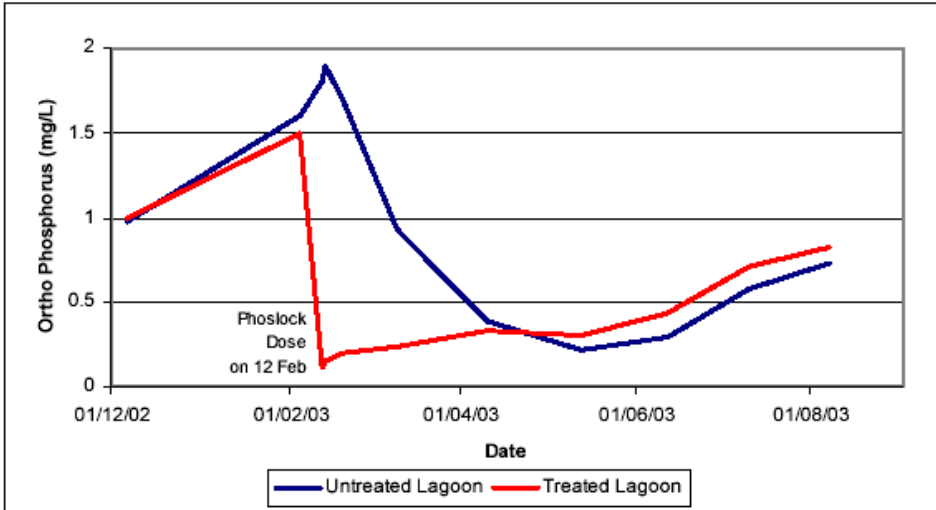


Fig. 3: OP Levels for the Treated and Untreated Lagoons

It is believed that the reduction in OP levels in the untreated lagoon from March 2003 is related to an algal bloom of *Microcystis aeuriginosa*, which would have uptake OP out of solution (Figure 4. shows algal bloom). From May 2003, the two lagoons behave similarly suggesting minimal influence of Phoslock after this time. The pH appears little affected (Figure 4).

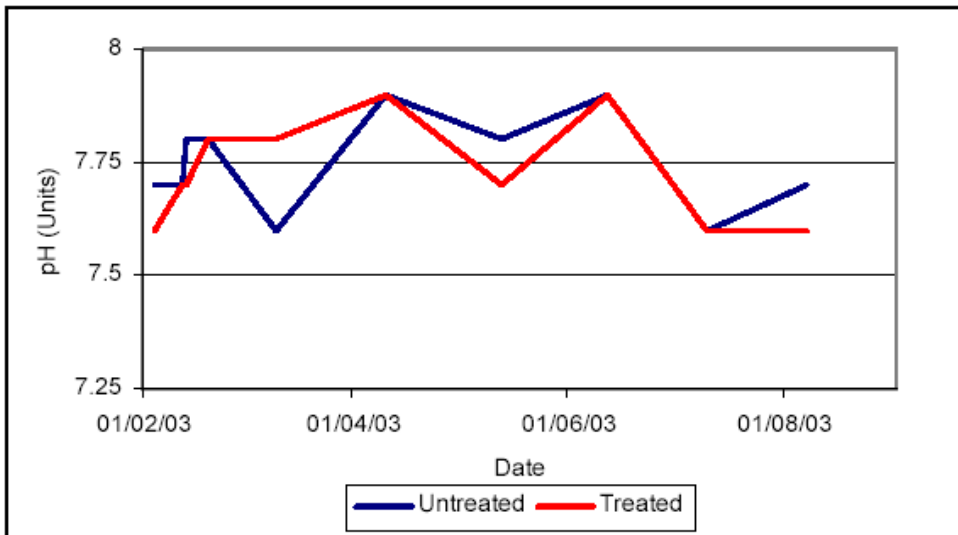


Fig 4: Impact on pH of Phoslock application – comparison of treated and untreated lagoons over six month monitoring period

Hartbeespoort Dam is located 37 km west of Pretoria on the Crocodile River (NIWR, 1985). It is classified as hypertrophic due to the runoff from fertilized fields and the inflow of sewage plant effluents from the Northern suburbs of Johannesburg that contain high

amounts of salts, phosphates and nitrates. Of particular interest is the high pH of 9.0 in this study and the effect this would have on the activity of Phoslock™.

Extensive cyanobacterial growth poses several severe implications on the general water quality as well as the maintenance of water treatment standards set for potable water. Massive blooms such as those found in the Hartbeespoort Dam can deplete the dissolved oxygen content resulting in fish kills and discolouration of the water by pigments released from the cells. High phosphorus levels remain the greatest factor influencing the development of algal blooms.

Laboratory tests have shown that Phoslock™ is capable of flocculating algal cells from water, and can bind phosphorus under these bloom conditions.

The site was approximately 2.5 hectares in size, had an average depth of 3m, and had an opening into the main dam, about 8m wide.

The phosphorus levels were 0.09 mg/l and the pH 9.8 while the phosphorus levels of the sediment were FRP 0.2 mg/l was used to calculate the amount of Phoslock™ necessary to treat the site.

At neutral pH, a ratio of 230:1 Phoslock™ to phosphorus is recommended, but the high pH of the Hartbeespoort Dam water required a higher dosage.

For large water bodies, the manufacturers recommended a Phoslock™ dosage of 250 g/sq m in order to achieve a 1 mm sediment capping. As the water body was approximately 2.5 ha in size (25 000 sq m surface area), 6000 kg of Phoslock™ was used. At a 0.2 mg/l phosphorus concentration, this will result in a Phoslock™ to phosphorus ratio of 400:1, and an 800:1 ratio for a 0.1 mg/l concentration of phosphorus. This dose was enough to overcome the negative effects of the high pH.

The concentration of FRP decreased by more than 50% in the first 24h after treatment from 0.09 mg/l to 0.043 mg/l. The FRP of the control area remained constant. After 48 h, the FRP concentration in the treated area had decreased to 0.017mg/l, and then stabilised at approximately 0.02 mg/l for the remainder of the first week of testing. The FRP concentration of the control area remained high; Phoslock™ therefore removed 73% of the FRP from the treated site.

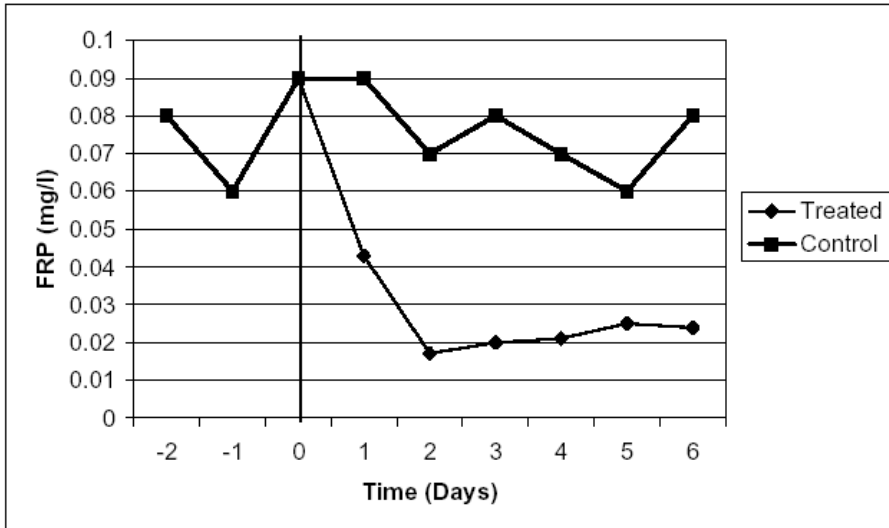


Fig 5. FRP values of the treated and control areas two days prior to treatment and 6 days after treatment (Day 0 represents the day of treatment)

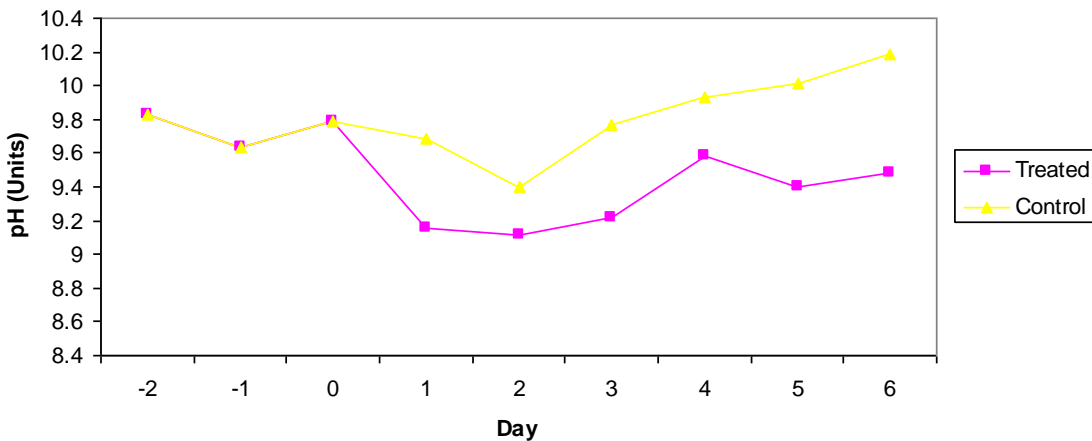


Fig 6. pH values of the treated and control areas two days prior to treatment and 6 days after treatment (Day 0 = day of treatment)

The pH values of the control and treated areas remained very similar throughout the trial. Following Phoslock application, the treated area showed a decrease in pH when compared to the control. However, by the second week after treatment, both the control and treated areas were once again of similar pH, and followed a similar trend.

