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Trends in the recovery of phosphorus in bioavailable forms from wastewater

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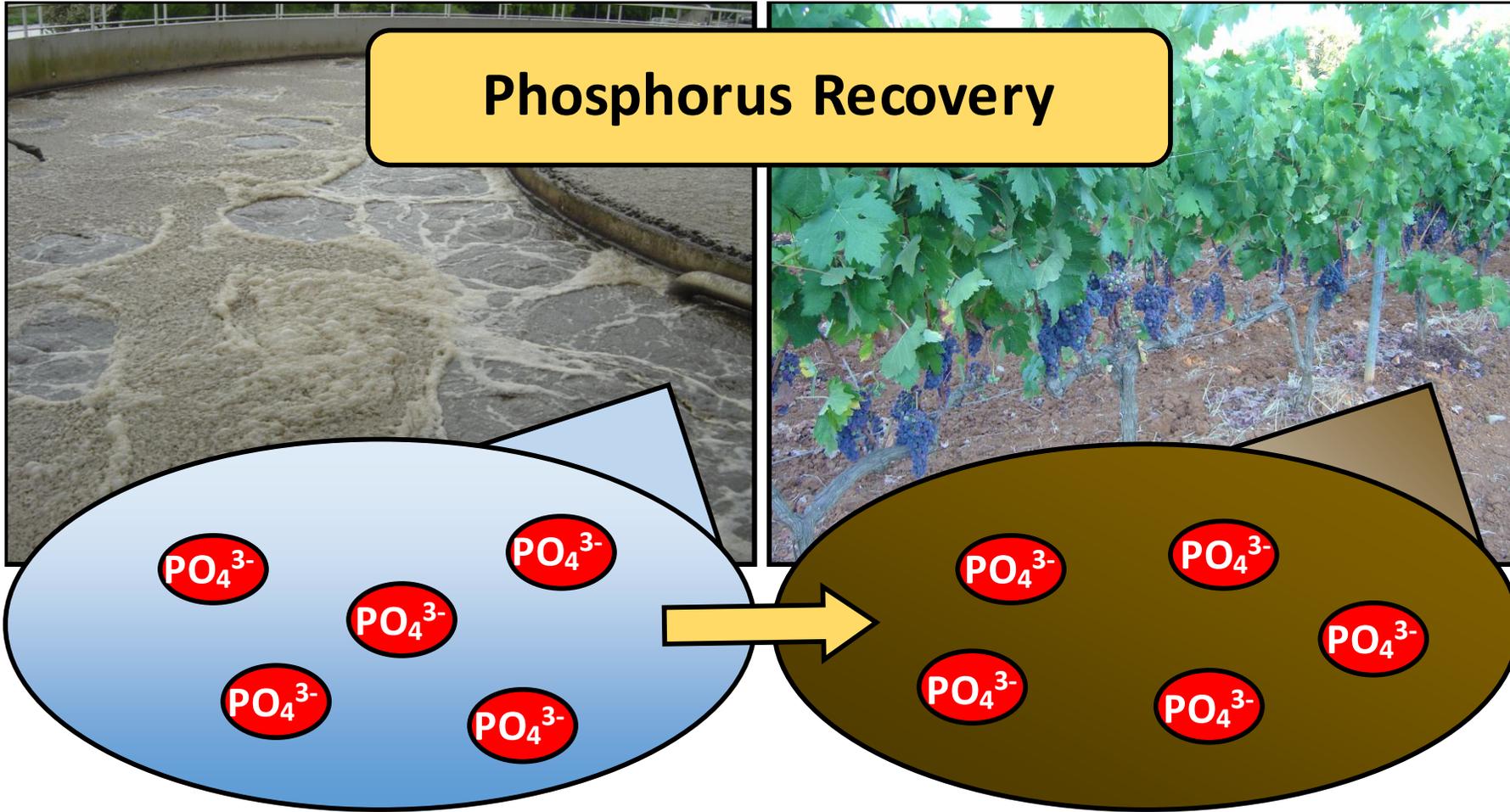
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Phosphorus Recovery



1 **Trends in the recovery of phosphorus in bioavailable forms from wastewater**

2

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19 **Abstract**

20 Addressing food security issues arising from phosphorus (P) scarcity is described as one of
21 the greatest global challenges of the 21st Century. Dependence on inorganic phosphate
22 fertilisers derived from limited geological sources of P creates an urgent need to recover P
23 from wastes and treated waters, in safe forms that are also effective agriculturally – the
24 established process of P removal by chemical precipitation using Fe or Al salts, is effective
25 for P removal but leads to residues with limited bioavailability and contamination concerns.
26 One of the greatest opportunities for P recovery is at wastewater treatment plants (WWTPs)
27 where the crystallisation of struvite and Ca-P from enhanced biological P removal (EBPR)
28 sludge is well developed and already shown to be economically and operationally feasible in
29 some WWTPs. However, recovery through this approach is limited to <25% efficiency
30 unless chemical extraction is applied. Thermochemical treatment of sludge ash produces
31 detoxified residues that are currently utilised by the fertiliser industry; wet chemical
32 extraction can be economically feasible in recovering P and other by-products. The
33 bioavailability of recovered P depends on soil pH as well as the P-rich material in question.
34 Struvite is a superior recovered P product in terms of plant availability, while use of Ca-P and
35 thermochemically treated sewage sludge ash is limited to acidic soils. These technologies, in
36 addition to others less developed, will be commercially pushed forward by revised fertiliser
37 legislation and foreseeable legislative limits for WWTPs to achieve discharges of <1 mg P/L.

38

39

40 **Keywords:**

41 Phosphorus recovery; wastewater; sewage sludge; struvite; sorption; bioavailability.

42	Abstract
43	Keywords:
44	1 Introduction
45	2 Management of P within WWTPs
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63 1 Introduction

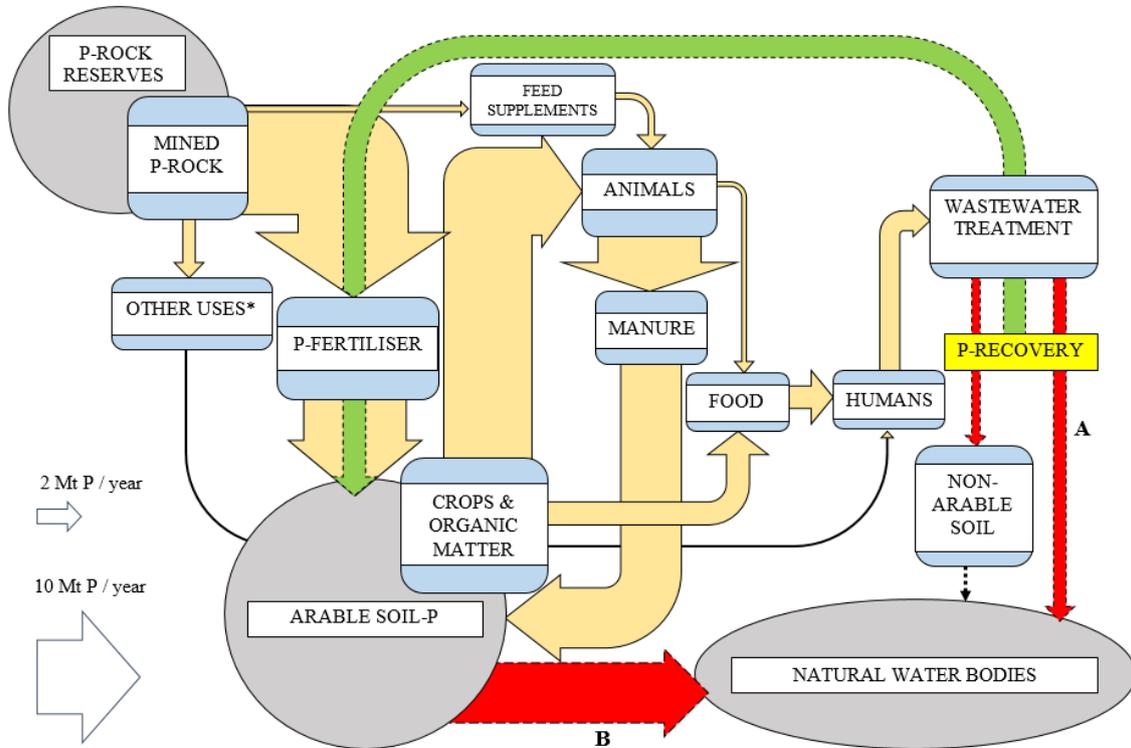
64 Phosphorus (P) is an essential plant nutrient and makes up around 0.2% of plant dry weight
65 (Jiang and Yuan, 2015; Schachtman et al., 1998). In aquatic ecosystems, low concentrations
66 of P benefit the biological productivity of freshwater lakes, reservoirs and rivers.

67 Concentrations of just ~0.02 mg P/L can be considered to cause eutrophication (Correll,
68 1998), having negative ecological effects where promoted algal growth (Yao et al., 2013) can
69 cause hypoxia and negative effects from algal toxins (Bláha et al., 2009; Žegura et al., 2011).

