1   # Guiding principles for the development and application of solid phase

2   # phosphorus-adsorbents for freshwater ecosystems

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21 **Abstract**

22 While a diverse array of phosphorus (P)-adsorbent materials is currently available for application to

23 freshwater aquatic systems, selection of the most appropriate P-adsorbents remains problematic. In

24 particular, there has to be a close correspondence between attributes of the P-adsorbent, its field

25 performance, and the management goals for treatment. These management goals may vary from a

26 rapid reduction in dissolved P to address seasonal enrichments from internal loading, targeting

27 external fluxes due to anthropogenic sources, or long term inactivation of internal P inventories

28 contained within bottom sediments. It also remains a challenge to develop new methods and materials

29 that are ecologically benign and cost-effective. We draw on evidence in the literature and the authors'

30 personal experiences in the field, to summarise the attributes of a range of P-adsorbent materials. We

31 offer 'guiding principles' to support practical use of existing materials and outline key development

32 needs for new materials.

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1. Introduction

Persistent eutrophication is a response to nutrient enrichment that often arises from anthropogenic modifications to catchments of freshwater systems (Smith 2003; Oliveira and Machado 2013; Zamparas and Zacharias 2014). The deleterious effects of eutrophication may include: changes in phytoplankton community structure, often leading to blooms of toxin-producing species, loss of aquatic habitat, fish kills, large releases of phosphorus (P)from bed sediments associated with anoxia, degradation of water quality, and loss of visual and social amenity (e.g. Nikolai and Dzialowski2014).

There is vigorous debate about the role of nitrogen (N) and P in limiting phytoplankton biomass in order to control eutrophication in freshwater systems. In the context of the applications of P adsorbent materials we provide a brief overview of this debate. Schindler et al. (2008) used a 37-year study on Lake 227 (Ontario, Canada) to conclude that P reduction should be the focus of efforts to manage eutrophication. The central tenet of their argument was that N fixation by cyanobacteria made up for N deficits at the system (lake) scale.Several subsequent publications have reinforced this viewpoint (Schindler 2008; Carpenter 2008; Patterson et al. 2011; Schindler 2012). Alternatively, Scott and McCarthy (2011) disputed the analysis of data that led to the original conclusions of Schindler et al. (2008) and a number of authors present arguments that N deficits are not necessarily compensated for by N-fixing cyanobacteria in eutrophic systems (e.g., Howarth and Paerl 2008; Conley et al. 2009). The proliferation of N-fixing cyanobacteria is often associated with the presence of anoxia in bottom waters, which enhances both P release from bottom sediments and N losses from denitrification (e.g., Downing and McCauley 1992, Dodds et al. 2002; Smith 2003; Ma et al. 2015), resulting in low water column N:P ratios (e.g. Bergstrom et al. 2015).

What is clear is that effective eutrophication management demands that both external supply as well as internally stored nutrients be tackled (Cooke et al. 2005). The latter has been most effectively achieved by the application of P adsorbent materials. In many cases phytoplankton growth limitation cannot be attributed solely to one nutrient, and co-limitation or switches in the limiting nutrient have been observed amongst different phytoplankton assemblages (e.g. Burger et al. 2007; Muller and Mitrovic 2014), over time scales such as seasons (Muhid and Burford 2012; Kolzau et al. 2014;

65   Trochine et al. 2014, Xu et al. 2015) or with location within a single system (Abell et al. 2014). Here

66   we recall Liebig's barrel – a barrel illustration published in 1903 by Hans Arnold von Dobeneck –

67   which visualizes that once the limitation of one element is lifted, another element becomes limiting

68   (Gröger 2010). Indeed, it is obvious that dual N and P enrichment can boost phytoplankton biomass

69   more than only single N or P addition. Put simply, all elements are needed in abundance to supply the

70   building blocks necessary for sustaining phytoplankton production. If stores remain sufficiently

71   elevated for a period of time, the consequence will be eutrophication. It is not necessary to control all

72   the nutrients that are in abundance. In fact, it is efficient to control only one element to prevent

73   excessive phytoplankton proliferation and blooms. Mitigation aimed at the external nutrient supply,

74   unfortunately, may not be especially effective in the short-term because of the need to mitigate

75   legacies of nutrients in the bottom sediments.

76   In many cases, internal loading of nutrients from bottom sediments may be sufficient to support

77   elevated phytoplankton biomass and delay return to an earlier pre-eutrophication state (Marsden 1989;

78   Jeppensen et al. 2005). The nutrient inventory contained within bottom sediments can be substantial,

79   and a sustained reduction in nutrients derived from both internal and external loading, is generally

80   required, irrespective of seasonal or persistent N, P or N+P limitation. Xu et al. (2015) suggest that

81   reducing nutrients to below a threshold concentration can still be cost-effective and manageable even

82   when it may not be possible to restore a system to its pre-human-impact status (i.e. reference state)

83   because of such legacies. Specifically, they claim that "61−71% TN and 20−46% TP reduction are

84   necessary to bring [Lake] Taihu's phytoplankton biomass to "acceptable" sub-bloom conditions of

85   less than 20 μg L^{-1} chlorophyll-a". Such reductions are already challenging in themselves, but in 2009

86   atmospheric N deposition in Jiangsu province (where Taihu is located) was 4890 kg N km^{-2} $year^{-1}$

87   (Han et al. 2014). Consequently, the 11,000 tonnes N $year^{-1}$ from atmospheric deposition is substantial

88   in relation to the estimated 46,000 tonnes N $year^{-1}$ derived from river inflows (Xu et al. 2015).

89   Therefore, it seems highly unlikely that the suggested N load reduction can be realized. In contrast, P

90   control may be more feasible. The bioavailability of P can be reduced to a point where it limits algal

91   growth (Douglas et al.in press; Waajen et al.in press). This inactivation can be accomplished through

92   formation of salts with varying degrees of solubility, including with aluminium, calcium, iron,

93   lanthanum or other metals, while such immobilization for nitrogen is generally not possible. Also,

94   based on its relative abundance in phytoplankton and in water, P-reduction is the single logical target;

95   the Redfield ratio (P:N:C is 1:16: 106) shows that P limitation is likely to be stoichiometrically the

96   most efficient mechanism to achieve limitation as ratios of P:C in the water are generally considerably

97   lower than the Redfield ratio.

98   Addressing P legacies is critical (e.g., Jarvie et al. 2014), and could be aided by the development of a

99   "tool box" of complimentary nutrient mitigation or intervention strategies. A major component of this

100   tool box may be the use of solid-phase P-adsorptive[1]or flocculation materials to reduce bioavailable P

101   concentrations, either directly in the water column or indirectly via reductions in P release from the

102   bottom sediments to the overlying water. Use of P-adsorptive materials is one of the commonly

103   deployed 'geoengineering' approaches (*sensu* MacKay et al. 2014) to manage internal nutrient

104   loading. In this review we examine current applications of a range of solid-phase P-adsorptive

105   materials and discuss guiding principles for their development and application in freshwater

106   ecosystems. We acknowledge the development of these materials is rapid and will therefore not

107   provide a complete coverage of all P-adsorptive materials. Instead we focus on those with an

108   established body of laboratory and/or field based evidence.

109   Over the past 50 years, a range of amendments has been applied to freshwater aquatic systems in an

110   attempt to manage internal Ploading on an intra- to inter-annual basis (Douglas et al. 2004). Initially,

111   dissolved chemical reagents were directly applied to a waterbody, and most commonly included alum

112   or Al-containing compounds and nitrate-containing compounds that are briefly discussed here as a

113   prelude to the discussion on solid P-adsorbents.