While a drop in pH was recorded, the size of the fall may not be considered significant.

The temperature of the dam water was between 24°C and 29°C and appeared to have no effect on the activity of Phoslock™.

LITERATURE REVIEW

Table 2. Results of tested parameters before and after treatment with Phoslock™

		Day -2	Day -1	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Week 2	Week 3	Week 4	Week 5	
Treated	<i>FRP</i>	(mg.l-1)	0.08	0.06	0.09	0.043	0.017	0.02	0.021	0.025	0.024	0.2925	0.0925	0.1225	0.055
	<i>Nitrate</i>	(mg.l-1)	2.5	4.15	3.75	4.53	2.9	6.4	7.5	5	6.2	3.4	4.2	2.575	3.425
	<i>pH</i>		9.824	9.63	9.791	9.16	9.11	9.22	9.58	9.4	9.48	9.255	9.2875	10.5725	9.0825
	<i>Turbidity</i>	(NTU)	36.8	32.7	24.2	13.3	9.6	12.2	15.2	19	18.4	38.75	32.75	63.75	21.75
	<i>Dissolved Oxygen</i>	(mg.l-1)	9.04	7.45	6.83	3.75	6.03	3.65	5.78	4.5	4.83	4.875	4.95	5.65	6
	<i>Water Temperature</i>	(°C)	27.7	27.6	27.3	26.8	26.6	28.6	26.5	25.2	25.4	25.25	25.75	25.25	24.65
		Day-2	Day -1	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Week 2	Week 3	Week 4	Week 5	
Control	<i>FRP</i>	(mg.l-1)	0.08	0.06	0.09	0.09	0.07	0.08	0.07	0.06	0.08	0.22	0.72	0.22	0.36
	<i>Nitrate</i>	(mg.l-1)	2.5	4.15	3.75	3.9	4.7	6.4	6.6	5.2	9.5	2.2	1.1	3.3	1.7
	<i>pH</i>		9.824	9.63	9.791	9.69	9.4	9.77	9.93	10.01	10.19	9.55	9.41	10.77	8.92
	<i>Turbidity</i>	(NTU)	36.8	32.7	24.2	39	26	17	25	45	23	23	18	75	18
	<i>Dissolved Oxygen</i>	(mg.l-1)	9.04	7.45	6.83	4.4	6.5	4.4	5.8	5.2	4.2	4.6	4.9	5.1	5.6
	<i>Water Temperature</i>	(°C)	27.7	27.6	27.3	26	27	29	25	25	25.2	25	25	24.6	24.1

Days – 2 to 0 represent days before treatment (Day 0 samples taken immediately prior to treatment). Day 1 onward represents post application sampling.

The categorical effectiveness of Phoslock in the reduction of the FRP levels from the water column has been demonstrated in a number of studies (laboratory and field trials) over the last decade (Douglas, Adeney *et al.*, 1998; Douglas and Adeney, 2000; Douglas, Adeney *et al.*, 2000).

In the largest study of P removal from four peat lakes, Faithfull *et al.*, (2005) reviewed the use of Phoslock, Alum, Zeolite, carbon and iron making slag with their reaction to the lake's pH of between 5 and 7.5, tannins and sedimentation rates. The study concluded that Phoslock advantages were:

- Non toxic under a wide range of environmental conditions (Martin & Hickey, 2004)
- Effective under a wide range of pH values and alkalinities
- Binding of P to Phoslock is less influenced by humic substances than alum (Omoike & Vanloon, 1999)
- Does not affect pH levels following treatment (Flapper, 2003).

The study suggested consideration should be given to:

- Toxicity of Phoslock: Martin & Hickey (2004). Laboratory filtering methods exclude the any of the effects of the bentonite component of Phoslock which could prove to be toxic given the inherent natural environmental variability.
- The concentration of lanthanum required to produce acute effects in soft water for *Daphnia carinata* is 33 µg/l at pH range 7.5 -7.8 and 22 mg CaCO₃ per litre (ANZECC, 2002). Based on this data and due to lack of available data on toxicity effect, ANZECC (2002) set a trigger value of lanthanum at 0.44 µg per litre which gives a safety factor of c.1000 fold. This trigger value is set close to limit of detection and of lanthanum in freshwater and ANZECC (2002) recommends that any detection should be investigated.
- The potential for the capping layer to affect the survival and behaviour of benthic organisms as well as influencing macrophyte reestablishment. There is not published data on this effect. As the bottom sediments of watercress settlement ponds are unlikely to be of any biological significance with the sediment being frequently removed, this issue is unlikely to be of any significance.
- In laboratory trials, Phoslock bound less phosphate than aluminium based treatments such as Baraclear and modified zeolite at equivalent application rates (Yang *et al.*, 2004). Unfortunately this study is not in the public domain.

Alkalinity

There are no research studies to refer to on the effectiveness of Phoslock where alkalinity has been measured before and after its use to determine impact.

Lanthanum associated with bentonite clay preferentially binds with PO_4 , forming a highly stable mineral, Rhabdophane. However, it can also bind with CO_3 or other oxi-anions. Among all other interactions, the lanthanum phosphate bond is the strongest (approx. 300 times stronger than between lanthanum and carbonate). Carbonate competes with phosphate and therefore causes a delay in the phosphate binding of Phoslock (which requires more than 24 hours) in high alkalinity waters. Therefore, in addition to the concentration of FRP, the alkalinity of water needs to be considered in determining the dose rates of Phoslock®. In low alkalinity water, the Phoslock® dose rate should be based on available phosphate only because there is less or no potential to bind CO_3 with Phoslock® active sites (i.e. lanthanum).

Settlement rate

Phoslock remains suspended in the water column for a substantial amount of time; generally 1-2 days are required for settling (Greenop & Robb, 2001). This might be seen as a disadvantage where settlement to the bottom of the lake is required. In the watercress settlement pond, where SRP is in solution, this prolonged activity appears advantageous, giving longer for contact and adsorption, although the limited residence time in many settlement ponds may mean that its full potential is not realised.

Organic matter

Organic matter as dissolved organic carbon. Haghseresht & Schoeman (2006) found that Phoslock could remove > 99% of the FRP in the absence of DOC (as humic acid), with the first 80% of it being removed after the first hour in its optimum performance pH range of 6–7. However, when the solution pH is raised above 9, the efficiency dropped to 70% and in the presence of 100 mg/l humic acid, the adsorption rate of FRP is reduced to 40%. Watercress farms would have to consider some filtration of the organic matter prior to treatment with Phoslock where the pH of the water is 8 or more.

The equilibrium adsorption capacity of Phoslock™ (q_e) in the effluent lake water was less than that observed in the synthetic water columns at either pH 8 or pH 9. This may be due to the presence of humic acids in the water, which lowered the phosphorus adsorption capacity of Phoslock, especially at higher pH values (Douglas *et al.*, 2000).

Temperature

There is no data to provide evidence for constant P uptake by Phoslock at different temperatures. The Hartbeespoort Dam study reported on the effective use of Phoslock with temperatures between 23°C and 27°C while in the Silbersee report, the lake temperature was between 8°C – 16°C. However, laboratory studies (Haghseresht, 2004), showed that P uptake is reduced by approximately 15% when the water temperature is reduced from 30°C to 10°C.

Environmental impacts

- *Release of lanthanum and effects on aquatic organisms*

The first three studies referenced were commissioned by Phoslock.

Early toxicological studies using Phoslock slurry.

Prior to the development of granular Phoslock, a slurry form of Phoslock™ was used for all applications. As a result, nearly all of the available toxicological data, including any studies on the effects of Phoslock™ on the physiochemical properties of the water and living organisms, are based on Phoslock™ slurry.

One of the earliest studies was carried out during the application of Phoslock™ in the Canning River in Western Australia. This was conducted by the Water and Rivers Commission and CSIRO Land and Water Division. The study concluded the use of Phoslock™ poses minimal risk of acute and chronic toxicity to fresh water organisms.

Table 3. Concentrations of selected metals before and after the application in Canning River, Australia

Elemental Concentration in Filtered Water samples (µg/l)						
Element	<i>Untreated site</i>			<i>Treated site</i>		
	-1 day	+1 day	+1 Week	-1 day	+1 day	+1 Week
Calcium	40	41	41	42	42	43
Magnesium	22	22	22	22	22	23
Copper	<1	3	2	4	7	4
Zinc	3	8	2	16	2	9
Lanthanum	<10	<10	<10	<10	50	40

In a recent study (Haghseresht, 2003), using a sample of the Phoslock™ granules produced from a given slurry batch with a known dissolved lanthanum concentration, the reduction of the available lanthanum in the granular form was illustrated. It has been demonstrated that as a result of the combined effects of the dewatering and drying stages, the level of dissolved lanthanum was reduced from 1.25 mg per g of the solid to 0.011 mg per g.

Table 4. Ecological data of Phoslock™ granular application

Eco-toxicological Data		
EC ₅₀ (ppm):	>1000	<i>Daphnia magna</i> 24 hr immobilization test
	>10,000	Rainbow trout 4 day static study

In the **Barensee study 2007** (Institut dr Nowak) the total lanthanum content was measured at 130 µg/l following the application of Bentophos. During the monitoring period, lanthanum concentrations dropped to <10 µg/l (Figure 3). This was interpreted as both lanthanum and phosphate being deposited firmly in the sediment and as such were considered safe.