70 Negative impacts within ecosystems caused by an excess of P has led governments to limit
71 the P concentration in waters. As a whole, the Water Framework Directive 2000/60/EC
72 (European Commission, 2008) in conjunction with the Council Directive 91/271/EEC
73 concerning urban wastewater treatment (European Commission, 1991), identify sensitive
74 areas where high levels of P would have large ecological impacts – and enforce the control of
75 P in wastewater discharges, respectively. As an annual average, it is required that P
76 concentrations within wastewater effluents are below 1–2 mg P/L, depending upon the
77 sensitivity of the receiving environment and the size of the wastewater treatment plant
78 (WWTP), or are reduced by 80% from the influent concentration (European Commission,
79 1998, 1991). Austria, Germany and Switzerland have now made P recovery mandatory from
80 municipal sewage sludge (European Sustainable Phosphorus Platform, 2017).

81 The P loading within many ecosystems is a result of P discharges from WWTPs or the use of
82 P in agriculture. Figure 1 summarises key P flows and losses throughout the global
83 agricultural production and food consumption system. The inorganic P cycle is extremely
84 inefficient and wasteful. Losses of P to natural water bodies from wastewater discharge
85 represents approximately 10 % of inorganic P derived fertiliser applied to arable soil globally
86 (see “A” in Figure 1). These losses create both a need and an opportunity, with respect to P

87 recovery and re-use, needed not only to ensure good ecological status of waterways, but also
 88 to maintain the global productivity of agriculture.



89

90 **Figure 1.** Diagram of key P flows. The widths of the arrows semiquantitatively represents
 91 figures reported by Cordell et al. (2009) in million tonnes (Mt) of P per year. Yellow, red and
 92 green arrows represent flows of P between major points of use in the food production and
 93 consumption system; key P losses and the potential flow of recovered-P from WWTPs,
 94 respectively. Losses such as those arising from fertiliser production and distribution,
 95 agricultural residues, and food chain losses are not shown. The blue boxes indicate major
 96 points of use. The grey ovals indicate major P sinks. Point “A” denotes the flow of P
 97 contained in treated or untreated sewage to natural water bodies and represents approximately
 98 1.5 Mt P/year. Point “B” denotes the flow of P contained in erosion losses and is about 8 Mt
 99 P/year. *Other uses includes industrial uses such as the production of some detergents.

100

101 With increasing global populations and increased difficulty in accessing P reserves, many

102 studies have raised concerns regarding depletion of mined P sources (Childers et al., 2011;

103 Cordell et al., 2011, 2009; Cordell and Neset, 2014; Gilbert, 2009; Smil, 2000; Withers et al.,

104 2014). Mined P rock exists mostly in ancient marine sedimentary deposits, the majority of

105 which are situated in Morocco and Western Sahara (Van Kauwenbergh et al., 2013).
106 Estimated at ca 67 000 Mt (USGS, 2014), the global production of P rock is widely thought
107 to hit a peak this century (Walan et al., 2014), with some predicting that economically
108 mineable P rock reserves could become scarce or exhausted within 100 years (Childers et al.,
109 2011; Cooper et al., 2011; Smil, 2000). The decreasing quality of P rock, in terms of
110 contamination with cadmium for example (Mar and Okazaki, 2012), and price spike events
111 (Mew, 2016) are additional concerns. With an expanding global population relying on
112 decreasing and deteriorating P resources, the development of technologies for improved
113 recovery and re-use of P is becoming an increasingly urgent environmental, economic and
114 societal issue. The rising cost of P rock extraction will inevitably favour the development of
115 these technologies.

116 WWTPs provide one of the biggest opportunities for P recovery (Schoumans et al., 2015;
117 Smil, 2000) given the relatively high and constant P load in sewage. The recovery of P from
118 wastewaters can provide an array of benefits: (1) meeting the effluent P limits required by
119 legislation; (2) reducing eutrophication problems; and (3) providing a potential source of
120 fertiliser of agricultural and economic value. The latter simultaneously reduces the reliance
121 on inorganic (rock-P derived) fertilisers in agriculture.

122 However, municipal wastewaters contain many contaminants, both organic and inorganic,
123 including heavy metals and metalloids (Nguyen et al., 2013), pesticides (Köck-Schulmeyer et
124 al., 2013), pharmaceuticals (Antoniou et al., 2013), personal care products (Brausch and
125 Rand, 2011), nanomaterials, perfluorinated compounds (PFCs) (Richardson and Ternes,
126 2014), hormones (Loos et al., 2013), recreational drugs (Wilkinson et al., 2016) and
127 pathogens (Cai and Zhang, 2013). Therefore, the application of untreated effluent to
128 agricultural land would pose associated risks to human food consumption (Schoumans et al.,

129 2015). Hence, wastewaters generally require recovery processes with a certain degree of
130 selectivity to remove P into a solid form that can be safely and effectively used as fertiliser.
131 Here we critically review P recovery technologies currently used in WWTP processes
132 (chemical precipitation, enhanced biological P removal (EBPR), various sludge treatments,
133 struvite and Ca-P crystallisation, and thermochemical treatment) and other emerging
134 technological options, particularly with respect to recovery efficiency and the use of
135 recovered P as a mineral-P substitute. We conclude this review by providing some
136 recommendations for future work, namely the diversification of technological approaches to
137 recover P and further consideration of the bioavailability and potential contamination of
138 recovered products.

139 **2 Management of P within WWTPs**

140 **2.1 Capture and accumulation of P – an overview**

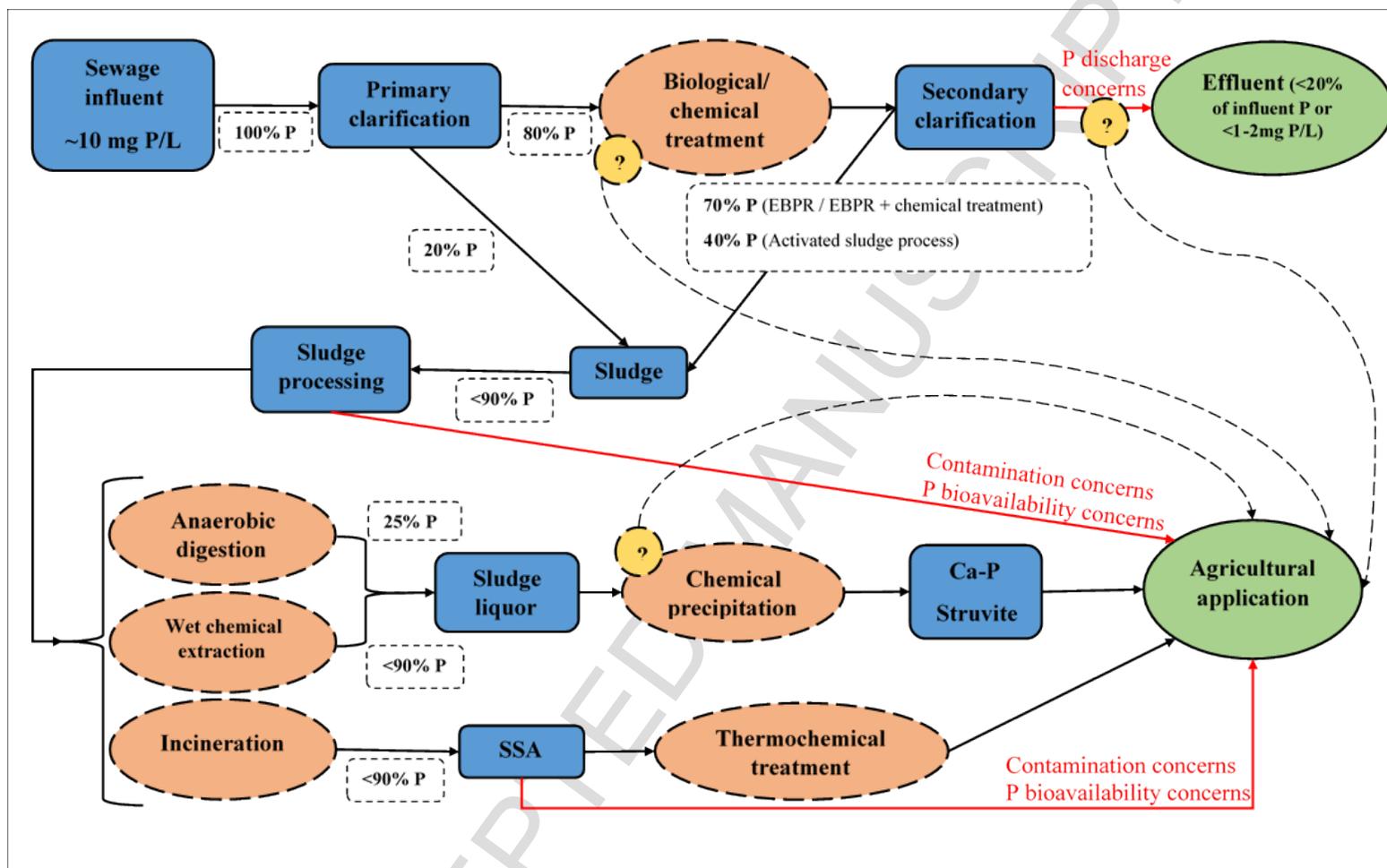
141 P exists in a variety of forms within wastewater and these vary throughout the WWTP
142 process; P in particulate forms are more easily and completely removed through clarification
143 steps (Dueñas et al., 2003) whereas dissolved P species, both organic and inorganic, require
144 more targeted chemical or biological processes for their removal. P concentrations reported
145 for municipal wastewaters are generally below 10 mg P/L (Kim and Chung, 2014; Petzet and
146 Cornel, 2013; Qiu and Ting, 2014; Yuan et al., 2012).