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[1] For consistency we have used the term "P-adsorptive" throughout to describe P-uptake, however, it is recognised that many materials may be either P-adsorbents (surface complexation/binding or precipitation) or P-absorbents (internal/intra-particle binding), or a combination thereof when more than one mechanism is operative. It is also recognised that the nature of P-uptake and occupancy/speciation, particle size or association may change over time (e.g. due to processes such as internal diffusion, crystal overgrowths or Ostwald ripening).

114   The use of alum to reduce concentrations of soluble phosphorus in aquatic systems appears to have

115   been first suggested by Lund (1955), with the first documented application occurring in a Swedish

116   lake (Jernelov 1971). Since that time alum or similar aluminium based amendments (*e.g.* aluminium

117   hydroxide, Browmanet al. 1977) have been applied to a number of aquatic systems, in particular lakes

118   in North America (*e.g.* Cooke and Welch 1993) in an attempt to control both algal and macrophyte

119   biomass (*e.g.* Haumann and Waite 1978;Wolter 1994). These applications continue in both Europe

120   and North America despite concerns over toxicity associated with either the application or the re-

121   release of applied Al (Reitzel et al. 2013) or changes in ecosystem function (e.g. Nogaro et al. 2013).

122   An alternative to alum has been the use of nitrate salts, most often ferric nitrate or calcium nitrate

123   injected into bottom sediments to increase redox status (via nitrate) and provide P-binding metal

124   cations (Fe or Ca). This technique was initially developed in the mid 1970s (Ripl, 1976, 1994; Ripl

125   and Lindward 1978) as a method to oxidise the upper layers of bottom sediments using calcium

126   nitrate. The calcium nitrate injection technique which is also known under various commercial names

127   *e.g.* 'Riplox' (Europe) and 'Limnofix' (North America), has been applied to a number of lakes,

128   particularly in Europe (*e.g.* Bjork 1988; Søndergaard et al. 2000; Yamada et al. 2012) with varying

129   degrees of success.

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131   **2.   A brief review of P-adsorptive materials for application in freshwater aquatic systems**

132   Several studies document different P-adsorptive materials and techniques that may be used to bind P

133   in the water column or to intercept the P that might arise from internal loading, or scavenge dissolved

134   P from the water column (e.g. Robb et al.2003; Douglas et al. 2004; Egemose et al. 2010, Gibbs et al.

135   2011, Pan et al.2012; Spears et al. 2013). In general, P-adsorptive materials applied in standing

136   waters, including constructed wetlands, can be divided into four categories (Table 1, modified after

137   Douglas et al. 2004):

138   •   naturally occurring minerals, soils, suspended particles or earth materials;

139   •   natural or synthetically produced materials;

140 • modified clay mineral or soils; and

141 • mining, mineral processing and industrial by-products.

142 Most P adsorbents with substantial uptake capacity are generally enriched in Ca, Fe and/or Al or a

143 combination thereof, however, it has also been demonstrated that rare earth elements, in particular

144 lanthanum (La), the most abundant, non-redox-sensitive rare earth element, may also form strong

145 associations with P (Firsching and Brune, 1991; Douglas 1997, 2002; Robb et al. 2002; Yuan et al.

146 2009). In the last decade, and nearly 20 years after the development of La-modified bentonite for P

147 adsorption, a large number of studies have sought to exploit the utility of La-modified materials or La-

148 bearing compounds to remove P from natural aquatic ecosystems (Table 1).

149 Interactions of Ca, Fe, Al or La-bearing materials with P may involve a number of geochemical

150 associations. These include the formation of discrete secondary minerals, ion exchange via surface

151 adsorption, internal ion exchange, or the formation of less well-defined associations such as complex

152 multi-component surface adsorption or precipitation processes (e.g. Booker et al., 1999; Douglas et al.

153 2004). Many of these associations may also change over time due to diffusion or recrystallization.

154 Confounding the uptake of P, however, may be the presence of interfering species including simple

155 (e.g. carbonate) or complex polyelectrolyte anions (e.g. dissolved organic carbon). A detailed

156 summary (modified after Douglas et al. 2004) of the four main groups of P-adsorbent materials is

157 given below and in Table 1.

158 *2.1. Naturally occurring minerals, soils, suspended particles or earth materials*

159 **2.1.1 Carbonates**

160 A range of carbonates including limestone, dolomite and magnesite has been investigated for the

161 uptake of P from natural and wastewaters (Shilton et al.2005; Karaca et al.2006; Mateus et al. 2012;

162 Jaouadi et al. 2013; Xu et al. 2014). As a consequence, carbonates or lime have been extensively

163 tested in the removal of soluble P from both natural (*e.g.* rivers: Jack and Platell 1983; Futaedaniet et

164 al. 1992, lakes or other impounds: Prepaset et al. 1990) and waste waters (*e.g.* piggery effluents:

165 Takeuchi and Komada 1998), stormwaters (Babinet al. 1989), soils (Anderson et al. 1995), and

166   wetlands (Drizoet et al. 1999; Arias et al 2000; Vohla et al. 2011; Mateus et al. 2012). In addition to

167   carbonate, calcined derivatives such as partially calcined dolomite (Roques et al. 1991) and granular

168   magnesia clinker (Kaneko and Nakajima 1998; Suzuki and Fuji 1988) and calcined magnesia

169   (Wendling et al. 2012) have also been assessed as substrates for P removal.

170   **2.1.2 Soils, sands and suspended particles**

171   Phosphorus adsorption to soils, particularly in an agricultural context, has been the subject of

172   extensive research for a number decades (Bray and Kurtz 1945; Barrow 1970, 1999), however, a

173   more recent focus has been on the utilisation of these material to remove dissolved P from natural

174   and wastewaters (Arias et al. 2000; Degens et al. 2000; Kim et al. 2014; Dai and Pan 2014: Pan et al.

175   2002, 2013). A range of P uptake capacities reflect the mineralogical and physico-chemical

176   heterogeneity of the soils used. The most adsorptive soils are generally enriched in one or more of

177   Ca-, Fe- or Al- bearing mineral phases. Arias et al. (2000) concluded that Ca was the most important

178   parameter in determining P uptake by sands, presumably due to the precipitation of calcium P phases

179   including apatite, however, under more moderately acidic conditions Fe and Al were also important

180   in P-uptake and precipitation reactions. More recently, chitosan-modified soils or cationic starch

181   modified soils have been investigated, although the focus has been on the flocculation of

182   cyanobacteria (and P contained therein) in lakes (Pan et al. 2006, 2011; Shi et al., 2015). However, it

183   is likely that these chitosan-modified soils may also simultaneously remove substantial P (e.g. Chung

184   et al. 2005; Dai et al. 2011). A similar study focusing on the removal of cyanobacteria using

185   polyaluminium chloride (PAC) or chitosan and a red soil collected on the banks of a eutrophic

186   reservoir in Brazil showed P adsorption maxima of 3.0 mg P g^{-1}soil under oxic and 0.5 mg g^{-1}under

187   anoxic conditions in ultrapure water (Noyma et al. 2015).