Eco-toxicity tests on lanthanum ions

On account of concerns regarding the use of agents containing lanthanum in bodies of water, the Institute also conducted acute eco-toxicity tests on lanthanum.

This involved determining the effective concentration at which lanthanum has a toxic effect on test organisms according to the appropriate DIN tests. Parallel to this, eco-toxicity tests were also undertaken using lanthanum solutions to which a corresponding amount of phosphate had been added.

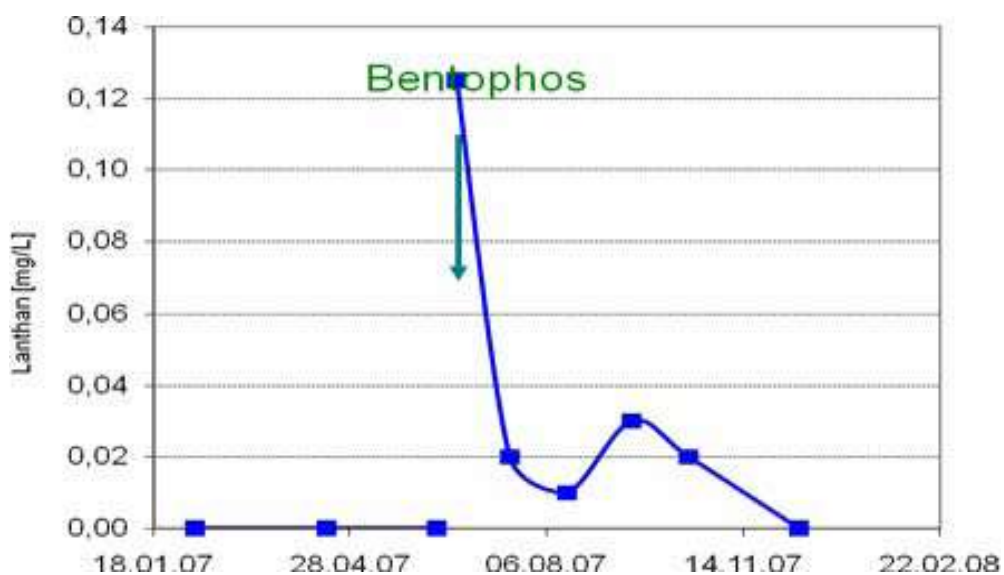
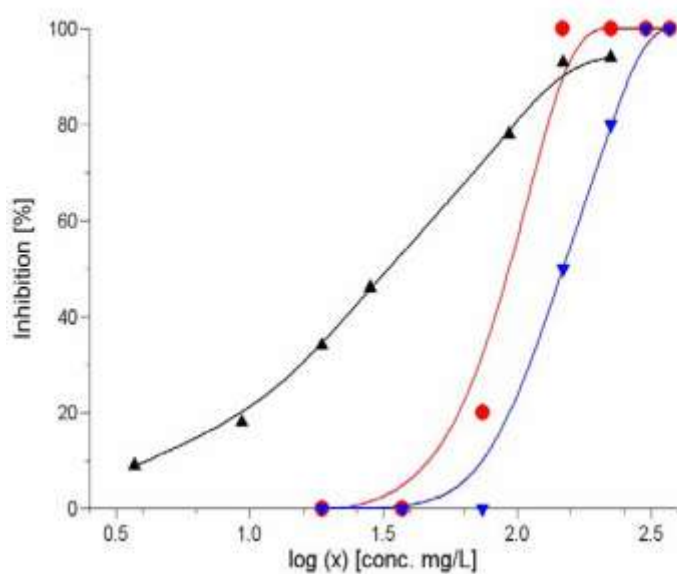


Fig 7. Lanthanum concentrations in Bärensee water after application with Bentophos (Phoslock)



Bacterial luminescence test (ISO 11348-3)

$$EC_{50} = 37 \text{ mg La}^{3+} / \text{l}$$

Toxicity test with *Daphnia magna* (DIN 38412-L30)

$$EC_{50} = 103 \text{ mg La}^{3+} / \text{l}$$

Fish egg toxicity test (DIN 38415-T6)

$$EC_{50} = 150 \text{ mg La}^{3+} / \text{l}$$

Fig 8. Dose-effect relationships between lanthanum and the respective test organism

Table 5. Fish egg test (pursuant to DIN 38415 Part 6, modified as “Contact”-Test)

Bentophos / cavity [mg]	pH	O ₂ [mg/l]	Coagulated eggs (N)	No somite created (N)	Tail not separated from yolk (N)	Heartbeat not determinable (N)	Sum of dead embryos (%)
5	7	“	/	/	/	/	0
10	7	“	/	/	/	/	0
25	7	“	/	/	/	/	0
50	7	“	/	/	/	/	0
75	7	“	/	/	/	/	0
100	7	“	/	/	/	/	0
125	7	“	/	/	/	/	0
150	7	“	/	/	/	/	0
175	7	“	/	/	/	/	0
200	7	“	/	/	/	/	0
Internal controls	6,8	9,5	/	/	/	/	0
External controls	6,8	11,7	9	/	/	/	9

Comment: external controls: 3.7 mg/l 3,4-Dichloanilin solution, N=number

The results reported were:

Effective concentrations on the test organisms (EC₅₀) were at least 1000 times higher than the lanthanum levels measured following the application on the Bäreensee (Table 4). With the addition of phosphate in the corresponding amount to the concentrations found in the Bäreensee, no toxic effect could be detected. The modified fish egg test shows that even direct contact with an amount of Bentophos[®] which was four times higher than the standard dosage would have no effects on sensitive water organisms (Table 4). After binding with phosphate, the lanthanum is no longer bio-available and therefore the amount of lanthanum used in the Bäreensee would have had no toxic effect on the organisms in the lake.

This implies that if there is a surplus of lanthanum that has not bound with phosphorus, there is likelihood that lanthanum levels could be considerably higher.

Haghseresht laboratory study for Phoslock evaluated the FRP properties if addition of the modified clay affected the toxicity of the water significantly, such that concentrations of a number of heavy metals were determined. Examination of Table below shows that the application of the clay did not affect the concentration of the metals in the water sample.

Table 6. Concentration of various metals prior and post modified clay addition to the water column

Element	Before application (ppm)	3 days after application (ppm)
As	<0.02	<0.02
B	0.2	0.2
Fe	0.1	0.05
Cr	<0.003	<0.003
Hg	<0.001	<0.001
Zn	0.04	0.03
Pb	<0.02	<0.02

Table 7. Recommended ANZECC sediment quality guidelines for a range of elements

Element	High ($\mu\text{g/g}$)	Low ($\mu\text{g/g}$)
As	70	20
Cr	370	80
Cu	270	65
Ni	52	21
Pb	220	50
Zn	410	200

Levels sampled appear to be well within the recommended level ANZECC guidelines for metals but the complete list is not provided.

In the Sibersee lake study (Institut dr Nowak) both the release of lanthanum into the water sediment and the effect on fish were studied. Total lanthanum concentrations in the lake water were measured at 100 $\mu\text{g/l}$ following the application. These dropped during the monitoring period to 4 $\mu\text{g/l}$ after 6 weeks.

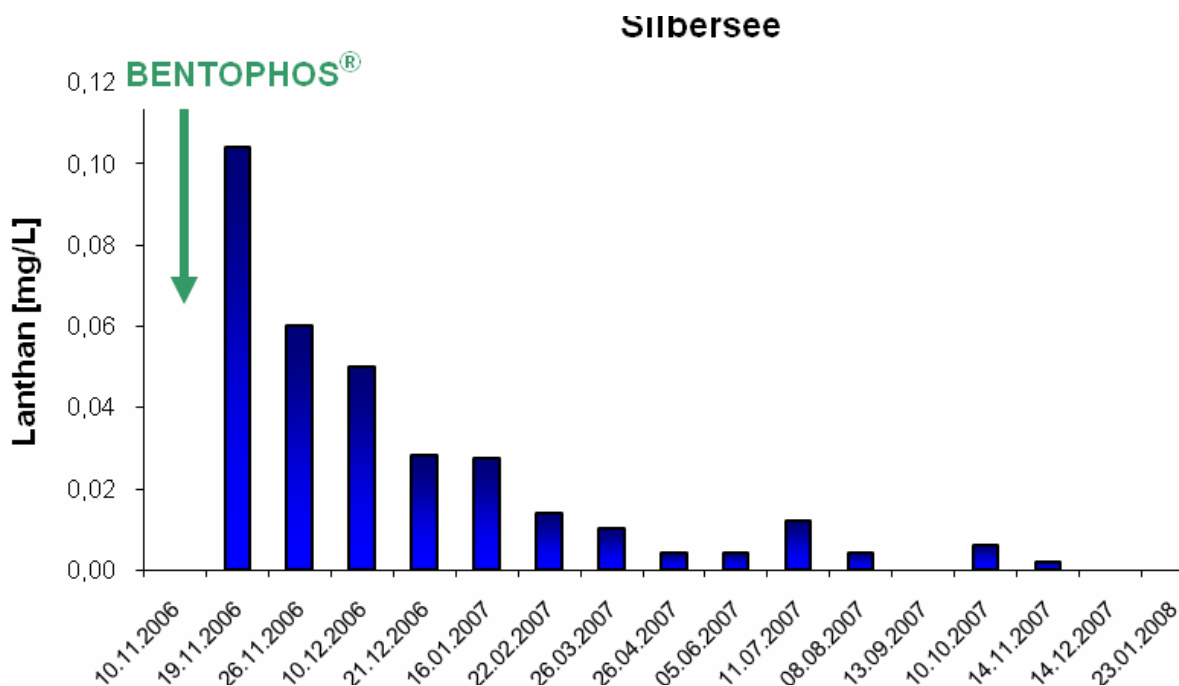


Fig 9. Lanthanum concentrations in the lake water following the application

Table 8. Lanthanum concentrations detected in fish on the 26.03.2007

Fish	Organ	La ³ (mg/kg DW)
Perch	Liver	2.3
	Skin	2.3
	Tissue	0.12
Pike	Liver	0.32
	Skin	2.2
	Tissue	0.03

Lanthanum was detected in both perch and pike most noticeably in the skin of both fish and in the liver of perch. Unfortunately, no tests were undertaken on fish prior to the application of Bentophos but measurements were taken of fish from a nearby lake for comparative purposes. The analytical level for lanthanum was not low enough to make effective comparisons (>5 mg/kg).