147 Preliminary screening is firstly applied in WWTPs to remove larger particles followed by a
148 primary treatment step. This involves the settlement and removal of suspended solids and
149 organic fractions, which can be achieved by chemical addition or filtration (Tchobanoglous et
150 al., 2014). Petzet and Cornel (2013) report that 17–26% of an incoming total P load,
151 predominantly in particulate forms, can be transferred to primary sludge in initial settlement

152 at a WWTP. Secondary treatment, especially in larger WWTPs and those discharging to
153 sensitive environments, is then applied (European Commission, 1991). This can involve the
154 use of microbes to break down soluble organic compounds that remain after the preliminary
155 and primary treatment steps (through trickling filter beds or other treatments), and/or the
156 addition of chemicals to promote the coagulation and flocculation of solids. Other than
157 particulate P removed here through secondary clarification, specific P removal techniques
158 such as chemical precipitation or enhanced biological phosphorus removal (EBPR) can be
159 integrated into the treatment process to target dissolved forms of P. Tertiary and advanced
160 treatments are applied for the further removal or degradation of dissolved contaminants,
161 especially when the treated water will be reused. Aside from addressing ecological and
162 statutory issues, P removal at WWTPs prevents the build-up and blockage of pipes by
163 crystalline deposits and precipitates of P (De-Bashan and Bashan, 2004; Rittmann et al.,
164 2011).

165 Standard primary and secondary treatments often do not remove sufficient P to meet the
166 required discharge concentration. Under normal secondary treatment (the activated sludge
167 process) around 31–48% of influent P can be transferred into sludge (Petzet and Cornel,
168 2013). With the P removed through primary settlement, this can leave up to approximately
169 50% of the total influent P load to be removed by an enhanced P removal technique before
170 discharge into a receiving water body (Desmidt et al., 2015).

171 Techniques specifically used to remove P from wastewaters can be operationally categorised
172 as chemical, biological or physical. They include the established techniques of chemical
173 precipitation and enhanced biological phosphorus removal (EBPR). In each case P is
174 removed by the conversion of the various dissolved P forms into a solid (De-Bashan and
175 Bashan, 2004).



176 **Figure 2.** The flow of P through a typical WWTP process, the positions of P recovery technologies (dashed circles) and routes of application of
 177 recovered P to agriculture with concerns highlighted in red. Percentage of P (white boxes with dashed line) represents what can be
 178 approximately assumed to be removed or carried over to the next treatment stage as a percentage of the influent P load. The dashed yellow
 179 circles with question marks indicate where emerging technological approaches could target P recovery.

180 **2.2 Chemical precipitation**

181 Precipitation was first attempted to control eutrophication problems in the 1950s (Morse et
182 al., 1998) and is the main commercial approach to P removal today (Wendling et al., 2013).
183 The precipitative removal of P is usually achieved through the addition of di- or trivalent
184 metal salts of Fe, Al or Ca (Table 1). P in the form HPO_4^{2-} , H_2PO_4^- or H_3PO_4 (dependent
185 upon reaction pH), as well as organic P and particulate P fractions, are coagulated to form a
186 metal phosphate sludge and subsequently removed after flocculation and settlement.
187 Chemical precipitation is more efficient at earlier stages in the waste water treatment process
188 when the concentration of P in solution is highest. Processes involving seeded precipitation,
189 where crystallisation is encouraged and controlled through the addition of a seed material, are
190 being developed to offer more efficient and less costly treatment (Petzet et al., 2012; Song et
191 al., 2006).

192 Fe and Al salts are considered the most suitable and are generally added as chlorides or
193 sulphates (Morse et al., 1998), calcium can also be used and is generally added as lime
194 ($\text{Ca}(\text{OH})_2$). Fe salts are generally preferred as they are cheaper than Al – Fe-P chemistry
195 relating the municipal wastewater is discussed in detail elsewhere (Wilfert et al., 2015).

196 In terms of emerging options, a recent study has investigated the use of potassium ferrate for
197 P precipitation combined with water disinfection (Kwon et al., 2013). The latter arises from
198 its status as a powerful oxidant while precipitation and coagulation of Fe-P occurs through
199 reduction of Fe (VI). The disinfection rate obtained was faster than for chlorine of the same
200 concentration. Within secondary effluent (1.46 mg total P/L), ferrate was able to remove
201 more than 80% of P in the dosage range of 5–25 mg Fe/L. The two most obvious
202 disadvantages of chemical precipitation are the requirement and cost of chemical additions,

203 and the generation of large volumes of sludge that are often unsuitable for reuse due to the
 204 low recoverability of P and possible incorporation of contaminants in the P-rich precipitate.

205

206 **Table 1.** Details of the three metals conventionally used in the chemical precipitation of P in
 207 WWTPs, including the optimal pH for the process, the most common precipitates formed and
 208 the advantages and disadvantages of using each.

Element	Optimal pH	Most common precipitate form	Advantages	Disadvantages
Fe	4.5-5 (Thistleton et al., 2002)	Strengite (FePO ₄ · 2H ₂ O) (Grzmil and Wronkowski, 2006)	<ul style="list-style-type: none"> • Relatively inexpensive • Effective in the precipitation of P 	<ul style="list-style-type: none"> • Precipitate unsuitable for use as fertiliser.
Al	~6 (Lin and Carlson, 1975)	Variscite (AlPO ₄ · 2H ₂ O) (Lin and Carlson, 1975)	<ul style="list-style-type: none"> • Most effective precipitant. (Yeoman et al., 1988) • At pH 6, both biological treatment and precipitation with Al could be operated. 	<ul style="list-style-type: none"> • Expensive • Precipitate unsuitable for use as fertiliser • Doses of >60mg Al/L have a toxic effect on autotrophic bacteria within a membrane bioreactor (Zahid and El-Shafai, 2012) – dosage must be carefully considered.
Ca	>10.5 (Jenkins et al., 1971)	Hydroxyapatite (Ca ₅ (PO ₄) ₃ OH)	<ul style="list-style-type: none"> • Relatively inexpensive • Ca-P precipitates can be similar in form to rock-P and suitable for use in industry • Potentially suitable as fertiliser 	<ul style="list-style-type: none"> • High pH requirement • High pH can create detrimental conditions for biological treatment • Additional neutralisation step may be required • Large volume of generated sludge

209

210 Numerous by-products and wastes have also been investigated as potential precipitants. Red
211 mud, an abundant mining waste, has been studied for its potential for precipitation of P due to
212 its high content of Al and Fe. Through the treatment of red mud, Poulin *et al.* derived a solid
213 product that had P removal efficiency similar to commercial coagulants, namely 70–98% in
214 solutions containing 5–100 mg P/L respectively (Poulin et al., 2008). Municipal solid waste
215 fly ash has also been investigated, with reported removal rates of approximately 6 mg P/g
216 (Zhong et al., 2014). Hydrated oil shale ashes in subsurface flow filters have been assessed in
217 long period pilot-scale experiments treating municipal and landfill leachate wastewater in
218 Estonia, achieving 99% removal from wastewaters ranging in P concentration from 0.13–17.0
219 mg total P/ L (Kõiv et al., 2010). In this case the direct precipitation of Ca-P was suggested to
220 be the controlling P removal mechanism.

221 Other waste materials providing strong precipitation effects include calcined waste paper
222 sludge. The formation of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was found to be the main mechanism
223 controlling P removal in a laboratory scale study, which reached 1.5 mmol P/g (46.6 mg P/g)
224 calcined paper sludge (Wajima and Rakovan, 2013). Drinking waterworks sludge was also
225 found to be effective for P removal in laboratory scale experiments due to its high content of
226 Al and Fe: 99% removal could be achieved from an initial concentration of 2 mg P/L and a
227 sludge dose of 10 g/L in synthetic wastewater, at pH value 5–6 (Yang et al., 2014).

228 **2.3 Enhanced biological phosphorus removal (EBPR)**

229 EBPR was developed during the 1970s (Barnard, 1975; Yuan et al., 2012), and is extensively
230 used today. Most full-scale P recovery technologies currently applied require the pre-
231 accumulation of P (as bio-P sludge) using EBPR processes. EBPR relies on polyphosphate
232 accumulating organisms (PAOs) or denitrifying PAOs to accumulate P intracellularly as
233 polyphosphate granules, thus avoiding any requirement for chemical precipitants (Oehmen et

234 al., 2007; Wong et al., 2013). The process is enabled by alternating anaerobic and aerobic
235 conditions; PAOs take up volatile fatty acids under the anaerobic phase, which are stored as
236 polyhydroxyalkanoates and subsequently metabolised in the aerobic phase to supply the
237 energy needed by the PAO to accumulate P (Kristiansen et al., 2012). Sludge, highly enriched
238 in PAOs, can accumulate as much as 20% cell dry weight as P, compared with 1–2% in non
239 PAO-enriched sludge (Tchobanoglous et al., 2014). Bacterial genus *Acinetobacter* was at first
240 thought to be the primary PAO (Fuhs and Chen, 1975) in EBPR, however members of
241 Actinobacterial genus *Tetrasphaera* (Kong et al., 2005) and the bacteria *Candidatus*
242 *Accumulibacter Phosphatis* (He and McMahon, 2011; Hesselmann et al., 1999) are now
243 considered to be more responsible for P accumulation in WWTPs (Kristiansen et al., 2012).
244 In addition to bacterial strains, microalgae have been investigated as suitable PAOs for P
245 assimilation in wastewater treatment (Solovchenko et al., 2016).