188   *2.2. Natural or synthetically-produced materials*

189   **2.2.1.   Allophane and imogolite**

190   Both allophane and imogolite occur in nature as secondary aluminosilicate minerals in soils (*e.g.*

191   Farmer and Russell 1990; Barrealet al. 2001; Moro et al. 2015) and can also be synthetically

192 produced (Wada 1989; Denaixet al. 1999). A high P-uptake capacity for allophane and imogolite has

193 been demonstrated in laboratory studies. Uptake can vary strongly as both a function of pH and

194 salinity. Optimal P-uptake is typically near pH6 while above pH9 P-uptake is minimal, with cation

195 uptake (e.g. Na, Ca) the predominant reaction (*e.g.* Wada 1959; 1980) as a result in changes in

196 surface charge with pH. Studies of the plant availability of P adsorbed to allophane suggest that the

197 initially adsorbed P, or that bound for an extended period, might not be bioavailable, although later-

198 bound P may become available (Parfitt et al. 1982, 1989). The ability of allophanic soils to retain P

199 has been documented by Degenset al. (2000). This study revealed that 91% of the P in a dairy

200 effluent applied to allophanic soils (*ca.* 1-12% allophane) over a period of 22 years was retained in a

201 75cm depth profile, with 81% retained within the upper 25cm.

202 **2.2.2. Fe-Al (oxy)hydroxides**

203 Numerous studies over many decades have documented the adsorption of P to both Fe- and Al-oxides

204 and (oxy)hydroxides in soils and sediments (Parfitt 1989; Goundaret al. 2014; Bakenet al. 2015) and

205 synthetically prepared materials (McLaughlin et al. 1981, Borggaard 1983, 1990). Some Fe- and Al-

206 oxides may also form a solid solution series such as Al in goethite, or amorphous oxides. In light of

207 this often close association of Fe and Al in nature, their mineralogical similarity and their common

208 evaluation as P adsorbents, Fe- and Al-oxides and oxyhydroxides are discussed together. The most

209 common Fe-oxides that occur in soils are goethite and ferrihydriteand both may contain significant

210 concentrations of other elements such as Al and Si, respectively. Many other types of oxide may also

211 occur in nature and as part of industrial wastes such as haematite and magnetite, which have a range

212 of P uptake capacities. Gibbsite is the most widely occurring Al-oxide in soils and bauxite deposits

213 (Hsu 1989). Studies of Fe- and Al-oxides in soils suggest that P is predominantly associated with Fe-

214 oxides at concentrations 4-20 times greater than that of Al-oxides (Norrish and Rosser 1983). In

215 contrast, comparative studies of the adsorption of P on synthetic Fe- and Al-oxides consistently

216 indicate that Al-oxides have a substantially higher P uptake capacity (*e.g.*Borggaard 1983). An

217 approximate order of P adsorption to Fe- and Al-oxide minerals is Al-gel > Fe-gel >>, haematite,

218 goethite, magnetite > gibbsite. This order of P adsorption may also be dependent on factors such as

219 particle size, age, drying, degree of crystallinity of particular minerals and pH, ionic strength, the

220 period of P adsorption and initial P concentration (*e.g.* Bolan et al. 1986). Iron oxides derived from

221 industrial processes such as the Bayer process (red mud) and mineral sand processing have also been

222 evaluated as P adsorbents (e.g. Douglas et al. 2012; Wendling et al. 2012, 2013).

223 **Hydrotalcites**

224 Hydrotalcites are layered double hydroxides most commonly formed by the co-precipitation of

225 divalent (*e.g.* Mg^{2+}, Fe^{2+}) and trivalent (Al^{3+}, Fe^{3+}) metal cation solutions at high pH (Taylor 1984;

226 Vucelic et al. 1997; Shin et al. 1996). Hydrotalcites occur naturally as accessory minerals in soils and

227 sediments, but may also be synthesised such as from industrial waste materials by the reaction of

228 bauxite residue (red mud) with seawater (*e.g.* Thornber and Hughes 1987), by the reaction of lime

229 with fly ash (*e.g.* Reardon and Della Valle 1997) or from wastewaters (Douglas 2014). A number of

230 studies have been conducted to investigate ways to exploit the anion exchange properties of

231 hydrotalcites. These studies have focussed on the removal of P and other oxyanions and humic

232 substances from natural and wastewaters (Miyata 1980; Misra and Perrotta 1992; Shin et al. 1996;

233 Seida and Nakano 2000). A major obstacle to the use of hydrotalcites for P removal in natural and/or

234 wastewaters is the selectivity for carbonate over P, with a selectivity series in the approximate order

235 $CO_3^{2-} > HPO_4^{2-} >> SO_4^{2-}$, $OH^- > F^- > Cl^- > NO_3^-$ (Miyata 1983; Shin et al. 1986; Cavaniet al. 1991).

236 Many hydrotalcites are also synthesised with carbonate as the predominant anion and thus require

237 anion exchange before they can be used as P-adsorbents. When carbonate is also combined with

238 sulphate, nitrate and chloride (as might commonly occur in natural or wastewaters) the reduction of

239 P adsorption to the hydrotalcite is further decreased (Shin et al. 1996).

240 *2.3. Modified clay mineral or soils*

241 **2.3.1. Expanded/thermally treated clay aggregates**

242 Expanded clay aggregates, where clay interlayers are expanded or exfoliated via heating, have been

243 extensively investigated in laboratory and constructed wetland systems, to evaluate their potential for

244 P-uptake (*e.g.* Johansson et al. 1995). The P uptake capacity of expanded clay aggregates is mostly

245 determined by the Ca concentration (Zhu et al. 1997), with the adsorbed P probably precipitating as

246 hydroxyapatite (Zhu 1998). Alternatively, thermally-treated palygorskite has also been demonstrated

247 to be an effective P-adsorbent in aquatic systems (e.g. Gan et al, 2009; Yin et al., 2013).

2.3.2.   Rare earth modified clays, zeolites and soils

249 Rare earth element (REE)-modified clays such as lanthanum (La)modified bentonite were initially

250 developed in the 1990s as a method to remove dissolved P from the water column and also to form a

251 reactive layer of bottom sediments to intercept and bind P released from underlying sediments

252 (Douglas 2007, 2007; Douglas et al. 2004, 2008;Robb et al. 2003). Extensive laboratory testing

253 demonstrated that in the presence of a strong oxyanion such as P, a stable mineral (LaPO$_4$.nH$_2$O –

254 rhabdophane) is formed (Douglas et al. 2000). This mineral is an analogue of other REE-P minerals

255 that were demonstrated to be resistant to weathering over geological time. Other studies suggested that

256 the newly precipitated rhabdophane is resistant to microbial attack from endemic sediment micro-

257 organisms at least in the short-term (days to months, Douglas et al. 1997). A study on sediments from

258 ten La-modified bentonite-treated lakes again demonstrated formation of rhabdophane (Douglas et al,

259 2000) and slow transition to the extremely stable mineral monazite (Dithmer et al. in press). Large-

260 scale field trials of lanthanum-modified clays suggest that they are effective in capturing a substantial

261 proportion of P released from bottom sediments when applied as a thin (*ca.* 1mm) reactive capping

262 (Douglas and Adeney 200l). Following on from the development of rare earth modified clays, similar

263 materials which incorporate lanthanum into an aluminosilicate matrix, including lanthanum modified

264 vermiculite, zeolite, and soils, have been synthesised and evaluated (Huang et al. 2014; Yuan et al.

265 2009; Ning et al. 2008).