In order to properly assess the use of a material containing lanthanum in bodies of water, the Institute carried out ecological toxicity examinations in relation to the acute toxicity of lanthanum. The effective concentration at which lanthanum has a toxic effect on the test organisms was measured in accordance with the guidelines of the DIN standards for the appropriate tests. In parallel, tests were also undertaken with lanthanum and a corresponding concentration of phosphate.

The results concluded that the effective concentrations for the test organisms (EC_{50}) were at least 1000 times higher in the investigations than the highest lanthanum quantity measured in the lake water of the Silbersee. (That does not mean they were not toxic). With the addition of phosphate, which is present in the Silbersee in the corresponding quantities, no toxic effect was detectable at all. The modified fish egg test shows that there is no effect on sensitive water organisms, even with direct contact at up to four times higher quantities than the standard Bentophos dosage. After combining with phosphate, the lanthanum is not bioavailable. The quantity of lanthanum used in the Silbersee therefore has no toxic effect on the organisms in the lake.

In the Fyshwyck STP (Flapper, 2003) the author concluded that lanthanum concentrations in the water column of the treated lagoon were slightly elevated for at least one month after application, compared to the control lagoon. These levels however, were below those found to have an acute impact on fish and water flea during ecotoxicology trials conducted for NICNAS approval by CSIRO. Two scientific papers one Asfar & Groves (2009), and Watson-Leung, (2008), contain an extensive review of the environmental profile of Phoslock and Phoslock toxicity testing with sediment dwelling, rainbow trout and *Daphnia*. In reviewing previous eco-toxicity trials, Asfar & Groves (2009) evaluated both acute and chronic studies on *Daphnia*, rainbow trout, shrimps, amphipod, mayfly and midge larvae. The report states in the early paragraph that at low alkalinity and low P concentrations, small concentrations of lanthanum may leach out of Phoslock™ due to anion concentrations. In high carbonate situations (hard water) the lanthanum is likely to bond to $Ca = LaCO_3$, rendering the La unavailable to subsequent biota.

However, it has also been found that the free/unbound lanthanum can be toxic to aquatic organisms depending on its concentration and application rate (Douglas *et al.*, 2004) which has been resolved by binding the lanthanum into the clay carrier bentonite, as in the product Phoslock, rather than in the original slurry formulation.

Most of the results in the review showed that Phoslock™ is not toxic to aquatic organisms and humans at normal dose rates applied in to water bodies (NICNAS Public Report, 2001; Martin & Hickey, 2004; Watson-Leung, 2008). However, some results indicated that Phoslock™ may be toxic to some organisms at higher dose rates in certain waters, e.g. low alkalinity.

In the review, only ecotoxicity tests conducted in moderately high alkalinity (120 mg/l) and pH 7.8 are considered relevant being the conditions operating at watercress farms on chalk streams. As most of the lab studies to establish acute and chronic effects require soft or de-ionised water to be used as part of the protocol, this eliminates most tests undertaken. In hard water (160 mg/l of $CaCO_3$), the acute toxicity of lanthanum chloride to *Daphnia*

carinata was dramatically reduced; 48 h EC50 was determined as 1180 µg/l which is 27 times higher than the value of tap water EC50 (Barry & Meehan, 2000).

Watson-Leung, (2008) using a direct solution of Phoslock™ granules (not leachate) dissolved in high alkalinity Scanlon pond water (203 mg/l as CaCO₃). Results demonstrated that Phoslock™ exhibited some toxicity to *Daphnia* only at very high concentrations (3,400 mg/l and 6,800 mg/l). The 48 h EC50 was calculated as >6,800 mg/l. Concentration of dissolved La in 6,800 mg/l of Phoslock™ treatment was measured as 14,000 µg/l. However, it was not clear why the concentration of dissolved lanthanum was lower (14,000 µg/l) in the 6,800 mg/l of Phoslock™ treatment than it was in the 3,400 mg/l concentration of Phoslock™ (dissolved lanthanum was 63,270 µg/l). The highest concentration of Phoslock™ used in this experiment was 6,800 mg/l.

Phoslock™ has never been applied in a Canadian ecosystem prior to the toxicity study conducted by Watson-Leung (2008). Alkalinity in Canadian water is usually high (203 mg/l as CaCO₃ measured in Scanlon pond water during *Daphnia* toxicity test). Therefore laboratory toxicity testing was necessary using high alkalinity Canadian natural lake/pond water. Phoslock™ application rates tested by Watson-Leung (2008) varied across the tests performed but in most cases were much greater than the proposed dose rate suggested by the Technical Division of Phoslock Water Solutions Ltd. Excessively high application rates of Phoslock™ (up to 13,600 mg/l) were tested to examine the worst case scenario: such as if a concentrated pulse of Phoslock™ entering the ecosystem due to equipment malfunction or human error.

Studies on rainbow trout (*Oncorhynchus mykiss*) in hard water are few. Watson-Leung. (2008) showed no sign of toxicity up to the highest concentration of 13,600 mg Phoslock™/l (direct solution of granules, not leachate) in pond water. The concentrations of dissolved La were not measured unfortunately but were assumed to be similar to the concentrations of dissolved La in the dilution series of Phoslock™ used in the *Daphnia* toxicity tests. Concentrations of dissolved La in 3,400 mg/l and 6,800 mg/l of Phoslock® treatments were 63,270 µg/l and 14,000 µg/l respectively. The concentration of dissolved La in 13,600 mg Phoslock™/l (highest concentration used for trout toxicity test) would be higher than 63,270 µg/l which is much higher than the values of EC50 determined by the CSIRO (127 & <600 µg/l) for rainbow fish and considerably higher than the concentrations that would ever be used in an environmental application.

All studies on shrimps (*Macrobrachium* sp) were conducted using synthetic soft water and consequently are not considered relevant. However, some toxic effects by leachates of the highest concentration (800 mg/l) of Phoslock™ granules on the survival of juvenile freshwater shrimp were recorded.

Watson-Leung (2008) revealed that Phoslock™ was not toxic to the survival and growth of amphipod, *Hyalella azteca*, up to the highest concentration (3,400 mg/l) tested using natural pond water. The test media contained a direct solution of Phoslock™ granules dissolved in pond water up to the concentration of 3,400 mg/l. Results showed that there was no significant reduction in the survival and growth of amphipods exposed to all of the test sediments and treatments when compared to amphipod survival in the control sediment ($p > 0.05$). From this study, the 14 d EC50, NOEC and LOEC can be calculated for survival and growth of amphipods as $>3,400$ mg/l, 3,400 mg/l and $>3,400$ mg/l of Phoslock™ respectively.

The same author, demonstrated that Phoslock™ was not toxic to mayfly, *Hexagenia* spp, at the dose rate of 250:1 (250 mg Phoslock™ for 1 mg FRP) applied in Canadian pond water under laboratory conditions. Results of a chronic toxicity study (21 d) showed no toxicity when a direct solution of Phoslock™ granules dissolved in pond water at the concentration of 450 mg/l.

There was no significant reduction in the survival and growth of the mayfly exposed to the test sediments and treatments when compared to the mayfly survival in the control sediment ($p > 0.05$). The 21 d EC50, NOEC and LOEC can be calculated for survival and growth of the mayfly as >450 mg/l, 450 mg/l and >450 mg/l of Phoslock™ respectively.

Chronic toxicity study (10 d) of Phoslock™ to test the survival and growth of midge larvae, *Chironomus dilutus* in a direct solution of Phoslock™ granules dissolved in pond water (Watson-Leung, 2008) showed that there were no toxic effects up to the highest concentration (3,400 mg/l) tested. There was no significant reduction in survival and growth of the midge larvae exposed to all of the test sediments and treatments when compared to the midge larvae survival in the control sediment ($p > 0.05$). The 10 d EC50, NOEC and LOEC can be calculated for survival and growth of midge larvae as $>3,400$ mg/l, 3,400 mg/l and $>3,400$ mg/l of Phoslock™ respectively.

None of the above tests demonstrated toxicity of Phoslock™ to aquatic organisms at the proposed dose rate (i.e. 100 g Phoslock: 1 g P). Results from recent toxicity studies using a direct application of Phoslock™ granules that were dissolved in low and high alkalinity natural waters demonstrated no toxic effects of Phoslock™ to aquatic organisms in the solution using up to 13,600 mg Phoslock™/l which is several thousands times higher than that of the usual Phoslock™ application dose rate.