246 The accumulation of P within bio-P sludge and its settlement can facilitate the recovery of P
247 and allow for direct utilisation as fertiliser, depending on contaminants present. Alternatively,
248 further treatment can facilitate the solubilisation and recovery of P in a form such as struvite
249 ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Baur, 2009). A recent paper investigated the use of microalgae and
250 cyanobacterial strains for the accumulation of P from parboiled rice mill effluent. These P
251 enriched PAOs showed moderate P release as a biofertiliser and was comparable to that of
252 commercial fertilisers (Mukherjee et al., 2015).

253 In full scale WWTPs, EBPR processes can typically remove over 85% of P in municipal
254 wastewater influent, often to concentrations $<0.1\text{mg P/L}$ (Gautam et al., 2014; Gebremariam
255 et al., 2011). Although efficient in many cases, there are however questions over the stability
256 of its performance (Oehmen et al., 2007; Zheng et al., 2014). Various process inefficiencies
257 and failures are reported to be associated with EBPR. One of the largest causes of
258 deterioration and failure in EBPR systems arises from the occurrence of glycogen

259 accumulating organisms (GAOs) (López-Vázquez et al., 2008), which compete with PAOs
260 for carbon substrate (Oehmen et al., 2007; Yuan et al., 2012). GAOs can function under
261 aerobic or anaerobic conditions (Zheng et al., 2014) and are found widely in EBPR processes
262 (Burow et al., 2007). Considerable effort has therefore been focused on establishing the
263 conditions that might limit their growth (Oehmen et al., 2006, 2005, 2004; Wang et al., 2010;
264 Whang and Park, 2006, 2002; Whang et al., 2007). This has established that at pH 8, the
265 abundance of GAOs is restricted while optimal PAO activity is maintained (Oehmen et al.,
266 2005). The type of carbon substrate and its concentration is also important (Shen and Zhou,
267 2016); propionate for example was found to be more beneficial than acetate for PAO growth
268 (Wang et al., 2010; Zeng et al., 2013). The presence of toxic substances in the influent, such
269 as Cr (VI) (≥ 0.5 mg/L), can also inhibit P removal, being toxic to PAOs (J. Fang et al., 2015).

270 Without carbon addition to ensure high and constant concentrations, the EBPR system can be
271 very susceptible to changes in the influent composition. Consequently, climates with a
272 tendency for sporadic heavy rainfall, which can drastically perturb nutrient concentrations,
273 can affect biological P removal (Manyumba et al., 2009). The addition of organic carbon to
274 the process however is unfavourable as it incurs additional cost to the EBPR process and
275 increases the overall carbon footprint (Guerrero et al., 2015). Organic carbon additions
276 derived from waste sources have been successfully investigated which may reduce cost and
277 increase the sustainability of the process; waste activated sludge fermentation liquid was
278 found to be a more effective carbon source than acetic acid (Ji and Chen, 2010), crude
279 glycerol, a biodiesel waste product, was successfully dosed in an EBPR process and resulted
280 in better control over P removal (Guerrero et al., 2015).

281 High temperatures, 30°C as opposed to 20°C, encourage GAO growth (Whang and Park,
282 2002) with lower temperatures found to be beneficial for PAO growth (López-Vázquez et al.,
283 2008) and therefore P removal. Low aeration rates and thus low dissolved oxygen (DO) also

284 favour PAOs over GAOs (Carvalheira et al., 2014). These variables may impact on the final
285 P concentrations in the treated effluents and discharges may exceed those permitted by
286 legislation.

287 EBPR processes are considered to be a more sustainable compared to chemical processes and
288 can often offer significant economic advantages in larger WWTPs (Manyumba et al., 2009).
289 EBPR requires less or no chemical addition and has the potential for the full-scale recovery
290 of P. However, where process inefficiencies are frequent and/or legislation requires
291 consistently low P concentrations in effluent discharge, it is also common for larger WWTPs
292 to deploy chemical precipitation in conjunction with EBPR to ensure requirements are
293 consistently met (Kim and Chung, 2014; Kwon et al., 2013). This reduces the amount of P
294 that can be solubilised and recovered through bio-P sludge digestion or direct application as
295 fertiliser. Other limitations include the complexity of operations and a large energy and space
296 requirement (Nguyen et al., 2014a). The future use of EBPR processes may therefore not
297 extend beyond those WWTPs with a relatively narrow geographic, spatial and economic
298 context.

299 **3 Sludge enhancement and P recovery from sludge**

300 A major disadvantage of chemical precipitation of P is the possible co-precipitation of toxic
301 ions such as arsenic and fluoride as well as organic contaminants, pathogens or viruses
302 (Mehta et al., 2014) among others. This is highly relevant in terms of the handling of the final
303 product and its suitability for land application. The potential for precipitation using Al and Fe
304 to yield suitable P-bearing soil amendments is limited, since Al can be toxic to many plants at
305 high concentration, especially in acidic soils (Poschenrieder et al., 2008), and P in Al- and
306 Fe-P solids may limit the P solubility to plants and is considered unrecoverable for the
307 purpose of fertiliser production (Donnert and Salecker, 1999; Wendling et al., 2013).

308 The direct application of dewatered bio-P sludge has been found to be as effective as mineral
309 fertiliser (Erdinçler and Seyhan, 2006; Kahiluoto et al., 2015), but similarly, there are
310 increasing concerns over the transfer of chemical and biological contaminants to the
311 environment, affecting food supply (De-Bashan and Bashan, 2004; Krzyzanowski et al.,
312 2014; Yuan et al., 2012). It has been shown that sewage sludge application to soil, although it
313 increases the available nutrient content of the soil, also increases heavy metal concentration
314 in both soil and plant. At a sludge application dose of 20 t/ha or higher, Cd concentrations in
315 rice grain were found to be above the Indian safe limit (Latare et al., 2014). Switzerland has
316 already banned the use of sewage sludge in agriculture (Franz, 2008; Schoumans et al.,
317 2015).

318 Other issues with the direct application of sewage sludge include the difficulty in its
319 transportation and application, given that sludges are bulky and dense. Dewatering of sludge
320 can reduce haulage costs and removes the necessity for specialist farm equipment, but incurs
321 energy and financial costs (Yuan et al., 2012). The recovery of P from WWTP sludges in
322 purer and more effective forms than that derived directly from sewage sludge is being sought
323 through the approaches outlined in the following subsections, which includes a number of
324 emergent technologies. These approaches are becoming necessary to ensure the safe recovery
325 of P and compliance with current and future legislation.

326 **3.1 Anaerobic digestion and dewatering**

327 Anaerobic digestion (AD) is the process most commonly used for stabilisation of sludge,
328 offering organic solids and pathogen destruction as well as energy recovery in the form of
329 methane (Mehta et al., 2014; Tchobanoglous et al., 2014). AD of bio-P sludges can generate a
330 liquor of approximately 10–50 times higher P concentration than the WWTP influent (Yuan
331 et al., 2012). The majority of the heavy metal load is retained within the sludge, whilst P is

332 released from the biodegradable fractions into the liquid phase. In terms of emerging organic
333 contaminants, it was shown that within AD processes, detected emerging contaminants such
334 as the antidepressant venlafaxine and benzoylecgonine, the main metabolite of cocaine, were
335 preferentially adsorbed and concentrated within the solid material; the majority of the 13
336 compounds detected were not degraded by AD processes (Boix et al., 2016).

337 Concentrations of P in the supernatant of AD processes can vary considerably: 30% of total P
338 has been estimated to be dissolved in the aqueous phase arising from AD of bio-P sludge,
339 whereas <10% is thought to be dissolved after AD of chemical sludges (Petzet and Cornel,
340 2013). This is due to the re-fixation of P into the sludge through precipitation with Fe, Al, Ca
341 and Mg or through adsorption (Petzet and Cornel, 2012). AD of bio-P sludge as a
342 solubilisation technique is a primary step in facilitating the precipitation of struvite in many
343 commercial P recovery processes such as Crystalactor®, NuReSys®, Pearl®, Phosnix® and
344 PHOSPAQ™ (Schoumans et al., 2015). Assimilation of solubilised compounds, in particular
345 emerging organic contaminants, found in AD supernatants into final recovered P products
346 such as struvite may be of particular concern and warrants further investigation.

347 **3.2 Wet chemical extraction**

348 Wet chemical extraction, involving either acid or alkaline dissolution, supports greater
349 solubilisation of P from sludge, sludge ash or other sludge residues, although it can
350 simultaneously solubilise contaminants, of which heavy metals/metalloids are of particular
351 concern. Therefore, the separation of metals and P is highly important when operating wet
352 chemical extraction for P recovery. Additionally, because in recovery through struvite
353 crystallisation, Fe, Al and Ca can compete with Mg to form complexes with orthophosphate,
354 their minimisation leads to improving the efficiency of the recovery process.

355 Through the acid digestion of various forms of digested sludge, using sulphuric acid (pH 1.8),
356 it has been established that incineration – compared to original, diluted and centrifuged
357 digested sludges – is the better preliminary step for precipitation of struvite. This is because
358 Al, Ca, and Fe could be removed to the greatest extent (98%, 97%, and 80% respectively)
359 (Güney et al., 2008). However, for the effectiveness of P solubilisation, Fe-PO₄-containing
360 raw sewage sludge was more beneficial for the release of P (Sano et al., 2012). Advantages to
361 using alkali extraction as opposed to acid extraction, is that the release of heavy
362 metals/metalloids can be suppressed to lower levels. This may limit the need for filtration
363 technologies, which can be costly and prone to fouling. However, alkali treatment can also
364 reduce the recovery of P to as low as 30% (Mattenberger et al., 2008).