266 *2.4. Mining, mineral processing and industrial by-products*

2.4.1.   Red mud/sand

268 The global inventory of red mud is estimated to be in excess of 2.7 billion tonnes, with an annual

269 increment of 120 million tonnes (Klauber et al. 2009; Pontikes and Angelopoulos, 2013). Red mud

270 has frequently been demonstrated to bind P from effluent or in soils. The degree of adsorption may

271   be strongly affected by pH (*e.g.* see Barrow 1982) and the amount of gypsum added to the red mud

272   as an amendment. This high affinity for P reflects the presence of high concentrations of Fe-

273   oxyhydroxides and/or Alspecies in the red mud, although little research has been undertaken to

274   elucidate the exact mechanism of P retention. Extensive field and laboratory trials have been

275   conducted with native red mud (or amended derivatives). Red mud has also been tested for its ability

276   to reduce P from aqueous solutions (Shiao and Akashi 1977) and from drain water (Ho and Mathew

277   1993). An inherent characteristic of red mud is that it is strongly alkaline as a legacy of the Bayer

278   process and thus, is usually neutralised (amended) prior to experimental use. This treatment, most

279   frequently with gypsum, may significantly increase the P adsorption capacity of red mud. However,

280   red mud may also contain high concentrations of dissolved salts that may have to be removed for

281   particular applications by washing. In addition, untreated and/or amended red mud may contain

282   substantial concentrations of chemically leachable or water extractable P (Ho and Mathew 1993).

283   The mixing of red mud with seawater, the lowest cost and most readily available material for

284   neutralization, results in the formation of hydrotalcites (Thornber and Hughes 1987). Extensive

285   testing of red mud, and in particular seawater-neutralised red mud, indicates that it may have some

286   P-uptake capacity but this is often reduced in the presence of bicarbonate (e.g. Wang et al, 2008).

287   **2.4.2. Slags**

288   A range of slags as P absorbents, including blast furnace slag, and related slags such as basic oxygen

289   furnace (BOF) slag and electric arc furnace slag (EAF), has been investigated extensively over the

290   past three decades (Yamada et al. 1986; Baker et al. 1998; Johansson and Gustafsson 2000;

291   Wendling et al. 2012). Blast furnace slag may occur in both crystalline and amorphous forms and is

292   principally composed of silica, aluminium derived from the parent iron ore with appreciable Ca

293   derived from the flux. The large proportion of CaO, and sometimes MgO, results in an alkaline slag,

294   which may impart a pH of between *ca.* 8-11 in leachates (Proctor et al. 2000) and when used in

295   laboratory and field trials (*e.g.* Johansson 1999; Drizo et al. 2002). Possible applications that have

296   been investigated at either laboratory or field scale include the capture of P released from bottom

297   sediments (Yamada et al. 1987), and as a substrate to enhance the P uptake capacity of constructed

298 wetlands (*e.g*. Mann and Bavor 1993; Sakadevan and Bavor 1998). Most studies have identified the

299 formation of Ca-P minerals such as hydroxyapatite as the predominant form of adsorbed P (*e.g*.

300 Johansson and Gustafsson 2000; Drizo et al. 2002).

301   2.4.3.   NUA

302 Neutralised Used Acid (NUA) is a by-product from the production of synthetic rutile from ilmenite,

303 formed by using sulphuric acid to leach impurities from ilmenite. The spent acidic wastewater is then

304 neutralised with quicklime to form NUA. This reaction results in an intimate mixture of Fe-

305 (oxy)hydroxides and related Fe-minerals (~30-35%), and gypsum (~60%), with minor quartz (~5%)

306 also present, with a high surface area, and a range of surfaces potentially amenable to P-uptake. A

307 long-term (ca. 1500 day) study using NUA as a 5% soil amendment demonstrated a 97% reduction

308 in leachable P. Observations of on-going gypsum dissolution from the NUA has likely resulted in the

309 formation of Ca-P minerals including apatite, whilst fine-grained Fe-(oxy)hydroxides also acted as a

310 substrate for P-adsorption (Douglas et al. 2012).

311 2.4.4. Coal Fly Ash

312 Coal Fly Ash (CFA) is produced in large quantities internationally. Recent studies indicated that

313 chitosan-modified CFA can effectively reduce the TP in the water column by flocculating algal cells

314 (Yuan et al., 2015). The Al and Fe contained in CFA facilitated chitosan binding for algal removal

315 due to improved charge neutralization, which may also contribute to P binding and depress P release

316 when settled on the sediment.

317   3.   Guiding principles for the assessment, application and development of P-adsorptive
318   materials

319 In the development and application of materials to freshwater ecosystems to address eutrophication,

320 and in particular to reduce bioavailable P concentrations, a number of common general guiding

321 principles should be employed in order to achieve an optimal outcome. These guiding principles can

322 be readily incorporated into a decision support system and risk assessment framework (e.g. Hickey

323 and Gibbs 2009) that is underpinned by characterisation of the system status and function, the mode

324 of application and intended target of the P-adsorptive materials, fiscal constraints, and stakeholder

325 buy-in and acceptance. The guiding principles are outlined below.

326 *3.1. Target setting*

327 In any lake management project it is essential to first set a series of realistic water quality targets

328 against which the success of the implemented measure can be assessed. The drivers of restoration will

329 be site specific and may include water quality targets dictated by policy (e.g. European Water

330 Framework Directive; EC 2000), human health risk thresholds of cyanobacteria biomass (e.g. WHO

331 2008), economic benefits to industry and society (e.g. Pretty et al.2003; Dodds et al.2009), reduction

332 of the need to control taste and odour problems in drinking water treatment plants (Codd 2000), and

333 biodiversity or habitat conservation interests (e.g. JNCC 2005). The likelihood that the use of any P-

334 adsorbent will achieve multiple non-target benefits (i.e. over and above the control of P) should be

335 considered fully prior to application. Similarly, the risk that P-adsorbents may have undesirable

336 effects on management targets (e.g., for external nutrient load targets) and ecotoxicity should also be

337 fully considered. For example, Gunn et al. (2014) report a range of responses in non-native invasive

338 aquatic macrophyte species in Loch Flemington following an improvement in water clarity associated

339 with a lanthanum-modified bentonite (LMB) application, although cause-effect was not quantified. In

340 this case, water quality and human health risk targets were met, at least in the short term, but

341 conservation outcomes were negatively impacted.

342 Lake management is rarely driven by simple targets for P or phytoplankton biomass reduction, but

343 instead by a myriad of interacting, and, at times conflicting processes driven by a diverse stakeholder

344 community. The diversity in the stakeholder community can in itself lead to conflicting demands in

345 relation to desired ecosystem services or goods. Of course, where wide reaching policy is relevant

346 (e.g. across EU WFD lakes), then some level of inter-calibration can support common standard/target

347 setting approaches across large numbers of lakes. For example, in the EU a relatively complex set of

348 metrics has been proposed and calibrated across member states, with which ecological status

349 following degradation and mitigation phases can be quantified (Birk et al. 2013). It is important that

any geo-engineering measures be assessed in line with these targets, especially where they are being used for reporting on statutory responsibilities of environmental regulators. In this case, monitoring procedures, metric calculation approaches and targets are standardised (Poikane et al. 2015) although each metric may have uncertainty associated with it (Carvalho et al. 2012).

It would be useful to develop material specific targets to ensure high confidence in their practical application. For example, the minimum concentration of the material in bed sediments relative to water column or sediment TP concentrations could be used to determine effective dose (e.g. Huser et al.2015). Reductions in TP flux measured using intact core incubations may also be a useful determinant to employ to indicate effectiveness of the control of internal P loading (Reitzel et al.2015). Similarly, where ecotoxicological issues are possible, minimum concentrations of high-risk components could be set and monitored as part of a licence agreement between water managers and regulatory bodies (e.g. the standard for dissolved lanthanum at 10.1 μg L^{-1} in place in the Netherlands; similar targets exist for Al in most countries). It is also important to explore the national scale inventory of lakes failing these targets, to produce estimates of the wider scale need for such management approaches and the potential for negative unintended consequences at the large scale (Spears and Maberly 2014).