Previous variations for toxicity results (Asfar & Groves, 2009), were explainable due to different experimental methods (TCLP method, direct solution of Phoslock™ granules and lanthanum chloride solution), type of material (early slurry versus later granules), water alkalinity (soft or hard), humic substances (La may interfere or mitigate toxicity),

Costs

- *Installation and application*

Phoslock™ can be applied during peak P discharge periods (bed cleaning, fertilizing, harvesting) as the water from the watercress beds enters the settlement ponds or scattered on the surface of the settlement pond at the inflow end. No specialist equipment is required for distribution.

- *Running costs (dosing rate, labour, management time)*

Phoslock™ as a polishing material costs ca £1,900 per tonne. 100 kg Phoslock™ will remove 1kg P from solution. To lower the P concentration in the settlement ponds from 0.2 mg/l to 0.06 mg/l = 0.14 mg/l requires 0.49 kg (0.14 X 3,500,000) Phoslock™ costing 0.95p per day where 3,500,000 litres water pass through the settlement pond per day.

ViroFilter™

ViroFilter™ is a stand alone filtration system that utilises a porous Bauxsol pelletised media, fitted 'in line' with existing secondary water treatment systems. This media is produced from the chemical and physical transformation of a by-product of aluminium extraction into a sustainable product for use in the treatment of water, wastewater or soils, to remove phosphate.

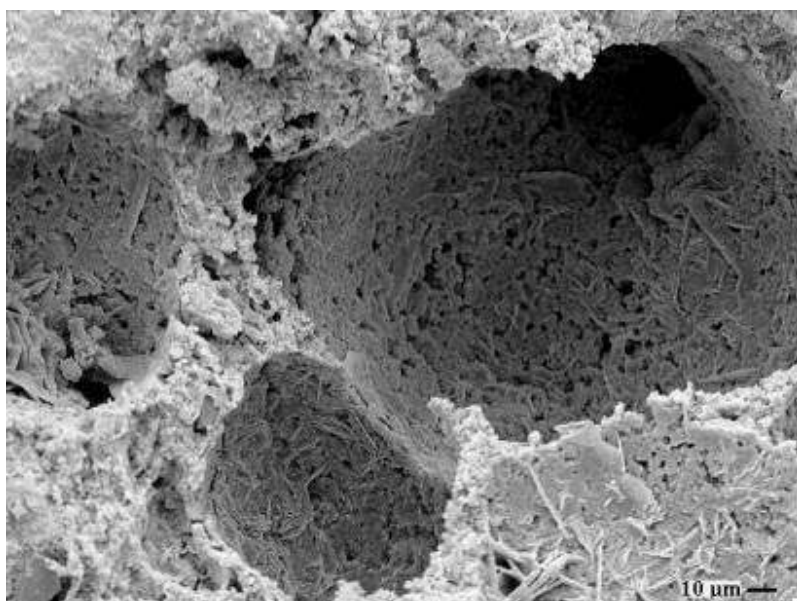


Fig 10. An SEM image of the interconnected pore space of the ViroFilter pellets

With ViroFilter Technology, effective phosphate removal to low concentrations can be achieved with no requirement to add flocculants or adjust influent pH. In addition to phosphate treatment, the Technology offers a solution for many of the problems associated

with conventional chemical dosing, producing an effluent reduced in BOD, ammonia, suspended solids, odour and colour, and successfully binds excess iron released in the effluent, therefore preventing iron carry-over. The immobilised pellet bed allows for variations in hydraulic flow and phosphate concentrations, and upstream chemical dosing is typically not required.

The technology offers a solution for the removal of phosphates and heavy metals from small and medium sized STP as it does not require the use of unsafe or hazardous chemicals but rather a fully automated flow-through system that requires no operator supervision. The phosphate removal capacity is projected to be 14 g of phosphate per kg of ViroFilter pellets.

The filter treatment beds can be positioned vertically or horizontally as a trickling filter to suit each specific location or available area. The system can be fitted retrospectively to submerged horizontal or vertical flow beds, biological or percolating filters and in parallel or series operation. The pellet bed can allow for variations in the hydraulic flow and phosphate concentrations so additional chemical dosing is not required.

Virotec is able to engineer Bauxsol™ pellets with specific characteristics for different applications, and in a variety of graded sizes. The size must ensure that pores will adsorb P and not rapidly block up from accumulation of solid substances present in the final effluent.

Where phosphate discharge consents of <2.0 mg/l are required, phosphate removal efficiency is approximately 80% per filter pass. Bed residence times are typically between 4 and 12 hours, depending on influent phosphate concentrations and treatment target levels.

Physical and chemical properties

Bauxsol is a trademark of Virotec International Ltd, for geochemically and physically modified red mud, produced during the refinement of alumina from bauxite (Bayer process) for environmental applications. Pure Bauxsol is a dry red solid that consists of a complex cocktail of minerals that usually includes: abundant hematite, boehmite, sodalite, quartz and cancrinite. However, specific mineralogies may vary according to source of the bauxite material, nature of the extraction process and what Bauxsol blends are chosen for the final product. Bauxsol™ media is available as highly porous pellets and is composed of haematite, magnesium minerals, calcium carbonate and titanium oxide.

Irrespective of the exact composition, pure Bauxsol has a large surface area; volume ratio and abundant Ca, Mg and Al ion availability, that facilitates a capacity to adsorb and complex a wide range of oxyanions such as phosphate from solution. Importantly, Bauxsol has a near-neutral reaction pH and consists of minerals that are not considered to pose an environmental risk.

The chemical properties of the ViroFilter pellets have a high metal binding capacity (up to 1,500 meq of metals/kg) and contain multi-charged surface for potential phosphate reaction sites. The physical properties of the raw materials in the pellets have a high charge-to-mass ratio and a high surface-to-mass ratio, composed of up to 80% solid grains 10 µm or less, are highly insoluble and non dispersive in water, display fast settling time when applied as a dry solid with a specific gravity of 3.2 g/cm³ and produce a stable sediment rather than a sludge when applied directly to water.

Case studies of P removal

Independent analyses and trials of ViroFilter Technology have been conducted in Australia and the United Kingdom. Initial research conducted by the Water Research Council (WRc) in the UK investigated the kinetics, chemistry and outcomes of applying ViroFilter Technology for phosphate treatment (Water Research Council, 2005). The research showed that while total phosphorus (TP) influent levels ranged from 6.0 mg/l to 9.0 mg/l during the trial TP effluent levels were at or below 2.0 mg/l when hydraulic residence time (HRT) was between four and 12 hours.

Two case studies are reviewed, both at wastewater treatment plants.

Yorkshire Water conducted a four-month trial of ViroFilter™ Technology to evaluate its potential to enhance the removal of phosphate from municipal wastewaters in accord with tightening consent standards in the Yorkshire region. The key objective of the work was to assess whether ViroFilter™ Technology offers a reliable, robust and economically viable solution for a small, rural, unmanned Sewage Treatment Plant (STP) to remain within its phosphate consent.

Specific objectives were:

- to assess the suitability of ViroFilter™ Technology for phosphate removal from wastewater in a trickling filter application
- to assess hydraulic retention times
- to assess the benefits of multi-stage filtration on lower media contact times against longer media contact times and single filter passes
- to assess the longevity of the ViroFilter™ media
- to assess the ability of ViroFilter™ Technology to remove Biological Oxygen Demand (BOD), ammonia and heavy metals from municipal wastewater

Treatments included three different designs:

1. Filter Pairing A consisted of two filters each containing approximately 0.75 m³ of 10 – 25 mm ViroFilter pellet media. Each filter had a Hydraulic Residence Time (HRT) of six hours for a total HRT of 12 hours. Operated for 4 months, samples were taken from the influent point, the intermediate point between filter 1 and 2 and at discharge.
2. Filter Pairing B consisted of a two-stage filter running in series, with each filter holding approximately 20 kg of 5-10 mm ViroFilter™ pellets. The filters were initially operated with a one hour residence time in each filter, giving a total HRT of two hours across the filter pairing. During the project hydraulic residence time was subsequently reduced to a total of one hour across the filter pairing (30 minutes in each filter) for a two-week period and then increased to a total of three hours across the filter pairing (one and half hours in each filter).
3. Filter Pairing C consisted of three small filters, each filter had a residence time of four hours, giving a total Hydraulic Residence Time (HRT) across the filters of twelve hours. The three filters, like Filter Pairing B, contained approximately 20 kg of 5-10 mm ViroFilter™ pellets. The three filters were designed to replicate Filter Pairing A, except using three filters. Three composite samples were taken daily, two intermediate samples (the points between each filter) and an effluent sample. The first intermediate sample was taken from a sample point between the outlet of the first filter and the inlet of the second filter; the second intermediate sample was taken from a sample point between the outlet of the second filter and the inlet of the third filter.

Results

Filter Pairing A had a Total Phosphorus (TP) load of 10.3 mg/l in the influent, and produced a TP load of 5.2 mg/l at the intermediate point, and a final treated effluent TP of 2.6 mg/l, indicating a 74% reduction in TP. On average about 5.0 mg/l of phosphate was removed by the intermediate stage and 2.5 mg/l of phosphate was removed by the second (final effluent) stage.