365 The PHOXNAN (Blöcher et al., 2012) process involves the release and accumulation of P
366 from sludge into a solution suitable for recovery through wet oxidation by the addition of
367 sulphuric acid (pH 1.5). P resides in the resulting solution as H₃PO₄, while the organic
368 content is decreased and other micro-organic pollutants are oxidised. An ultrafiltration
369 membrane separates the remaining solids, a step that is followed by nanofiltration to remove
370 cations. P is accumulated in the final solution mainly as phosphoric acid. In another study,
371 alkaline hydrolysis of excess secondary sludge from an anaerobic/aerobic process was carried
372 out at an optimal pH value of 13, with both P and N being recoverable from the supernatant
373 (Bi et al., 2014). The process enables the release and recovery of 42.0 % PO₄³⁻ (P) and 7.8 %
374 NH₄⁺ (N) in the form of struvite. The treatment of sludge with supercritical water gasification
375 was found to release up to 95.5 % P (Acelas et al., 2014). In this case, oxalic acid was
376 reported to have a better performance than sulphuric acid in the leaching of P.

377 Neither acid nor alkali treatments offer an ideal option for the full solubilisation and recovery
378 of P. The choice of treatment should be considered carefully with respect to the initial
379 accumulation of P in primary and/or secondary treatment. Petzet *et al.* reported that P

380 recovery via wet chemical treatment of sewage sludge ash (SSA) could be optimised by a
381 combination of both acid and alkaline leaching (Petzet et al., 2012). Through an acidic pre-
382 treatment, alkaline insoluble Ca-P fractions are converted to Al-P which can then be easily
383 dissolved through alkaline treatment and separated through the precipitation of Ca-P. The Al
384 fraction can then be reused in chemical precipitation processes in the primary stream. For
385 WWTPs using Al based precipitation and thus generating a high Al SSA, the P-recovery rates
386 were found to be as high as 70–77%. Even where Fe-based precipitation was operated, it was
387 reported that a considerable amount of the required Al is supplied by the decay products of
388 detergent zeolites (Petzet et al., 2012).

389 **3.3 Incineration and P release from sewage sludge ash**

390 The incineration of sludge provides complete oxidation of organic constituents at high
391 temperatures. Mono-incineration, where the sludge is incinerated separately to other wastes,
392 can be a favoured option since it can greatly decrease sludge volume, energy can be
393 recovered and, since phosphate is thermally stable and does not volatilise during the process,
394 P is retained and concentrated in the ash. SSA has been found to contain on average 11.6%
395 P_2O_5 (Cyr et al., 2007) (a form and content comparable to P-rock ores) (Aydin et al., 2010;
396 Weigand et al., 2013). SSA is not generally appropriate for direct application to land
397 however, due to the retention of heavy metals/metalloids and the strong binding of P (Ottosen
398 et al., 2014) due to higher crystallinity of P_2O_5 generated at higher temperatures. In solubility
399 tests with ammonium citrate, one indicator of short-term bioavailability, only 26% of P
400 present in SSA was found bioavailable (Krüger and Adam, 2015). The recovery of P in a
401 purer form may increase the bioavailability of P and reduce the contamination risk.

402 The release of P from SSA can be achieved by the dissolution of the ashes in acid, the
403 separation of heavy metals and the precipitation of calcium phosphate, ferric hydroxide and

404 aluminium hydroxide, as in the Ash2[®]Phos process. This process is reportedly economically
405 profitable since it is dealing with a waste which would otherwise incur a cost for disposal and
406 the commercial products produced (mono/di-ammonium-phosphate and Fe and Al
407 precipitants) (EasyMining-Sweden, 2017). P content (>95%) from SSA was recovered by
408 acidification with HCl (Xu et al., 2012). Heavy metals were subsequently removed from
409 solution using a cation exchange resin. P was recovered in the form of struvite (97% pure),
410 which has high P bioavailability of 94% and low metal content, thus comparable to a high
411 quality fertiliser. Electrodialysis was also studied as an option for the separation of heavy
412 metals/metalloids and P after pre-treatment with sulphuric acid. The process separated P from
413 heavy metals/metalloids effectively with up to 70% mobilisation of the P from the SSA
414 (Guedes et al., 2014).

415 **Table 2.** Examples of commercial processes for P recovery and the form of the final P product derived.

416

Process	Information and process description	Final product	Reference
AirPrex® process	Crystallisation of struvite applied directly in the digested sludge stream. CO ₂ is stripped to increase pH. MgCl ₂ is added. AirPrex® systems are currently operational at several WWTPs in Germany and The Netherlands. The world's largest AirPrex® system is being constructed at the WWTP of Amsterdam. Developed by Berliner Wasserbetriebe (Germany).	Struvite	(Eliquo Water & Energy BV, 2016; Tchobanoglous et al., 2014)
DHV Crystalactor®	The sludge side stream is fed into the reactor and recirculated. Quartz sand is initially added as seed material to accelerate precipitation. Pellets settle to the bottom. Developed by DHV (NL).	Struvite, Mg-P or Ca-P	(Giesen, 2016; Tchobanoglous et al., 2014)
NuReSys® process	Air is initially added and CO ₂ is stripped from the side stream followed by MgCl ₂ addition in the stirred crystalliser tank where struvite forms pellets. NaOH is added to maintain pH in the range 8.1-8.3. Pellet size can be controlled by stirring speed. Developed by Akwadok/NuReSys (Belgium).	Struvite	(NuReSys, 2016; Tchobanoglous et al., 2014)
Ostara Pearl® process	Struvite crystallisation is achieved through treatment of sludge side stream in a fluidised bed crystalliser. Effluent is recirculated and MgCl ₂ and NaOH are added as the Mg source and for pH maintenance respectively. Developed at the University of British Columbia and introduced at full-scale by Ostara Nutrients Recovery Technologies Inc. (USA).	Struvite (Crystal Green®)	(Ostara, 2016; Tchobanoglous et al., 2014)
Phosnix® process	A cylindrical reaction zone with a conical bottom section is applied. Mg(OH) ₂ and NaOH added as a source of Mg and for the control of pH respectively, and aerated to strip CO ₂ . Struvite settles to the bottom where it is removed with the effluent recirculated. Developed by Unitika Ltd (Japan).	Struvite	(Katsuura, 1998; Tchobanoglous et al., 2014)
PHOSPAQ™ process	A side stream process consisting within an aerated zone. Air lift is designed to provide mixing, strip CO ₂ and increase pH, and provide DO for biological treatment. MgO is used as the Mg source for the precipitation of struvite. Developed by Paques (The Netherlands).	Struvite	(PAQUES, 2016; Tchobanoglous et al., 2014)

FIX-Phos	Calcium silicate hydrate (CSH) particles are added into the anaerobic digester. The CSH adsorbs P as Ca-P and controls struvite formation by reducing the P concentration in the digestate. The Ca-P on CSH can be separated and recovered from the digested sludge.	Ca-P on CSH	(Petzet and Cornel, 2012)
P-RoC®	P recovery from waste water similar to the Crystalactor® process however complex pre-treatment steps such as pH adjustment or CO ₂ stripping can reportedly be avoided. Crystallisation products showed a P content of 11 % to 13 % which was comparable to phosphate rock.	Ca-P on CSH	(Berg et al., 2001)
PHOXNAN	The process combines low pressure wet oxidation with two membrane filtration steps. High temperature and pressure at acidic conditions (sulphuric acid added to adjust pH to 1.5) are used for sludge oxidation with pure oxygen. Organic components are decreased and organic pollutants are oxidised. Due to the low pH, P exists in solution mainly as H ₃ PO ₄ and H ₂ PO ₄ . The first membrane uses ultrafiltration to separate solids, the second membrane uses nanofiltration to eliminate metal ions.	H ₃ PO ₄	(Blöcher et al., 2012)
Aqua Reci	Commercially, the process makes use of supercritical water oxidation. Leaching is accomplished with a base, which selectively dissolves P. By addition of calcium, P can be precipitated.	Ca-P	(Levlin, 2007; Stendahl and Jäferström, 2004)
EcoPhos®	HCl or H ₂ SO ₄ is used for the digestion of any phosphate raw material including P-rock or SSA. The EcoPhos® process involves the treatment of the obtained slurry to remove dissolved impurities and solid residues and produces a phosphate product such as dicalcium phosphate or H ₃ PO ₄ .	DCP or H ₃ PO ₄	(DeRuiter, 2014; Ecophos, 2017)
Mephrec	The process utilises temperatures of up to 2000 °C where the sewage sludge melts under the addition of oxygen, with all organic pollutants destroyed. The metals obtained can be recycled, the slag is a form of fertilizer with high plant availability, free of heavy metals/metalloids and organic pollutants – similar to Thomas phosphate fertiliser (a P-rich slag produced in the steel industry).	Detoxified mineral P	(Nuremberg GmbH, 2016)
AshDec	Ash and natural earth alkali salts are exposed to a temperature of 1 000-1050°C. The heavy metals/metalloids react with the salts, become gaseous and evaporate. The phosphate compounds are transformed into plant available species.	Detoxified mineral P	(Outotec, 2017)

418 **4 Recovered P products from treated sludge**

419 P recovery processes from sewage sludge, including commercial and large scale approaches
420 and the characteristics of the final products obtained are detailed in Table 2. Recent
421 description and comparison of commercial approaches for P recovery from municipal
422 wastewater is provided in detail elsewhere (Egle et al., 2016, 2015). Current EU fertiliser
423 regulation recognises only primary mineral-derived P products as fertiliser whereas the rest of
424 these recovered P products cannot yet be labelled as such (European Union, 2003) – the
425 legislation however is currently under revision to include recovered P residues such as
426 struvite, ashes and pyrolysis materials (European Commission, 2016; Huygens et al., 2017).
427 This revision also limits the composition of fertiliser products in terms of impurities and level
428 and bioavailability of nutrients, therefore selective routes to obtain these products will be
429 beneficial. Among the recovered products in Table 2, struvite stands out due to its usability
430 directly as a slow release fertiliser (Bouropoulos and Koutsoukos, 2000).