3.2. System characterisation and function

A holistic understanding of system function is fundamental to the effective application of any P-adsorptive material in a freshwater ecosystem. This understanding includes knowledge of the size of the inventory of labile nutrients associated with bottom sediments, the magnitude of sediment nutrient fluxes, and changes in nutrient speciation related to, for example, anoxia. A further basic requirement is knowledge of temporal changes in limnological characteristics of the waterbody, including water volume, nutrient concentrations, phytoplankton biomass and composition, temperature and dissolved oxygen through the water column and duration of stratification. These measurements should be part of a water quality monitoring program that has ideally been established prior to any material application. In addition, external nutrient inputs should be quantified (e.g. Welch et al. 2015), so that a nutrient budget can be established to better understand the potential longevity of an application (e.g. Catherine

377 et al. 2010). Additional variables, including macrophyte cover, zooplankton, benthic

378 macroinvertebrates, fish and avian populations, should also ideally be part of the monitoring

379 programme and can provide valuable evidence of either acute (e.g., ecotoxicological) or long-term

380 responses to geoengineering (Wang et al. in press). For example, one of the premises of geo-

381 engineering for eutrophic, phytoplankton-dominated shallow lakes is to bring about a regime shift to

382 macrophyte-dominated vegetation; sampling of both phytoplankton and macrophyte populations

383 would provide documentation of such a change. While the collection and synthesis of the above data

384 constitutes an on-going financial encumbrance, particularly if monitoring is maintained over a number

385 of years, it must be balanced with the intrinsic ecological and social value of the aquatic system, and

386 the requirement to be able to make sufficiently well-informed assessments of the management

387 requirements.

388 Monitoring can also provide information about nutrient limitation of phytoplankton growth, which

389 may be based on measurements of total and dissolved nutrient species, often augmented with

390 laboratory-based trials (e.g. bioassays) to provide more direct indications of nutrient limitation. In an

391 ideal scenario, the collective system knowledge could also be integrated into a biophysical model of

392 the system (e.g. Battin et al., 2008). Importantly, this model can then inform the development of water

393 quality targets for dissolved P and other nutrient species (e.g. Polkane et al. 2014), as well as the

394 timing and dose(s) of one of more P-adsorptive materials. Modelling can also assist with testing

395 different dosing scenarios refine the procedure with the aim of reducing the extant water column P

396 concentration in addition to the internal loading, and decreasing phytoplankton biomass and the

397 occurrence of undesirable species.

398 *3.3. P-adsorptive materials – a multiplicity of roles in freshwater aquatic systems*

399 Performance testing of P-adsorptive materials in terms of reaction kinetics, total uptake capacity,

400 influence of other chemical species, and physicochemical conditions is essential to best estimate

401 dosage and select the most suitable materials for application in eutrophic freshwater systems. We

402 differentiate below three scenarios which can involve performance testing.

403 *Water column (days to weeks):* In the initial phase where the P-adsorptive material is applied to

404 surface waters, the material may be fully dispersed into constituent particles or aggregates to

405 maximise the available surface area, the reactivity and hence the potential for P uptake. The

406 immediate focus here is to reduce the bioavailable P inventory in the water column. Settling of the

407 added material, particularly if there are flocs or aggregates, would normally occur in quiescent

408 laboratory conditions within two days but may be longer (e.g. weeks to months) under natural

409 conditions, particularly in deep waters, under well-mixed conditions or via wind-induced resuspension

410 or convective overturn (Spears et al. 2013b).

411 *Reactive capping (weeks to months):* Once settled, the role of the P-adsorptive material fundamentally

412 changes. If distributed evenly and in sufficient quantity over the bottom sediment, it forms a pervasive

413 barrier of P-adsorptive material to act as a reactive (absorptive) capping agent in intimate contact with

414 the bottom sediments. Hence the role of the P-adsorptive material is to act primarily as a reactive

415 capping to intercept P migrating upward in the sediments, with varying fidelity depending on the

416 thickness, extent of sediment coverage, and P mass in the bottom sediments. The reactivity of the

417 settled P-adsorptive material will likely be less than that when present in the water column due to

418 aggregation, and possibly compaction, limiting ingress into, and interaction with, P-rich porewaters in

419 the bottom sediments. This is likely to be balanced in part, however, by the thickness of the applied

420 P-adsorptive material, (e.g. typically 1-2 mm for lanthanum-modified bentonite), such that there will

421 be substantial physicochemical interaction between any P migrating upwards from the bottom

422 sediments and the reactive capping layer. The longevity of the reactive capping of P-adsorptive

423 material will be a function of any remaining P-uptake capacity at the time of sedimentation to the

424 bottom, the bottom-sediment P flux and physical transport of the material due to resuspension or

425 bottom currents. Of primary importance, however, is how quickly the material is buried vertically

426 (Meis et al. 2011; Reitzel et al.2015) or translocated horizontally (Yasseri et al., 2015) as a result of

427 deposition of material from the overlying water column (related to catchment P loads) and physically

428 and biologically induced bed disturbance and sediment focussing, which are discussed below.

429 *Buried or redistributed reactive capping (months to years):* In the majority of freshwater systems two

430 processes induce the burial of any applied P-adsorptive material. The first is bioturbation, particularly

431 where fish or benthic fauna create deep conduits within the bottom sediment and migrating P bypasses

432 the reactive capping (e.g. Nogaro et al. 2006; Huser et al. 2015). In general, disturbance of the

433 capping layer by benthic fauna will redistribute the P-adsorptive material and lead to heterogeneous

434 coverage that potentially may reduce its effectiveness. The dosage should be based on this interacting

435 sediment depth to avoid dilution of the P-adsorptive material in relation to the potential P pool.

436 The second key process is the addition of new particulate material to the bottom sediments.

437 Deposition rates increase in the presence of storm events but these events may also elevate nutrient

438 concentrations and increase rates of deposition of organic material to the bottom sediments. This

439 process alone may be sufficient to bury any applied P-adsorptive materials, although production of

440 autochthonous organic matter (e.g. phytoplankton) will be reduced in the treated water column. In

441 addition, focussing (preferential deposition) of new sediment or the applied P-adsorptive material may

442 compromise the integrity of the reactive capping layer and physically mix and dilute the capping

443 layer. Although some redistribution and progressive burial of the P-adsorptive material is to be

444 expected, materials that are insensitive to changes in redox status and form highly insoluble

445 compounds may, depending on whether they retain any remaining P-uptake capacity, still function

446 effectively as a P-sink whilst buried within the bottom sediments.

447 *3.4. Composition, mineralogy and physical morphology of potential nutrient adsorptive materials*

448 The composition and mineralogy of a potential nutrient adsorptive material are major determinants of

449 its function, effectiveness and potential viability and efficacy. The goal is to be able to precisely

450 match the attributes of the P-adsorptive material to the nature of the system to ensure effective P

451 reduction. Relevant attributes include the composition, particle size and density of the material, as

452 well as its performance under pH and redox conditions that approximate but also extend beyond those

453 expected in the system. Relevant attributes in the context of different materials are given in Table 1.

454 On the basis of composition and mineralogy, many prospective materials, including some natural soils

455 or industrial by-products derived from the mining, mineral processing or other industries, although

456 potentially possessing one or more promising characteristics, may be deemed inappropriate.