Filter Pairing A had an ortho-phosphate load of 9.6 mg/l in the influent, and produced an orthophosphate load of 4.6 mg/l at the intermediate point (between filters #1 filter #2), and a final treated effluent ortho-phosphate concentration of 2.1 mg/l, representing a 77% reduction of orthophosphate concentration. Final effluent pH was on average 9.1

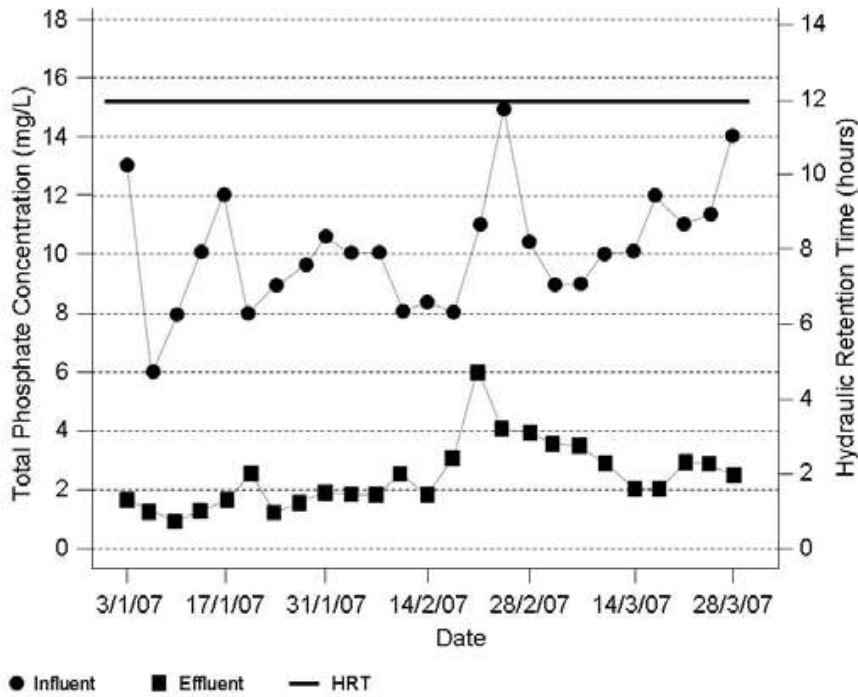


Fig 11. The influent and effluent total phosphate levels and HRT times for filter pairing

Filter Pairing B had a Total Phosphorus (TP) load of 9.6 mg/l in the influent, and produced a TP of 3.6 mg/l at the intermediate point (between filters #1 filter #2), and a final treated effluent TP of 1.8 mg/l, representing an 81% TP removal. On average, about 6.0 mg/l of phosphate was removed by the intermediate stage and 2.0 mg/l of phosphate was removed by the second (final effluent) stage. Final effluent pH was on average 8.6.

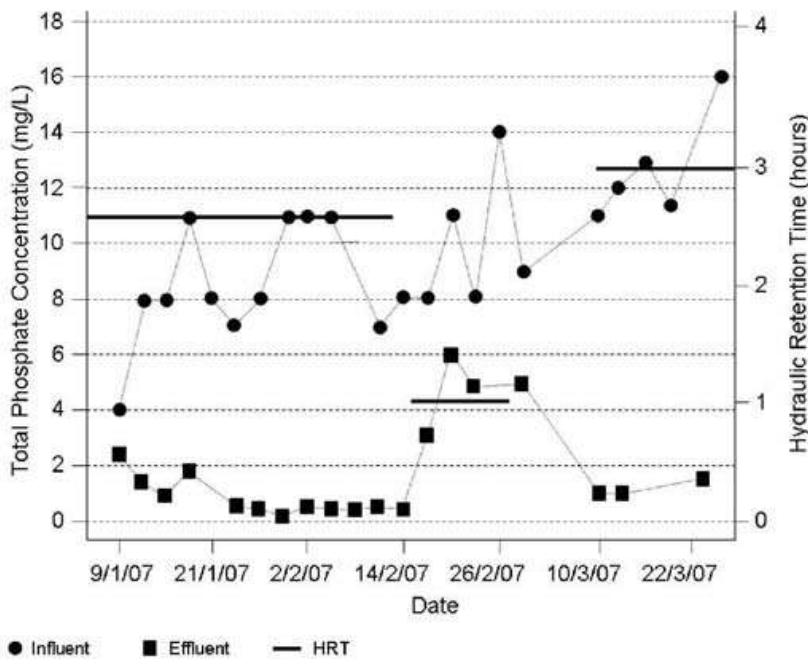


Fig 12. The influent and effluent total phosphate levels and HRT times for filter pairing B

Filter Pairing C had a TP load of 9.6 mg/l in the influent, and produced a TP load of 1.1 mg/l at the first intermediate point, a TP load of 0.5 mg/l at the second intermediate point, and a final treated effluent TP of 0.37 mg/l, representing a 95% TP reduction. On average, about 6.0 mg/l of phosphate was removed by the intermediate stage and 2.0 mg/l was removed by the second (final effluent) stage. Final effluent pH was on average 8.6.

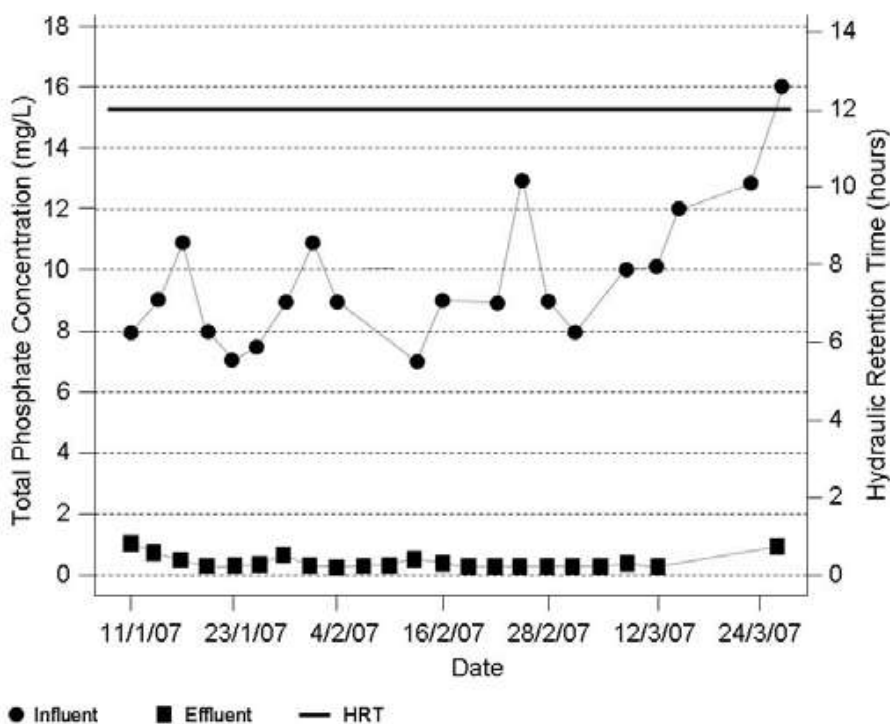


Fig 13. The influent and effluent total phosphate levels and HRT times for filter pairing C

The conclusions from this trial focused on the longevity of the material. Assuming ViroFilter™ media remove 14 g/kg, and Filter Pairing A holds a total of 1,500 kg, the ViroFilter™ media has the potential to remove 21,000g of phosphate. The total amount of phosphate removed over the duration of the project was calculated to be 2,035 g, thus the filter system had the potential to remove a further 18,965 g. From this it can be calculated that at a 12-hour Hydraulic Residence Time (HRT) the average removal rate of phosphate over the duration of the study was 6.6 mg/l.

In summary, this research concluded the following:

- ViroFilter Technology removed total phosphate and total ortho-phosphate to approximately 80% from wastewaters in a trickling filter type application
- HRTs for the trial showed that Filter Pairing B (two hours) and Filter Pairing C (12 hours over three filters) resulted in phosphate discharge levels below 2.0 mg/l

- multi-stage filtration resulted in greater phosphate removal rates
- the estimated bed life of the ViroFilter media was between 2.5 and 9.5 years, depending on HRT and levels of phosphate to be treated

Disposal costs were considered minimal while providing a source of beneficial P to soil grown crops.

The cost per kilogramme of phosphate removed from chemical dosing is extremely sensitive to the size of the works, and substantial increases are seen when consent levels for phosphate reduction to <2.0 mg/l are imposed. The operating cost of chemical dosing for small to medium-sized WwTPs is £15-£93 per kilogram of phosphate removed (at an average of £46 per kilogram of phosphate removed), depending on phosphate consent level when heavy metal consents are not imposed, and £23-£146 per kilogram of phosphate removed (at an average cost of £72 per kilogram of phosphate removed), depending on the phosphate consent level when heavy metal consents are imposed (Environmental Data Services, 2006d).

ViroFilter Technology has a price bracket of £23-£27 per kilogram of phosphate removed at small to medium-sized WwTPs, and thus appears to be cost-competitive with alternate chemical dosing methods.

The report concluded that ViroFilter provides a robust, low-maintenance means of achieving phosphorus removal to extremely low levels, with very competitive longevity of the system. It is easily fitted (or retro-fitted) to existing treatment systems, and achieves effluent total phosphorus concentrations of 1.0 mg/l - 2.0 mg/l. A ViroFilter Technology treatment system will operate effectively without the need for chemical dosing or influent pH adjustment. This removes the need for chemical handling and storage, and reduces operator intervention requirements, thereby reducing cost and risk. Its average operating cost of £25 per kilogram of phosphate removed also makes ViroFilter Technology cost competitive for small and medium-sized works, with a clear cost differential (particularly over chemical dosing) for works where the population equivalent is up to 10,000. ViroFilter

Technology's competitive phosphate removal costs and low maintenance requirements make it a robust and cost-effective solution to meet stricter discharge consents set for phosphorus by regulators.