431 **4.1 Struvite**

432 Struvite precipitation has been the main focus for P recovery commercially, and is widely
433 recommended for treatment of sludge digester liquors in large WWTPs operating EBPR
434 processes (Martí et al., 2010). Struvite crystallises as hard crystalline deposits when a molar
435 ratio and concentration of $Mg:NH_4:PO_4$ exists of 1:1:1 and exceeds the product solubility
436 constant, respectively (Crutchik and Garrido, 2016). For crystallisation to occur readily, a
437 concentration between 100 and 200 mg PO_4^{3-}/L is required (Rittmann et al., 2011), which
438 tends to be at least 10 times higher than typically found in the liquid phases of municipal
439 wastewater treatment. The crystallisation of struvite and other P-rich precipitates results in a
440 very low degree of impurities. This is advantageous because the selectivity of this process

441 leads to a safe product that can be applied to soil directly, despite the possible presence of
442 heavy metals and other contaminants in the EPBR effluents. Solution pH can be increased by
443 the addition of a base or through CO₂ stripping (Petzet and Cornel, 2013); struvite becomes
444 highly insoluble at alkaline pH and therefore increasing solution pH can lead to increased and
445 accelerated struvite formation (Ariyanto et al., 2014). The effective precipitation of struvite
446 has been shown feasible in the treatment of side streams originating from the digestion of
447 EBPR sludge (Mattenberger et al., 2008). Practically and economically, however, struvite
448 production is currently viable only in large WWTPs where enhanced biological accumulation
449 of P can be applied.

450 The precipitation of struvite is usually initiated with the addition of a Mg source as most
451 municipal wastewaters contain more N and P than Mg (Rahman et al., 2014), however some
452 streams can require PO₄³⁻ additions where the P content is low. The source of Mg used may
453 contribute up to 75% of the overall production costs of struvite (Dockhorn, 2009), however if
454 P is accumulated using EBPR then Mg may be the only chemical requirement in the WWTP
455 process. The most common source of additional Mg is MgCl₂ or MgO, though many other
456 materials have been used experimentally. Lahav *et al.* (2013) investigated using concentrate
457 from seawater nanofiltration as a cheap Mg (II) source for precipitating struvite from
458 municipal sludge centrifuge wastewater. Wood ash and bittern salts have also been found to
459 be good sources of Mg in struvite crystallisation processes (Lee et al., 2003; Sakthivel et al.,
460 2012).

461 Where chemical precipitation is operated, Fe or Al may be present at high concentrations. P
462 may consequently co-precipitate during solubilisation in AD or other WWTP processes. A
463 stream of sufficiently concentrated P may then not be available to support effective struvite
464 precipitation and ensure high rates of P recovery. High Ca²⁺/PO₄³⁻ ratios have been found to

465 be detrimental to struvite formation in pilot- and full-scale plants treating potato and dairy
466 wastewater, respectively (Moerman et al., 2009).

467 Uncontrolled precipitation of struvite can occur within centrifuges, digesters and sludge
468 liquor pipes (Petzet and Cornel, 2012). Where the controlled precipitation of struvite is
469 carried out in side stream processes, after the dewatering of the digested sludge, this
470 undesired precipitation can make the processes less efficient with potential additional costs
471 being incurred from the maintenance of equipment. The commercial Airprex® process (Table
472 2) precipitates struvite directly in the sludge stream and can therefore have economic benefits
473 regarding scaling of pipes and sludge dewatering equipment. The recovery of the struvite
474 then depends on the subsequent separation of digested sludge. Waternet, Amsterdam, which
475 recovers P as struvite from bio-P sludge using the Airprex® process, reportedly makes an
476 annual saving of €500 000 due to improved dewatering and reduced scaling problems – the
477 recovered struvite product is sold to the fertiliser industry for between €50–100/t for fertiliser
478 production (Waternet, 2017). For the use of struvite in agriculture it is important to minimise
479 contaminants, for example heavy metals and metalloids may become incorporated into the
480 precipitated struvite. Arsenic, for example, has been found sequestered into a synthetic
481 struvite at concentrations of up to 547 ± 15 mg/kg (Lin et al., 2013). This potentially renders
482 struvite recovered from some waste streams unusable in agriculture without removal of heavy
483 metals/metalloids.

484 Struvite has an economic value as an effective slow release fertiliser, for example it was sold
485 in Japan at a USD value of \$250 per tonne in 2001 (Forrest et al., 2008; Ueno and Fujii,
486 2001). Other than in municipal WWTPs, struvite precipitation has recently been investigated
487 in a broad variety of wastewater streams from bakery production (Uysal et al., 2014); the
488 semiconductor industry (Warmadewanthi and Liu, 2009); swine and poultry farming (Jordaan
489 et al., 2010; Taddeo and Lepisto, 2015; Yang et al., 2012); slaughterhouse wastewater

490 (Kabdaşlı et al., 2009); landfill leachate (Huang et al., 2014); human urine (Lind et al., 2000)
491 and within the potato processing industry (Uysal and Kuru, 2013). Some studies have been
492 found effective, in precipitating struvite from agro-industrial wastewaters, at pilot- and full-
493 scale (Moerman et al., 2009), whereas largely, studies still remain to be proven effective at
494 full-scales.

495 **4.2 Ca-P precipitates**

496 P content in recovered Ca-P products can vary from 12–20% and can be assumed to have a
497 higher solubility than that of well-crystallised Ca-P (Cabeza et al., 2011). From a commercial
498 viewpoint, however, the recovery of P in the form of Ca-P is beneficial since it has more
499 diverse applications in industry than struvite (Okano et al., 2013). Calcium phosphate (mainly
500 as hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) reflects the composition of rock phosphate and should be
501 easily adopted as a secondary P source in existing industry and infrastructure (Song et al.,
502 2006; Tervahauta et al., 2014). Indeed, many established commercial processes already
503 derive Ca-P precipitates as the final product (Table 2).

504 Hydroxyapatite is the most common form of Ca-P precipitate and forms at high pH, typically
505 >10 (Rittmann et al., 2011). At lower pH, dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$)
506 and octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) are expected to be the more stable phases.
507 However, these precipitated phases are thought to transform into the more
508 thermodynamically stable hydroxyapatite over time (Desmidt et al., 2015; Seckler et al.,
509 1996).

510 Calcium silicate hydrates (CSHs) have been studied as a seed for Ca-P precipitates.
511 Amorphous CSHs (Okano et al., 2013) and tobermorite-rich waste materials from the
512 construction industry (P-RoC) (Berg et al., 2001) have been investigated. Other calcium rich
513 materials investigated include cattle bone (Jang and Kang, 2002). In the precipitation of Ca-P,

514 bicarbonate alkalinity often requires control as competition between hydroxyapatite and
515 calcium carbonate precipitation can occur. This is often provided through the removal of
516 carbonates by acidification and CO₂ stripping, but the addition of a base such as NaOH to
517 increase pH can increase the cost of the process. It has been noted, however, that using CSH
518 as a seed material avoids the need to modify the influent and that removal of carbonate was
519 unnecessary, with phosphate and carbonate co-precipitated to the solid surface (Song et al.,
520 2006).

521 Commercial processes based on Ca-P precipitation include *FIX-Phos*, in which Ca-P is
522 directly precipitated (on CSH) into sludge. This holds the same risks identified for the
523 corresponding struvite process (see section 4.1).

524 **4.3 Thermochemically treated sewage sludge ash**

525 Thermochemical treatment is an option for deriving a metal-depleted solid with higher
526 bioavailable P. After mono-incineration, the addition of Mg and Ca chlorinated salts and
527 water, thermochemical treatment at approximately 1000°C was found to increase P-
528 bioavailability due to the formation of Mg- and Ca- bearing phosphates such as chlorapatite,
529 farringtonite and stanfieldite (Adam et al., 2009). Heavy metals/metalloids are depleted
530 mainly due to their volatilisation as heavy metal chlorides. The legal limits of Fertilizer
531 Ordinance in the EU were reportedly met in most cases. KCl added to SSA favoured Cu
532 removal over Zn, but the converse was the case for MgCl₂ (Mattenberger et al., 2008). This
533 has relevance to the thermochemical treatment of incinerated biological sludges since they
534 tend to contain higher concentrations of Cu and Zn (Franz, 2008). In most cases Cd, Cu, Zn
535 and Pb can be removed up to at least 90 wt% from SSA. However, even with higher Cl
536 addition at the same incineration temperatures (1000°C), Cr and Ni have been found to have
537 low volatility (Fraissler et al., 2009; Vogel and Adam, 2011).