457 Examples might include materials containing fibres, leachable/labile trace elements including metals

458 and metalloids, or in specific cases, naturally occurring radionuclides. Nonetheless, if assessed and

459 considered on a case by case basis, many natural materials such as shales, serpentinite, soils and

460 sands, and mining or mineral processing by-products such as red mud and slags, may also be

461 considered for specific applications (Table 1). Materials manufactured from well-defined precursor

462 materials, however, such as allophane and imogolite, and modified clay and zeolite have a distinct

463 advantage of tighter quality control and composition, with less natural variation. In addition, the

464 active constituent is not diluted by other inert or inactive components such as may be the case in

465 mining or mineral processing by-products, and hence tends to have a higher and more consistent P-

466 uptake capacity.

467 Of fundamental importance when considering the development of a P-adsorptive material is its

468 sensitivity to changes in redox status (e.g. Douglas et al. 2004). Many eutrophic aquatic systems are

469 characterised by large external loads of labile organic carbon and/or high rates of generation of

470 organic carbon within the system. Microbially-mediated degradation of this material will facilitate

471 often spatially extensive and sustained periods of water column anoxia and low redox state. Thus, the

472 majority of Fe-based materials, while possessing some potential as soil amendments within

473 catchments or as reactive media in constructed wetlands, are unlikely to be suitable for deployment in

474 eutrophic aquatic systems. These materials are highly redox sensitive and are likely to release

475 previously accumulated P during reductive dissolution. Under circumstances when anoxia occurs,

476 even if only briefly, the appropriate P adsorbents will include hydrotalcites, allophane/imogolite, rare

477 earth modified clays, carbonates/calcined derivatives or soils and soil derivatives (depending on

478 composition), all of which are insensitive to redox status (Table 1).

479 The sensitivity of P-adsorbent materials to other physicochemical conditions in the water column,

480 besides redox status, also requires *a priori* evaluation, for example using laboratory- or mesocosm-

481 scale assessments. The most important of these physicochemical conditions is pH. Changes in pH

482 may affect both uptake capacity and kinetics of P-adsorbent materials, and in the worst case can

483 potentially lead to massive releases of accumulated P due to dissolution or ion-exchange reactions.

484 Ideally the P-adsorbent material will have a wide operational pH range that spans both moderately

485 acidic conditions of pH 5-6 up to pH of at least 10, corresponding to values attained during major

486 phytoplankton blooms in poorly buffered systems. In this respect, La-based materials are often ideal

487 given the wide pH stability of lanthanum phosphate minerals (Table 1 and Copetti et al., 2015),

488 although some lanthanum may potentially be released to the water column above pH 9 (Reitzel et al.,

489 2013). Alternatively some materials such as carbonates (circumneutral pH) and calcined derivatives

490 (high pH) may possess a degree of buffering capacity, albeit at substantially differing pH. In the

491 specific case of carbonates this may be undesirable for application in a freshwater aquatic system

492 where the final pH may increase to above 9.5.

493 System-specific factors such as the composition of the water in terms of both major and trace

494 elements, dissolved organic carbon and alkalinity, may also affect uptake kinetics and in some cases

495 have a major impact on total P uptake capacity. This may occur, for example, due to the precipitation

496 of unintended secondary phases in place of the target nutrient such as lanthanum carbonates instead of

497 lanthanum phosphates associated with DOC complexation at exchange sites(e.g. Lurling, et al. 2014;

498 Spears et al. 2015).

499 In addition to considerations of the composition, mineralogy, physicochemical behaviour and water-

500 P-adsorbent interactions outlined above, the morphology, and in particular particle size distribution

501 and density, are also key considerations in the development of P-adsorptive materials. In the context

502 of aquatic system applications this may in some cases be advantageous as materials can be rapidly

503 conveyed to the bottom sediments by virtue of their large particle size and/or high density, and may

504 also be more resistant to resuspension and transport. Conversely, however, these characteristics may

505 also increase the rate of burial via displacement of less dense particles or aggregates extant in the

506 bottom sediment. Generally, the reactivity of P-adsorptive materials will decrease with the ratio of

507 particle surface area to volume.

508 *3.5. Ecotoxicity*

509 The ecotoxicological profile of a P-adsorptive material is of paramount importance and is often

510 closely aligned with its mineralogy, physical form, chemical composition and origin (e.g. slags and

511 fly ash, Table 1). A suite of detailed ecotoxicological tests should be undertaken in order to assess the

512 extent of possible acute and chronic ecotoxicological impacts on a range of biota relevant to the

513 aquatic system to be treated (e.g. Stauber 2000; Stauber and Binet 2000; Lurling and Tolman 2010;

514 Reitzel et al.2012; Spears et al. 2013a; Van Oosterhout and Lurling 2011, 2013; Wang et al. 2015).

515 For estuary applications the ecotoxicological testing may also need to encompass both fresh and

516 saline waters. Tests on biota should also include considerations due to physical changes in sediment

517 composition; from burial to changes in sediment particle size and impacts on sediment irrigation

518 processes.

519   *3.6. Evaluation of P-adsorbent materials prior to full-scale implementation*

520 Given the inherent diversity of freshwater systems in terms of both bottom-sediment composition and

521 water quality, and the diversity of potential P-adsorbents available (Table 1), a fundamental

522 prerequisite to full-scale application of P-adsorbent material is a suitably scaled assessment of P-

523 uptake performance, which may also help to foreshadow any unforeseen or unintended treatment

524 consequences.   Once the most appropriate P-adsorbent material(s) has been chosen, a suite of

525 potential evaluation steps may be employed.   These may range, in increasing order of scale,

526 complexity, time and cost, from laboratory testing of water samples alone to core samples

527 incorporating both bottom sediment and water, both stirred and unstirred to simulate sediment–water

528 exchange, to small (metre-scale) and/or larger (many metres or isolated portions of an aquatic system)

529 mesocosm studies incorporating many of the major elements (water, sediment, biota, atmospheric

530 exchange, mixing, stratification) of the aquatic system (e.g. Douglas et al. 2008; Pan et al., 2011).

531 Importantly, with increasing scale comes an increased understanding of the performance of, and

532 confidence in, the P-adsorbent material in the system of interest. In addition, other fundamentally

533 important variables such as dose, performance in terms of kinetics, total uptake capacity and potential

534 longevity, are able to be better simulated, but ability to achieve replication or carry out multiple

535 treatments is usually not possible. Ideally, mesocosm-scale trials, where appropriately replicated, and

536 with suitable controls, can provide a convenient *in-situ* 'laboratory' to evaluate aspects of changes, if

537 any, in benthic biota due to physical (*e.g.* smothering of benthic biota), chemical (interaction of the

538 adsorbent with the water column) or ecotoxicological (*e.g.* from chemical interaction or direct

539 ingestion) effects from the application of the P-adsorbent material (Douglas et al. 2004). For instance,

540 an enclosure experiment testing lanthanum-modified bentonite (LMB), dredging and their

541 combination (Lürling and Faassen 2012) also revealed gradually increased filterable La

542 concentrations in the LMB treated enclosures, to concentrations of above 100 µg La L^{-1}, that made the

543 authorities conclude LMB was not an option as these concentrations exceeded the Dutch La standard.

544 *3.7. Cost-benefit analysis*

545 The cost of eutrophication and the cumulative effects of phytoplankton blooms and changes in

546 ecosystem function can be considered on five levels:

547 • the loss of ecosystem function and values with eutrophication;

548 • a status quo, "do nothing", approach;

549 • the implementation of one or more technologies to reduce nutrient loads and concentrations;

550 • the implementation of existing P-adsorbent technologies (Table 1);and

551 • the development of novel interventions or management technologies.