This trial did not consider the SRP (only the TRP) and neither did it mention the volume of liquid being processed through the ViroFilter system. Clearly with the very large volume of water containing low SRP from the watercress farm, the HRT that was required to reduce the TP levels in this trial may not be feasible in the watercress situation.

A second study, an **Independent evaluation of Virofilter technology for enhanced phosphate removal** by the Water Research Council (2005) at a wastewater treatment works with the main objective to study the effect of influent pH and bed residence time on the extent of phosphorus removal capacity. This report is protected by copyright so can not be reported directly.

The trial used a submerged horizontal flow reed bed with influent flowing continuously in a horizontal path through a bed of gravel (3-6 mm) to the outlet. Beds were typically about 0.6 m deep and 10 m long. Horizontal-flow systems tend to be oxygen-limited and essentially remove organic matter by settlement and filtration. Their simple design and construction suit the topographies of most sites and they continue to find widespread use in the UK as a final polishing stage at small WwTW.

Selection of the media size was partly based on what had previously been used on the laboratory scale to enable a comparison of the results at the two different scales and also on reed beds which have media sizes between 2 and 12 mm. The majority of the media chosen for this project was A2 Bauxsol™ pellets (2-8 mm in size), except for the first 2 m of Reactor B, which was filled with pellets in the size range from 5-12mm.

The conclusions of this study were:

- While two different reactors were used operating between pH 6.5 to 6.8 and at 7.5, there was no difference in the P removal capacity.
- The target effluent level was 2 mg/l (from influent level of 7 mg/l) achieved initially in 4 hours HRT after 300 to 400 treated bed volumes but extended to 12 hours to maintain the target level for 6 months.
- An overall P removal efficiency of 80% was achieved.
- P removal capacity of the two reactors was 5.46 and 4.96 kg/tonne indicating durability of the media for 10 years. Up to 14 kg P/tonne media have been previously achieved by Virotec.
- The fertiliser value of the spent media requires further investigation.

The study suggested:

- Careful selection of the media materials and pore size is critical for optimum P removal efficiency based on operating environment. Suspended solids or organic matter in the water will need to be fully removed or will block the pores in the media material.

- The ideal media is dependant on pH with high pH favouring the use of calcium to precipitate calcium phosphate while at low pH, the use of Fe or Al will precipitate insoluble iron or aluminium phosphate.
- That the Bauxsol™ media has a high removal capacity, which exceeds the capacity of the other types of media namely calcite media (Arias *et al.*, 2003) with a P sorption capacity of about 2 kg P/m³, expanded clay (Mæhlum and Stålnacke 1999; Zhu *et al.*, 2003) at about 0.5 kg/m³ and sands/gravel (Rustige *et al.*, 2003) that while 50% of all the horizontal-flow units had an average P output concentration of less than 2.1 mg/l P, the vertical-flow units had an output concentration of 3.3 mg/l P.
- The durability for the Bauxsol™ media lasted considerably longer than the others reported.
- At the end of the media's working life, it can be crushed into powder suitable for disposal to agricultural land
- Suspended solids may be buffered for a period of about two weeks with initial removal of the larger size only while the smaller particles passed through. Up to 40 mg/litre of SS were removed.
- The optimum media and pore-size for Bauxsol™ pellets should be determined to gain maximum P-removal.

From these remark, it is clear that a customized media would be required specific to the levels of P (0.05 mg/l) that need to be addressed and the variations in pH while the quality of water leaving the settlement pond should contain limited suspended solids or organic matter. The report made no mention of the flow or volume of liquid being treated consequently the suitability of the technology for watercross discharges remains open.

Further to these two points, the largest issue that remains unresolved with Virofilter, is the HRT required to meet 0.05 mg/l from 2.00 mg/l where large volumes of water, ca. 5 million litres per day, need to be treated.

Environment for optimum adsorption capacity and properties

pH

The Virofilter would appear to operate efficiently irrespective of the pH but there is the need to have clarity on what the pH range will be when operating in order to allow accurate specification of the media to match the pH.

Alkalinity

There are no research studies to refer to on the effectiveness of ViroFilter where alkalinity has been measured before and after its use to determine impact.

Settlement rate

Not applicable.

Organic matter

Virofilter would appear to operate for a limited period (2 weeks) with up to 40 mg/l suspended solids without any detrimental effects on P adsorption removing larger particles only. However, where organic matter is suspended in the flow, this would need to be removed or will block the media filter. Back flushing of the system between high risk periods may remove solids attached to the media surface.

Temperature

Not considered in either report.

Environmental impacts

No adverse impacts reported. As the filter media varies according to the situation of use, there are no references to review.

BARACLEAR (trade name and US distribution company AquaBlok)

A commercially available product in the UK, sold predominantly for garden fish ponds to reduce green water and string algae by locking up available phosphate in the water column and pond sediment. In the US, it is sold by AquaBlok for industrial sediment restoration projects as a remedial cap or liner where it has EPA approval.

For many projects, AquaBlok use generally involves applying dry masses of the product through water and across the surface of contaminated sediments. In a matter of days, a homogeneous and relatively cohesive, low-permeability cap, or barrier, is formed between contaminated sediments and the overlying water column and its inhabitants. Barrier thickness will depend on a number of factors, including: type of formation, water depth and salinity, application thickness, number of lifts applied, and sediment characteristics. AquaBlok can also be used as a hydraulic/chemical barrier to the movements of water- or sediment borne contaminants into underlying groundwater resources, or to minimize leaching losses of water from reservoirs or wastewater discharge basins.

Physical and chemical properties

BARACLEAR consists of an alum polymer (aluminium sulphate or potassium aluminium sulphate) and calcium carbonate core wrapped in a clay-based bentonite outer shell. The product has the appearance of small pebbles, the size of which can be varied according to the settlement rate required. The formulations prepared ranged from a relatively bentonite-rich product (70% bentonite plus 30% aggregate (alum), referred to as 7030 FW) to a much leaner formulation (20% bentonite plus 80% aggregate, referred to as 2080 FW).

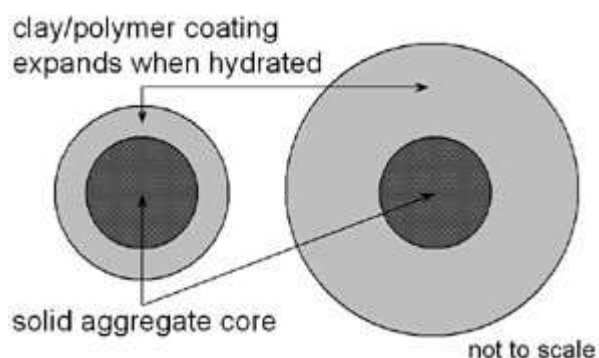


Fig 14. Diagram of Baraclear granule

Other types of clay materials, including attapulgite, can be incorporated into the product for saline applications. Likewise, a large variety of other minerals or materials (such as organo-clays, gypsum, zeolites, elemental sulphur, oxides, zero-valent iron, organics, sand, seeds, fertilizer, etc.) can also be incorporated to meet particular site- or project-specific needs.

Alum is commonly used for phosphorus control, due to its low metal to phosphorus ratio, required for formation of a precipitant. Theoretically, the ratio by weight of aluminum metal to soluble reactive phosphorus expressed as elemental phosphorus (P) is 0.87 ppm Al: ppm P.

Alum additions enter the water column where the aluminum ions bond with phosphate in solution, resulting in aluminum phosphate becoming insoluble in water and sinking to the pond bottom. Since the majority of the free phosphorus resides on the bottom (in the sediment), powder and liquid treatments primarily address phosphorus in the water column, but not directly at the primary source. The remaining untreated phosphorus on the bottom will continue to enter the water column over time. However, the goal of the BARACLEAR treatment is to deliver the active ingredient (alum) to the sediment on the bottom, where it can effectively bind the phosphorus.

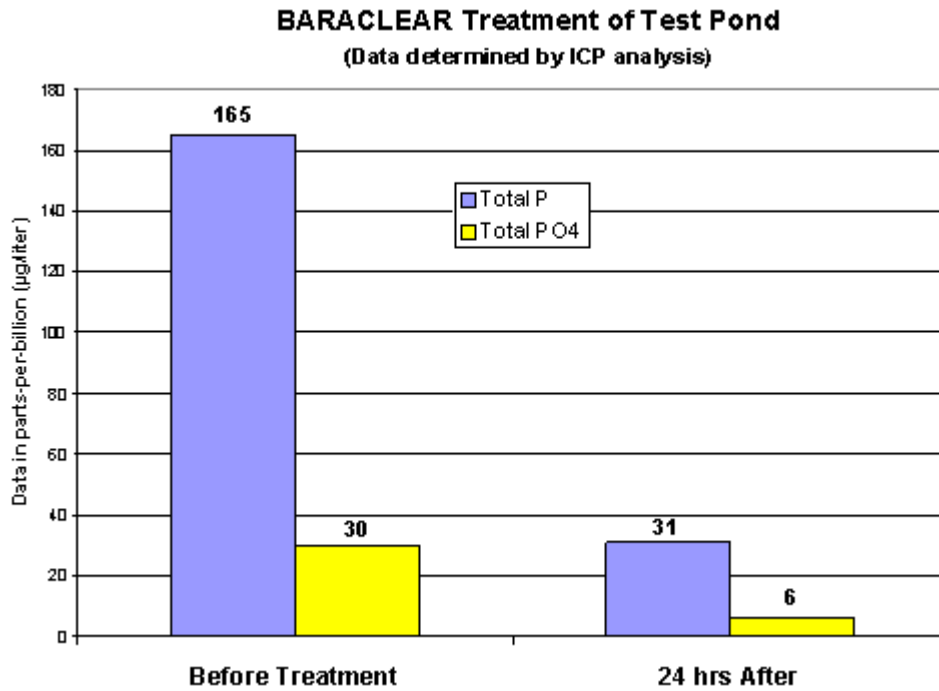


Fig 15. Baraclear phosphorus removal in water.