538 Two commercial processes in the literature, AshDec and Mephrec, offer recovered products
539 in the form of mineral-P from thermochemical SSA treatment. The AshDec process is a
540 calcination process based on fluidised bed technology (Outotec, 2017). The Mephrec process,
541 through metallurgic treatment at high temperature, provides a slag that contains P of high
542 plant availability, free from heavy metals/metalloids and organic pollutants, and similar in
543 form to Thomas-phosphate fertiliser. This is used by the fertiliser industry after further
544 processing but can be safely used in organic farming (Nuremberg GmbH, 2016).

545 **5 Experimental P recovery through sorption processes**

546 Several experimental technologies are being developed that have shown high efficiency for P
547 recovery at bench or small pilot scale: membrane filtration (Gerardo et al., 2015; Qiu and
548 Ting, 2014), electrodialysis (Zhang et al., 2013), and nanoparticle-based sorbents (Lu et al.,
549 2015; Su et al., 2015; Tu and You, 2014) as well as various modified mineral- and biological-
550 based sorbents (Chiou et al., 2015; C. Fang et al., 2015; Nguyen et al., 2014b; Yu et al.,
551 2015). However, cost and practicality have so far prevented these technologies from being
552 adopted in commercial scale operations.

553 Sorption techniques have been shown to have potential for removal of a wide range of
554 contaminants from dilute wastewater effluents (Busquets et al., 2014; Nguyen et al., 2013;
555 Sivasankar et al., 2013). The use of easily obtainable or synthesisable materials as well as
556 waste materials may reduce the need for more expensive chemical additives or modification
557 to existing WWTP infrastructures. As well as encouraging the precipitation of P by seeding,
558 mentioned in preceding sections, sorbent-based processes can include other coexisting
559 mechanisms such as ion exchange, ligand exchange, and electrostatic interactions to directly
560 sorb P from the waste stream. Such processes can potentially fit into existing WWTP
561 infrastructures and provide enhanced P removal and recovery. Sorbents have not been widely

562 employed in WWTPs as stand-alone P recovery processes. Similarly, the potential of
563 recovered sorbed-P fertiliser or soil amendment has not been widely considered or assessed.
564 However, a wide variety of materials evaluated for the sorption of P have shown high
565 potential, these have been compiled in Table 3.

566 An extensive review of agricultural by-products and wastes for the sorptive removal and
567 recovery of P recently concluded that organic materials require some form of pre-treatment
568 before use in P recovery, due to the lack of anion binding sites (Nguyen et al., 2014a).
569 Surface modifications can significantly enhance the capture efficiency, but poor reusability of
570 materials recycled from agriculture has been reported. Capture and recovery of P by biochars
571 has been investigated and modification of the feedstock, mainly through incorporation of Fe
572 or Mg, has been shown to be necessary to enable efficient uptake of P (Shepherd et al., 2016;
573 Yao et al., 2013). Although the application of P-bearing biochar to soil has been suggested,
574 the technology is still in its infancy. While efficient P removal can be brought about through
575 material modifications, the added cost to the process may make their application to soil
576 uneconomic. Among the potential mineral sorbents zeolitised fly ash, layered double
577 hydroxide (LDH) minerals and Li-intercalated gibbsite have exhibited high potential for P
578 sorption from solution (Wendling et al., 2013). Their subsequent direct use as nutrient
579 bearing soil amendments or as P fertiliser has been suggested, but not yet demonstrated.

580 **Table 3.** Sorbent materials used for the uptake of P: Sorption capacities, application and mechanisms.

Sorbent material	Sorption capacity/ efficiency	Information about study/ experiment	Reference
Powdered sulphate-coated zeolite	111.5mg P/g	Three novel composite adsorbents, sulphate- coated zeolite (SCZ), hydrotalcite (SCH) and activated alumina (SCAA). Sulphate coating improved sorption capacity in the case of SCZ and SCAA. Adsorption thought to have occurred fast. Main mechanism: ion-exchange between phosphate and sulphate on the surface of the adsorbents.	(Choi et al., 2012)
Powdered hydrotalcite	26.1 mg P/g		
Sulphate coated activated alumina	49.7 mg P/g		
Lanthanum hydroxide	107.5 mg P/g	Surface area 153.3 m ² /g. Performed well across a wide range of pH values. Main mechanism: ligand exchange.	(Xie et al., 2014)
Cerium-zirconium binary oxide nanoparticles	36.6 mg P/g	Ce/Zr binary oxide nanoparticles were synthesised with different structure, crystal size, surface properties, and phosphate adsorption performance. Main mechanism: inner-sphere complexing mechanisms were thought to dominate, the surface -OH groups playing a major role.	(Su et al., 2015)
Cement based materials	30.0 mg P/g	High Si, Ca, Al and Fe content within cement materials. Main mechanism: precipitation with Ca predominantly.	(Wang et al., 2014)
Zirconium loaded okara	14.4 mg P/g	The phosphate removal was rapid, reaching 95% in 30 min from an initial concentration of 5 mg P/L. Adsorption tested between 10 – 500 mg P/L.	(Nguyen et al., 2014b)
Magnetic Fe-Zr binary oxide	13.7 mg P/g	Incorporation of Fe into Fe-Zr oxide allows for magnetic recovery. Zr oxide was a suitable adsorbent for P. Main mechanism: ion-exchange of Zr species and partly originated from magnetite species of Fe-Zr binary oxide.	(Long et al., 2011)
Scallop shell synthesized ceramic biomaterials	13.6 mg P/g	Scallop shells, montmorillonite and starch (1:1:1) were mixed to a paste. The ceramic samples were dried at 105°C for 24 h in an oven and calcined at 600°C. A surface area of 53.74 m ² /g was reported.	(Chen et al., 2013)

Nano bimetal ferrites (CuFe₂O₄ – Green synthesis)	13.5 mg P/g	Manufactured from industrial sludge. Fast sorption rate within first 10mins reached equilibrium within 120mins. Magnetic. Large potential for desorption and recovery. Main mechanism: inner-sphere mechanisms.	(Tu and You, 2014)
Amine-functionalized silica magnetite	>~13 mg P/g	A magnetic adsorbent: amine-functionalized silica magnetite. The maximum adsorption was found to occur at pH 3.0.	(Chiou et al., 2015)
Zirconium loaded bifunctional fibers (fibrous ligand exchange adsorbent)	Breakthrough point at ~340BV	Adsorbent slightly preferred phosphate to arsenate. Sorbent reversible and suitable for multiple reuse cycles. Main mechanism: ligand exchange – sorption slightly enhanced due to co-ion and Donnan invasion mechanisms (Cl ⁻ and SO ₄ ²⁻).	(Awual et al., 2014)
Nano-sized iron oxide coated sand	69.1% P removal without magnetic field application, 75% with.	20mL/min flow rate through column of 20cm height, 5cm width. Main mechanism: precipitation of Fe-P deposits on the surface of sand.	(Khiadani Hajian et al., 2013)
Chemically surface-modified silica filter	Effective up to 1.5L of influent with 36 filters (900g) to remove P to below 1 mg/L. 20 seconds per 500mL with 36 filters.	Glass modified silica granules packed into 25g porous cylindrical filters. After regeneration, filters (36) unable to reduce P concentration to below 2 mg/L. Main mechanism: ion-exchange.	(Kim et al., 2012)

582 Using sorbent materials for the removal and recovery of P for subsequent direct use as a
583 fertiliser or soil amendment is attractive, provided that the sorbent material is economic and
584 has adequate P affinity without retention of contaminants. If modifications are required to
585 provide these, the cost and complexity of additional processing have to be considered. Rather
586 few materials shown to be effective as sorbents for P are also suitable for direct application to
587 agricultural land. Waste materials are an attractive option for having a low (or no) price and
588 for their often wide availability, but incur the cost of compliance with regulation (European
589 Union, 2003). Variability in composition is a further challenge. Also, materials showing high
590 affinity for P in sorption studies may also have minimal potential for P release. Effective
591 sorption is often brought about by high Fe or Al contents which, as discussed, may then limit
592 solubilisation of P within the soil, or may be toxic in surrounding aquatic environments.

593 Other issues regarding the sorption of P from wastewaters is the co-sorption of toxic
594 compounds that contain heavy metals/metalloids, or metals that compete with phosphate and
595 other anions for sorption sites; selective recovery of P should therefore be a key goal of any
596 recovery process. A Zn-Al LDH material reported in the literature provides an example for
597 such selectivity. Intercalated with pyromellitic acid this sorbent achieved 97.4% selectivity
598 toward P at pH 7 from complex solutions containing H_2PO_4^- , SO_4^{2-} , CO_3^{2-} , NO_3^- and Cl^- (Yu
599 et al., 2015). Although this material showed a selective and effective P sorption compared to
600 other options, the practicality of the material in terms of recyclability, usability or cost was
601 not discussed. For innovation in sorbent technologies to translate to WWTP use, their
602 potential feasibility should be assessed and demonstrated at an early stage. Their efficiency at
603 low or high P concentrations should be assessed in relation to their suggested use; as filtration
604 media in a tertiary process in the primary stream or for sorption of P within a side stream
605 process treating sludge liquors and dewatered sludge, respectively. But their end use is an
606 equally important consideration in developing sorbents for P recovery – the effective

607 bioavailability of P and its re-release into soil when used as a fertiliser or P-bearing soil
608 amendment, or its potential for regeneration, i.e. re-use after desorption of P and its separate
609 recovery. Sorption of P remains a flexible, efficient and potentially effective option; either as
610 a potentially lower-cost alternative to crystallisation technologies, or as an additional
611 technology that provides for enhanced P removal and recovery potential.