552 Estimates of the costs of eutrophication and phytoplankton blooms have been made in a number of

553 studies. Recently, Hamilton et al. (2014) estimated costs in a range of categories including

554 surveillance and monitoring, treating and managing surface water supplies and management of

555 nutrient catchment loads, with the conclusion that factors such as increasing nutrient export and

556 climate change are likely to lead to increases in management costs in the future. Hamilton et al.

557 (2014) provide a range of costs for cyanobacteria blooms in different freshwater systems across the

558 world, including a single bloom event in Lake Taihu (China) of costs c.US$20M. Dodds et al. (2009)

559 estimated the costs of eutrophication management in the USA to be approximately US $2.2B

560 annually. In Australia the costs of freshwater cyanobacterial bloom management have been estimated

561 to be between AU$180M and 220M annually (LWRRDC 1998). In England and Wales the cost was

562 estimated to be between US$105M and160M annually (Pretty et al. 2003) comprised of reduced

563 values to waterfront dwellings, additional drinking water treatment costs, reduced amenity of

564 waterbodies, removal of algal toxins and decomposition products from drinking waters, the reduced

565 value of non-polluted atmosphere (e.g. geosmin), ecological effects and tourist industry losses.

566 Contemporary management of eutrophication symptoms in freshwater and estuarine systems

567 emphasises source reduction from both diffuse and agricultural point sources through implementation

568 of best practice. In Australia, at least, changing agricultural practices and effecting behavioural

569 changes take considerable time and are reliant on the development of new approaches. Although

570 substantial effort is now being directed to fertiliser management and point source reduction, it will be

571 many years before effective reductions in nutrient losses to waterways will be achieved. In the

572 interim there is substantial pressure and public expectation to reduce algal blooms and fish kills. In

573 some cases there is no "Do Nothing" option as major highly developed estuaries are on the edge of

574 ecological collapse. Phosphorus adsorptive clays or materials allow P accumulated in sediments to be

575 treated and offer rapid topical treatment options for water bodies to address legacies of P within these

576 systems.

577 Placed in the context of whole catchment solutions, the cost of P adsorptive clay treatments is

578 relatively low, depending of course on the efficacy and cost of the material. In Western Australia

579 (WA) application of LMB in small cyanobacteria-prone water bodies showed an immediate reduction

580 of 95% to 99% in P available for algal growth for the expenditure of about $150,000 per application.

581 Similar reductions from primary nutrient sources would have taken years of behaviour change and a

582 substantially higher cost. Whole-of-catchment solutions that cost many millions of dollars over a long

583 time period are still required and P adsorptive materials offer promise when used as part of "treatment

584 train" approach. As a comparison, if P adsorptive materials were used as the sole treatment in

585 selected agricultural drains in WA the cost of $1M per year compares to estimates of $100M over ten

586 years to reduce nutrients at source. These estimates should not be taken to mean that the authors do

587 not advocate for sustainable long-term solutions involving catchment restoration. Rather, they indicate

588   that a balance of investment is required between catchment restoration and use of P adsorptive

589   materials where there is a prerogative to address eutrophication in a timely, cost-effective manner.

590   Based on the authors' experiences, we consider below the level of investment required in research and

591   development, from concept to application of novel P-adsorptive materials. We include considerations

592   of patenting and commercialisation. To this end, an estimate of the costs that may be typically

593   involved in product development is given after each component in parentheses below. These estimates

594   constitute what may be considered typical costs but may vary substantially on a case by case basis.

595   Conservatively, it may take two years for a material to be conceived and tested at a laboratory scale

596   prior to more extensive in-field assessment. For this we have assumed a nominal salary of USD$100K

597   for the researcher for each of the two years (USD$200K). Ecotoxicological evaluation may include

598   acute and chronic effects testing over at least four trophic levels commensurate with the likely

599   population of target aquatic ecosystems (USD$200K). Field trials are typically 1-2 seasons in

600   duration, involving both research and technical staff, construction, sampling and analysis costs

601   ($200K). Regulatory approvals may typically take a year in each separate jurisdiction or country,

602   however, requirements are often similar for each although local consultants may be required to

603   manage each on a case-by-case basis ($100K). If the nutrient adsorptive material is deemed

604   sufficiently novel then patenting for both national (country of origin) and international jurisdictions of

605   relevance may be undertaken (USD$250K). If it is deemed that the technology has potential

606   commercial value, project management, usually by the inventor but with legal and business

607   assistance, identification of a partner company and full technology transfer including initiation and

608   monitoring of field trials, stakeholder and regulatory liaison and reporting, may occur for at least two

609   years (USD$250K). Thus, there may be considerable delays in the testing of an initial concept,

610   through extensive laboratory and field trials over a variety of scales, upscaling of manufacture,

611   ecotoxicological testing, regulatory submission and approval (with the possible imposition of

612   conditions), and engagement of commercial partners. Many of these steps may also have to be

613   repeated in each new jurisdiction, placing a considerable cost and intellectual burden on the developer

614   or applicant, notwithstanding many years of trials and validation, before there is widespread

615   regulatory and public acceptance, as well as commercial return on investment.

616   Thus, based on some conservative estimates outlined above, the development of a novel, viable,

617   nutrient adsorptive material may cost in the order of USD\$1.2M. In addition to the above, however,

618   given the traditionally conservative nature of many management agencies and stakeholders of aquatic

619   systems, some years may elapse between recognition and ownership of the (eutrophication) problem.

620   After this recognition followsthe need for active intervention, the demonstration of successful trials,

621   regulatory and stakeholder acceptance, and the ability to quarantine and direct the requisite funding,

622   perhaps over a number of years, also involving the concomitant management of external loads, to

623   enable full-scale intervention.

624   *3.8. Regulatory approval*

625   In the majority of jurisdictions, regulatory approval is required to implement P-adsorptive materials

626   directly to lakes. While regulatory requirements may vary considerably between jurisdictions, and for

627   different P-adsorbents (Table 1), a demonstrable thread of characterisation including mineralogical

628   and chemical testing, ecotoxicity assessment and extensive laboratory trials are generally required to

629   determine both efficacy and safety. The Netherlands is the only country in the world that has an

630   official La standard of 10.1 μg L^{-1} as the maximum allowable concentration (MAC) in fresh surface

631   water (Sneller et al. 2000). Hence, the residual filterable La concentration following application of

632   LMB is of great importance. The MAC is based on studies performed by NOTOX B.V. in 1995

633   (NOTOX 1995). The reported No Observed Effect Concentration (NOEC) of 100 μg L^{-1} has been

634   divided by 10 giving the maximum allowable addition of 10.1 μg L^{-1}, which with an estimated

635   background concentration of 0.1 μg L^{-1}, yields the MAC of of 10.1 μg L^{-1} (Sneller et al. 2000). The

636   underlying chronic *Daphnia magna* reproduction test contained a period of several days in which the

637   test animals received less food and in the treatments showed lower reproduction, but reproduction was

638   restored to normal (similar to controls) when food supply was increased again. Since cumulative

639   reproduction was chosen as the endpoint, this unusual experimental condition led to the NOEC of 100

640   μg L^{-1}. In the period of less food in the highest La doses, precipitation and consequently food

641 limitation may have occurred (Lürling and Tolman 2010). In addition, calculating exposure

642 concentrations based on the geometric mean of the two extremes in the measured La concentrations

643 (NOTOX 1995) gave a value half or less than if all data had been used in determining a mean or

644 median. Hence, there are significant doubts regarding the validity of the official Dutch La standard.