Smaller particles tend to carry relatively higher percentages of clay than larger particles, particularly for relatively clay-rich formulations. This is also an artefact of the manufacturing process. For any formulation, smaller particles tend to be somewhat less dense than larger particles. This is because of the presence of higher proportions of the relatively less dense clay. This apparent relationship between particle size and density is generally accentuated in bentonite-rich formulations in which relatively greater percentages of each particle size are comprised of clay rather than aggregate.

BARACLEAR retains 99% of its particle integrity for several minutes in the water column (allowing it to travel all the way to the sediment floor) and, due to the cohesive properties of the clay additives, the active ingredients will remain available at the sediment/water interface to combat phosphorus cycling. Each particle contains the highest quality sodium bentonite products available on the market (originating from mines in Wyoming).

Case studies of P removal

Case studies of AquaBlok tend to major on its application for sediment capping where contamination has occurred and a clay cap is required. Numerous studies are available for alum as a phosphate stripping agent in still waters but the pH, alkalinity and CaCO₃ conditions are not similar to the conditions on watercress farms.

The performance of alum is compared with Phoslock (lanthanum encased in a bentonite clay) (Haghseresht, 2004). In this assessment, the physiochemical properties of the water

requiring to be cleared need to be carefully considered. The author asserts that when alum is added to water, hydrogen ions are released lowering the pH and potentially leading to the formation of toxic Al^{3+} . This is unlikely to happen with the level of alkalinity at 120 mg/l and the pH approximately 7.8. Further, the alum in the Baraclear material is buffered to prevent any drop in pH. Other issues related to toxic effects on surface biota are not relevant due, to pH buffering.

If the pH rises to above 10, intensive re-suspension of alum can increase the risk of P being released from the sediment in lakes less than 2 m depth (Van Hullebusch, 2002) and also in Lake Süsser in Germany (Lewandowski *et al.*, 2004) in a long term study of the effects of P reduction by alum. The literature would also indicate this phenomenon can also occur with Phoslock, although not reported (Haghseresht, 2004).

Environment for optimum adsorption capacity and properties

pH and alkalinity

For optimal results, the recommended water pH should be between 6.5 and 8.0, with an alkalinity of 50-200 ppm prior to product application. This is similar to the characteristics of water found on watercress farms. Despite the calcium carbonate buffer around the aluminium sulphate, a pH drop in the water is possible, suggesting that four to six weeks should lapse between treatments.

Settlement rate

Smaller BARACLEAR particles tend to settle slower than larger particles (Table 9). This is because smaller particles have lower densities and higher surface-area-to-mass ratios than larger particles.

Table 9. BARACLEAR particle average settling

Size fraction (inches)	Velocity (ft/sec)
1.00 – 0.75	1.94
0.75 – 0.38	1.55
0.38 – 0.19	1.03
0.19 – 0.08	0.72

Organic matter

In order to study the effect of dissolved organic matter on the P removal capacity of alum, Omoike & Vanloon (1999) chose tannic acid as a model compound. The P-removing capacity of alum in a number of solutions containing different amounts of tannic acid was then measured (using an Al:P ratio of 1:1). The performance of alum was reduced dramatically in the presence of tannic acid, with an increase in tannic acid from 4 to 14 ppm leading to a reduction in P removal from 50 to 10%. The authors attribute the observed results to the increase in the solubilisation of aluminium in presence of the organic matter. This view is also supported by other researchers (Van Hullebusch, 2002).

As a number of factors such as the organic matter content of the water can affect the Al(OH)_3 floc formation, the required Al:P ratio can vary from one application to another. This is further complicated by the number of different aluminium phosphate species that are possible. Haghseresht suggests a number of different molar ratios have been found. For example, Lewandowski *et al.* (2003) investigated Lake Süsser in Germany, which was treated almost annually with alum from 1977 to 1992. These studies showed that the molar ratio of added aluminium to additionally bound phosphorus was 2.1:1.

Conversely, Rydin *et al.* (2000), in a study of the sediment of the alum-treated Washington Lake, found that the ratio of the added Al to Al-P was 11:1 by weight, which would translate into 12.7:1 by molar ratio. The author proposed a 'jar test' be undertaken on each batch of water to determine the dose of alum before application. He points out that continuous application of alum to certain lakes to reduce P concentrations failed due to inaccurate dose applications and that a considerably higher weight of alum is required compared with Phoslock to have the same effect.

Addition of aluminum to wastewater in the presence of tannic acid forms aluminum hydroxyphosphate, hydroxy-alumino-tannate, and aluminum complexes containing both phosphorus and tannic acid. Tannic acid, as well as other organic matter, inhibits phosphorus removal. The extent of inhibition increases with increasing concentrations of organic matter. When aluminum is exposed to tannic acid, the organic matter coats the surface of the inorganic solid, preventing adsorption of phosphorus. It should be advantageous to add an alum treatment at the end of the cleaning process for harvesting more phosphorus when concentrations of organic matter are relatively low (Ozacar and Sengil, 2003).

Temperature

Haghseresht makes claim that there is a substantial reduction in P adsorption with reduced temperature when alum is used but cites no references to back this assertion.

Environmental impacts

The Materials Safety Data Sheet (MSDS) provides the following information on alum (aluminium sulphate) provided by General Chemical (US):

Ecological information

14 ppm/36 hr./fundulus/fatal/fresh water;

240 ppm/48 hr/mosquito fish/TLm/water type not specified;

TLm Mosquito fish, 235 ppm, 96 hours;

LC50 Large mouth bass, 250 ppm, 96 hours

Table 10. Ecological data of aluminium sulphate

Component	Freshwater fish	Freshwater flea
aluminum sulphate	LC50= 37 mg/l <i>Gambusia affinis</i> 96 h	EC50 = 136 mg/l 15 min
	LC50= 100 mg/l <i>Carassius auratus</i> 96 h	

Based on the limited dataset, alum is relatively non-toxic to fish. The test species are indicative only and would often be more than one species. The test durations are standard. There is no data on aquatic invertebrates, which may respond differently.

Claims by AquaBlok

AquaBlok make the following claims for BARACLEAR over both alum and non-alum based alternatives:

- BARACLEAR is non-toxic, with all its ingredients approved for use in water systems – no specialized safety equipment (beyond gloves to protect against possible mild skin irritation) is necessary during material handling – refer to MSDS for details
- Due to its coated and durable particle structure, BARACLEAR is easily transported and handled – its dry, stable state also dramatically reduces dust during handling and application
- The product is designed to be surface applied and can be readily broadcast without mixing tanks, injection, or any specialized equipment

- BARACLEAR mitigates suspended organic and inorganic materials that are the primary contributors which produce turbid or "murky" waters
- Product application does not leave significant suspended sediment in the water column
- The product can be used by informed water managers to directly target internal load phosphorus and suspended organic and inorganic colloidal material in water bodies up to 50 feet in depth
- BARACLEAR can be used in relatively high-energy flow regimes (e.g. canals, ditches, or streams)

Costs

Price quoted by Pulstronic is £2,800 per tonne. Reactivity is dependent on existing water chemistry. Historical data suggests that optimal results can be achieved when pre-treatment pH falls between 6.5 and 8 and alkalinity falls between 50 and 200 ppm (or mg/l CaCO₃). Dose suggested by AquaBlok is 0.3 kg/5000 litres water but there is no indication of the adsorption capacity this will provide or in what range. Dosing 3.5 million litres water per day, 210 kg per day, using would cost £ 588. Exactly how much P would be removed has not been calculated.

Summary

In the absence of replicated and widely reported independent scientific trials on Baraclear, this hampers widespread use on watercress farms. However, as levels of organic matter after bed clearing can be high, it suggests that Baraclear is not the ideal product, when compared with, for example, Phoslock as an alternative dosing material. There are also concerns over its optimum pH range, which suggest that 7.8 may be too high.

List of abbreviations

AA	Activated aluminium oxide
BOD	Biological oxygen demand
COD	Chemical oxygen demand
CW	Constructed wetland
DOC	Dissolved organic carbon
DP	Dissolved phosphorous/phosphate
DW	Dry weight
EA	Environment agency
EBPR	Enhanced biological phosphorous removal
EPA	Environmental protection agency (US)
FFP	Free floating plants (type of wetland)
FRP	Filterable reactive phosphorous
FWS	Free water surface (type of wetland)
GFH	Granulated ferric hydroxide
HAIX	Hybrid anion exchanger
HD	Habitats directive
HRT	Hydraulic residence time
HSSF	Horizontal sub-surface flow (type of wetland)
LA	Lanthanum
MSDS	Materials safety data sheet
OM	Organic matter
OP	Orthophosphate
P	Phosphorous/phosphate
PP	Particulate phosphate
PSC	Particle size coefficient
REE	Rare earth element
SRP	Soluble reactive phosphorous

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SS	Solid substances
STW	Sewage treatment works
TP	Total phosphorous/phosphate
VSSF	Vertical sub-surface flow (type of wetland)
WFD	Water framework directive
WTR	Waste water treatment residual
WW	Waste water
WWTW	Waste water treatment works

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