612 **6 Bioavailability of recovered P products**

613 Not all P in soil is bioavailable to plants and P is a key limiting nutrient in terrestrial
614 ecosystems (Elser, 2012; Maltais-Landry et al., 2014). Phosphorus therefore plays a critical
615 role in productive agriculture (Withers et al., 2014), but its plant availability however can
616 often be low: it forms sparingly soluble fractions due to adsorption, precipitation or
617 conversion to organic fractions in soil (Werner and Prietzel, 2015), via geochemical
618 processes that depend on several soil properties such as the abundance of Ca, Al and Fe
619 oxides, pH and organic matter content. The bioavailability of P in recycled P products can be
620 assessed using chemical analogues for plant acquisition (i.e. using extractants) or more
621 directly in pot or field trials. For P to be utilised by plants it must be soluble or solubilised,
622 but solubility and potential bioavailability depends on a number of soil-related factors, so its
623 assessment as an effective and suitable fertiliser should be undertaken in diverse
624 environments. The use of Ca and Mg in crystallisation processes has been shown to have high
625 potential for P recovery, owing to the solubility of precipitated Ca and Mg products in soil.
626 The bioavailability of struvite has been more widely investigated: i.e. through cultivation of
627 Chinese cabbage (Ryu et al., 2012); maize (Liu et al., 2011); maize and tomato plants (Uysal
628 et al., 2014); corn and tomato plants (Uysal and Kuru, 2013). Struvite-P has been found to be
629 relatively soluble and bioavailable across a wide range of pH conditions and soil types.
630 Recovered Ca-P products have been investigated to a lesser extent.

631 Struvite can be considered as the better product compared with Ca-P, in terms of
632 bioavailability. Through isotopic labelling techniques with ^{33}P , a reference hydroxyapatite
633 and a recovered product partly composed of hydroxyapatite, were found to be less effective,
634 in terms of the plant availability of P, than triple super phosphate (TSP), reference struvite
635 and a recovered product composed of both struvite and hydroxyapatite (Achat et al., 2014a).
636 However, using the same recovered products in pot and soil incubation experiments with
637 slightly acidic soil growing ryegrass and fescue, both were as effective as TSP and the
638 struvite reference material (Achat et al., 2014b). When the plant uptake of P derived from the
639 applied products was compared with that derived from the TSP, the reference hydroxyapatite
640 was found to have only 22% relative effectiveness, compared with 85-96% for the recycled
641 products and 111% for the reference struvite. This was likely due to higher solubility of
642 poorly crystallised phases of Ca-P associated with the recycled products (Achat et al., 2014b).
643 The recovered P products containing struvite and Ca-P were derived from pig manures and
644 dairy effluents.

645 The bioavailability of various recycled P products has also been compared with TSP and P-
646 rock in pot experiments with maize in two contrasting soil environments (pH (CaCl_2) 4.7 and
647 6.6) over a period of 2 years. Recycled struvite products were found to be as effective as TSP
648 in both soils, but the Ca-P product was only effective in the acidic soil (Cabeza et al., 2011).
649 The restricted effectiveness of Ca-P to acidic soils is due to the enhanced disintegration of the
650 P-rich material in higher H^+ concentrations and its relative stability in alkaline conditions.
651 Similarly, an alkali sinter phosphate made from meat and bone meal was as effective as TSP
652 in the acidic soil, while a cupola furnace slag was in the neutral soil (Cabeza et al., 2011).
653 Both the SSA and a meat and bone meal ash had low effectiveness, in terms of P uptake and
654 P concentration in the soil solution, and were comparable to rock-P. It was concluded that P
655 products obtained through chemical processes were suitable for direct application as

656 fertilisers, especially struvite, and the ash products could be potential raw materials for P
657 fertiliser production (Cabeza et al., 2011).

658 The thermochemical treatment of SSA is a promising technology in deriving heavy metal
659 depleted residues containing P in bioavailable forms. Two SSA products thermochemically
660 treated with either $MgCl_2$ or $CaCl_2$ were investigated for their plant availability in pot trials
661 with ryegrass using ^{33}P (Nanzer et al., 2014). The shoot uptake of P from the Mg treated SSA
662 was found to be higher than the Ca treated SSA (15.7 and 8.3 mg P/kg acidic soil,
663 respectively). The effectiveness of the Mg treated SSA relative to a water-soluble P fertiliser
664 was 88% in an acidic soil, 71.2% in a neutral soil but was reduced to 4% in an alkaline soil
665 (Nanzer et al., 2014).

666 Large gaps still remain in the understanding of the release and plant availability of P in soils
667 from recovered products derived from WWTPs. From review, the use of indirect isotopic
668 labelling techniques would appear to be the best method in assessing the contribution of
669 recovered-P to plant available P in soil and P utilised by the plant. Further investigation and
670 empirical information regarding the availability, plant uptake and cycling of P in soils related
671 to the application of recovered products and residues will lead to a greater understanding and
672 confidence in their use as alternatives to inorganic-P derived fertilisers. It is additionally
673 important that both the removal process and reuse of P are considered on a case-by-case basis
674 – not all recovery processes will be applicable to all wastewaters, and similarly not all
675 recovered products will be equally effective across different soil environments. As sorbent
676 materials can be derived from a wide variety of materials and processes, providing a myriad
677 of physical and chemical characteristics, P sorbed to and within the surface and structure of
678 these solids may have wide ranging applications.

679 **7 Conclusions**

680 The diminishing quantity and quality of P-rock reserves, and the eutrophication of water
681 bodies, are instigating a critical need to recover P from WWTPs in forms suitable for
682 agricultural application. There are numerous recovery options that vary in application (i.e.
683 sludge, sludge liquor, primary stream, SSA) and technology used (precipitation, EBPR, AD,
684 wet chemical extraction, thermochemical treatment). The chemical precipitation of struvite
685 and Ca-P, from the digested EBPR sludge stream, are the favoured routes that are
686 technologically well developed and already in operation in a number of WWTPs. The mono-
687 incineration of sludge followed by thermochemical treatment of the SSAs are also promising
688 steps in the production of secondary P residues suitable as a detoxified P fertiliser.

689 EBPR currently forms the basis of chemical crystallisation technologies in providing a
690 process stream of suitable concentration for efficient P recovery. The minimisation of Fe and
691 Al, especially where P is to be recovered from anaerobic digestate, is important to maximise
692 P release. Where chemical accumulation processes are required to be operated due to spatial,
693 economic or infrastructural requirements the metal salt applied and the resulting sludge
694 composition should be considered regarding the suitability of the sludge residue for
695 processing by the fertiliser industry or its use directly as a detoxified residue after
696 thermochemical treatment.

697 Technologies such as thermochemical treatment, wet chemical extraction and electro dialysis
698 may be used to increase the total recovery potential to around 90%, and in some cases, have
699 been shown to be economically feasible. However, the present cost of some existing and
700 novel technologies is not yet offset by a marketable product due the current omission of
701 recovered products from fertiliser legislation. Where P must be removed on in some cases
702 recovered, to comply with statutory limits and regulation, a range of approaches will be

703 valuable and necessary despite not being profitable – the inclusion of recovered P products
704 such as struvite and ashes in to the revised fertiliser legislation will then create a value and a
705 market for these products. This is important in enabling recovered-P products to substitute
706 and compete with primary fertilisers on the market and could foreseeably require
707 subsidisation or regulatory forcing until an increase in price of primary fertilisers ensures that
708 widespread agricultural adoption is economical.

709 Around 90% of the incoming P load can be incorporated into sewage sludge, however to
710 consistently achieve P limits of <1 mg/L, WWTPs require a further removal of P before
711 discharge, with future legislation foreseeably requiring increasingly lower concentrations of P
712 in discharge. Consequently, a gap in wastewater treatment strategy has presented itself; the
713 “polishing” of effluents, other than by additional chemical dosing, in a tertiary treatment
714 setting where EBPR may not be able to reliably meet required concentrations. Experimental
715 technologies (ion-exchange, novel sorption processes, membrane filtration, etc.), although not
716 yet commercially operational, may become key in providing an enhanced P removal and
717 recovery potential. Sorbents, if effective, may easily be incorporated into existing
718 infrastructures and may provide alternatives to technologies unachievable at smaller WWTPs
719 – currently the precipitation of struvite/ Ca-P can only be practically applied at large WWTPs
720 operating EBPR. The focus of experimental technologies and especially sorption processes is
721 deriving recovered-P products or residues of suitable purity, form, economy and
722 bioavailability for their safe and effective application as fertiliser to agricultural land.

723 Struvite compares well to TSP and other mineral-P fertilisers in pot trials under a range of
724 soil pH values, but full field trials and longer term tests are still lacking. The application of
725 recovered-P products and residues to soils and their use by crops needs further investigation
726 and empirical information – understanding the bioavailability and availability of recovered P
727 and its use by plants in a wide range of soils and environments is important to increase

728 confidence in the precise and effective use of these products as a substitute for conventional
729 inorganic-P derived fertilisers. This will be vital for the widespread recovery of P and the
730 adoption of recovered-P as fertiliser.

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Highlights

- P recovery is a pressing issue and wastewater provides a substantial opportunity
- Struvite/Ca-P **crystallisation** is limited to <25% **P recovery of the influent P load**
- **Crystallisation, thermo- and wet-chemical processes are being commercially applied**
- **Revised fertiliser legislation and P limits drives wider adoption of technologies**
- **All approaches should focus on obtaining agriculturally effective forms of P**