645 Nonetheless, filterable La has to be measured and values exceeding the Dutch La standard, even when

646 these are caused by insoluble and non-bioavailable La-oxyanion colloids, can lead to a 'no-

647 go'situation as was evidenced in Pond De Ploeg in 2009 (Lürling et al. 2012). The combined

648 application of LMB and a low dose flocculent (poly-aluminium chloride, PAC) needed a thorough

649 risk assessment prior to application in Lake Rauwbraken (The Netherlands, 2008; Lürling and van

650 Oosterhout 2013). However, a follow-up whole-lake experiment in Lake De Kuil (The Netherlands,

651 2009; Waajen et al.2015) situated in the jurisdiction of a neighbouring water authority to Lake

652 Rauwbraken met strong opposition from the legislator for Al treatment. Despite scientific

653 documentation and safety reporting, the legislator refused to licence a permit for PAC; instead

654 Fe(III)chloride had to be used as a flocculent. This example illustrates that regulatory approval may

655 differ even within a country depending on the interpretation of the legislator involved. It is evident

656 that only well-documented case studies can address such situations and thus applications should

657 include thorough long-term post application monitoring to validate treatment performance and

658 provide robust data that can be used to assist in determining safety and efficacy of whole of lake

659 experiments or prescribed treatments (e.g. Özkundakci et al. 2010).

660 *3.9. Public/social acceptance*

661 In the majority of freshwater ecosystems it is a fundamental requirement as a prelude to intervention

662 that robust, independent scientific assessment is obtained to underpin all interactions with

663 stakeholders in terms of both regulatory approval (as discussed above) and the general public (e.g.

664 Spears et al. 2013). Critically important in this process is to make available the scientific assessment

665 in a transparent, palatable, and user-friendly fashion. This is particularly so where P-adsorbents may

666 be nominally considered as industrial waste materials (e.g. slags or fly ash, Table 1) or are considered

667 novel or not naturally-occurring (e.g. La-substituted materials, Table 1). Ideally, the preliminary

668   dissemination of information will commence in parallel with the initial assessment or laboratory/pilot

669   trial stages such that elements of misinformation or scepticism are addressed in the first instance.

670   Ideally, the stakeholders will be engaged early and kept fully informed of the progress to facilitate a

671   partnership, garner acceptance and intellectual buy-in before, during and after full-scale

672   implementation of the nutrient management process.

673   A method to address the multiple issues raised above would be to establish a multinational Centre of

674   Excellence in P-adsorbent technology (Spears et al. 2013). The Centre would seek to bring a unified

675   approach and consensus to some of the critical steps, including public acceptance, regulatory

676   approvals, ecotoxicological tests and limit-setting, time periods from concept to full-scale application,

677   and provision of commercial quantities of the P-adsorbent. The Centre could leverage resources and

678   facilitate further research, development and validation of the performance of P-adsorbents in addition

679   to aligning approval processes for use, thus streamlining a process currently fraught with myriad

680   regulatory and other roadblocks both within and between countries.

681   **4. Conclusions**

682   The goal of effective interception, containment and long-term immobilization of phosphorus from

683   point and/or diffuse sources has gained increasing prominence over the past two decades. This is

684   particularly so as more efficient and environmentally acceptable methods are sought to combat the

685   effects of eutrophication in freshwater ecosystems.

686   The application of P-adsorptive materials to freshwater aquatic systems to manage the effects of

687   eutrophication constitutes a nexus spanning a range of considerations. These include meeting water

688   quality goals, including public health requirements, public perception and acceptance, and (partial)

689   restoration of ecosystem function, intended use (water column or reactive sediment barrier),

690   operational performance, and hence longevity of the efficacy of the P-adsorptive material.

691   It is evident that P is generally the nutrient that can be made limiting to such an extent that

692   eutrophication and some of its associated symptoms of harmful algal blooms and bottom-water

693   anoxia, can be minimised (e.g., Lürling and van Oosterhout 2013). Such intervention to reduce N to

694 concentrations similarly limiting to phytoplankton grow is often not possible. Hence, the development

695 of materials for the control of in-system P has been the focus of recent efforts in this field. These

696 developments have led to a better understanding of the operational performance of a wide range of P-

697 adsorptive materials as well as practical and socio-economic factors associated with their widespread

698 use in freshwater ecosystem management. To consolidate this evidence and expedite its practical

699 uptake we call for a multi-national collaboration and research centre to develop and test P adsorptive

700 materials, boost scientific insights, and reduce the delay from concept to market.

701 **5. Acknowledgements**

Table 1. Summary of common phosphorus adsorbents used in aquatic systems and their properties Modified after Douglas et al., (2004).

Material	Selected references	Composition	P-uptake	Cost	Advantages	Disadvantages
Naturally-occurring minerals or earth materials						
Carbonates	Shilton et al. (2005); ;Karaca et al. (2006); Mateus et al. (2012) ; Jaouadi et al. (2013); Xu et al. (2014)	Ca, Mg, carbonates	Low to moderate depends on source, particle size and composition	Low	Abundant, naturally occurring	May depend on limestone type
Soils, sands, suspended particles	Arias et al. (2000); Degens et al. (2000); Kim et al. (2014); Dai and Pan (2014): Pan et al., (2002, 2013)	Na-K-Ca-Mg aluminosilicates, Fe-oxides; Fe-(oxy)hydroxides	Low to moderate depending on composition. mineralogy, particle size	Low	Naturally occurring	May depend on soil type, siltation
Natural or synthetically-produced materials						
Allophane and imogolite	Wada, (1989); Farmer and Russell (1990);	Aluminosilicate	High uptake capacity	Mod-high	May occur in some soils	Industrial-scale synthesis
Fe-Al (oxy)hydroxides	Barrow (1999); Lu et al. (2014);	Fe-(oxy)hydroxides	Low - high depends on mineralogy/particle size	Low	May also occur in soils	Reductive dissolution (Fe), P-release
Hydrotalcite	Miyata, (1980, 1983); Shin et al. (1996); Yang et al. (2014)	Mg-Al hydroxide	High uptake capacity	Mod-high	Simple synthesis	Industrial-scale synthesis
Modified clay minerals or soils						
Expanded/thermally treated clay aggregates	Zhu et al. (1997), Johannsen et al. (1995); Adam et al. (2007) ; Gan et al., (2009), Yin et al., (2013)	Aluminosilicates calcined to form porous aggregates	Low to moderate	Low-Mod	Clay mineral	Industrial scale process
La-modified bentonite, vermiculite, zeolite or soils	Robb et al. (2003); Douglas et al. (2008) ; Huang et al. (2014); Yuan et al., (2009); Ning et al., (2008); Xie et al., (2014)	Na or K aluminosilicates modified with La	Moderate, depends on clay/soil cation exchange	Mod	Clay, simple synthesis	Suitable La, industrial process
Mining, mineral processing and industrial by-products						
Red mud/sand	Thornber and Hughes (1987);	Fe/Al (oxy)hydroxide, ± gypsum	Low to moderate, depends on composition		Abundant in certain regions, low cost	Often high pH, trace elements, potential ecotoxicity
Slags	Drizo et al (2006); Douglas et al. (2012); Wendling et al. (2012, 2013); Barka et al. (2014)	Alkali/alkaline earth aluminosilicates	Low to moderate, depends on composition		Abundant, low cost	Often high pH, trace elements, potential ecotoxicity
NUA	Douglas et al. (2012)	Fe-(oxy)hydroxides, gypsum	High to very high	Low	Low cost, high P uptake	High Ca, SO4 from gypsum dissolution

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