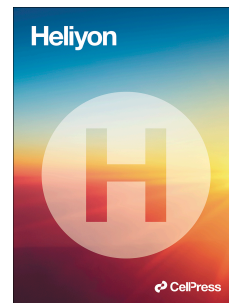


Journal Pre-proof

STRUVITE PRECIPITATION WITHIN WASTEWATER TREATMENT: A PROBLEM OR A CIRCULAR ECONOMY OPPORTUNITY?

P. Achilleos, K.R. Roberts, I.D. Williams



PII: S2405-8440(22)01150-1

DOI: <https://doi.org/10.1016/j.heliyon.2022.e09862>

Reference: HLY 9862

To appear in: *HELIYON*

Received Date: 18 February 2022

Revised Date: 17 May 2022

Accepted Date: 29 June 2022

Please cite this article as: Achilleos, P., Roberts, K.R., Williams, I.D., STRUVITE PRECIPITATION WITHIN WASTEWATER TREATMENT: A PROBLEM OR A CIRCULAR ECONOMY OPPORTUNITY?, *HELIYON*, <https://doi.org/10.1016/j.heliyon.2022.e09862>.

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Circular Economy from struvite recovery

- ✓ Recovery of nutrients.
- ✓ Displacement of fossil fuel derived fertiliser (Ammonia).
- ✓ Displacement of mined phosphate.
- ✓ Potentially reduced leaching/ eutrophication rate.
- ✓ Developing market emerging.
- ✓ Revenue stream from the fertiliser.

Journal Pre-proof

1 **STRUVITE PRECIPITATION WITHIN WASTEWATER TREATMENT: A PROBLEM**
2 **OR A CIRCULAR ECONOMY OPPORTUNITY?**

3

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11

12

13 **Abstract**

14 Enhanced biological phosphorus removal at wastewater treatment plants that use anaerobic digesters
15 for sludge treatment have historically encountered phosphate precipitation problems in the form of
16 struvite. Literature on struvite is thin which is surprising given it can foul/block the sludge return lines
17 and associated pumps and valves, causing significant operational problems. This study has evaluated
18 if a typical large wastewater treatment plant can overcome this problem by adopting circular economy
19 thinking. The struvite profile based on the supersaturation ratio of ($Mg:NH_4:PO_4^{2-}$), pH and
20 temperature demonstrates the potential operational hotspots that can present uncontrolled struvite
21 formation. Based on current struvite monitoring technologies and a cost-benefit analysis, the
22 controlled struvite recovery via an Ostara crystallization reactor has been demonstrated to be
23 economically viable with a pay-back period of less than a decade. An integrated evaluation illustrates
24 the positive environmental impact arising from the utilisation of the recovered product. Economic
25 viability and payback periods will vary according to circumstances, but we recommend that WWTP
26 operators globally consider fitting a crystallisation reactor to appropriate plants, The outcomes and
27 recommendation from this study are particularly timely given the global fertiliser shortage (2022) that
28 is driving up food prices and reducing crop sizes.

29

30

31 **Keywords:** wastewater treatment, phosphorus, struvite, cost-benefit analysis, circular economy.

32

33 1.0 Introduction

34 Wastewater treatment plants (WWTPs) incorporating secondary treatment and anaerobic sludge
35 digestion facilities have historically encountered phosphate precipitates in the form of struvite (Barr &
36 Münch, 2001; Jaffer et al, 2002). These agglomerates can foul and block the sludge return lines and
37 associated pumps and valves (Ohlinger et al, 1998; Jaffer et al, 2002; Mudragada et al, 2014).

38 Uncontrolled struvite precipitation increases pumping and maintenance costs, as well as reducing the
39 overall capacity of the plant piping system via hydraulic loss capacity. This also lowers the biological
40 treatment efficiency (Battistoni et al, 1997; Barr & Münch, 2001; Doyle & Parsons, 2002; Jaffer et al,
41 2002; Mudragada et al, 2014).

42
43 However, it is possible that controlled production and recovery of struvite could promote circular
44 economy (CE) opportunities for the wastewater treatment industry (Barr & Münch, 2001; Jaffer et al,
45 2002; Molinos et al, 2010; Siciliano et al, 2020), especially in coastal areas (Roberts et al, 2021). The
46 precipitated struvite can be recovered and sold as fertiliser, reducing resource depletion by replacing
47 fossil-fuel based P (Jaffer et al, 2002; Zhang & Mo, 2013). Mavhungu et al (2021) report that struvite
48 precipitation could act as a fast, efficient, and environmentally friendly pre-treatment step to remove P
49 and reduce N from wastewater. However, a potential concern is that the environmental impacts of
50 struvite recovery via the use of additional chemicals and energy are not offset by its benefits (Sena et
51 al, 2021). Nevertheless, removal of struvite can significantly decrease the operational and
52 maintenance costs of WWTPs, promoting the optimisation of operational and environmental
53 performance (Jaffer et al, 2002; Pastor et al, 2008).

54 Within WWTPs, enhanced biological phosphorus removal (EBPR) processes produce a P-rich
55 activated sludge, causing struvite deposit problems in anaerobic sludge digestion (Barr & Münch,
56 2001). Generally, struvite (MgNH_4PO_4) is a white crystalline mineral compound that forms under
57 conditions of elemental supersaturation within liquids (Barr & Münch, 2001). It can be found in
58 WWTP systems when Mg^{2+} , NH_4^+ and PO_4^{3-} (magnesium, ammonium and phosphate – MAP)

59 concentrations exceed solubility levels, supersaturation occurs and minerals combine and precipitate
60 into solid form (Wu & Bishop, 2004).

61 WWTP design generally incorporates flow and partial pressure reduction through pump
62 impellers and pipe bends, forcing the removal of dissolved CO₂ and increasing the pH of the liquor
63 (Battistoni et al, 1997; Fattah et al, 2010; Xavier et al, 2014). High pH levels (~7.5–10) are essential
64 for the struvite precipitation (Ohlinger et al, 1998; Barr & Münch, 2001; Wu & Bishop, 2004).
65 Reduction of the partial pressure of reject waters from 0.5 atm to 0.05 atm within the WWTP
66 contributes to the release of dissolved CO₂ and thus increases pH levels from 7.0 to 8.0, increasing the
67 chance of struvite precipitation (Fattah et al, 2010).

68 The most common P removal technologies include biological P removal, crystallization,
69 chemical precipitation via ferric chloride, tertiary filtration and ion exchange (Morse et al, 1998).
70 Crystallization of struvite is probably the most sustainable solution due to the minimal waste
71 production that needs to be managed (Marti et al, 2008).

72 The primary aim of this study was to determine and evaluate the economic and environmental
73 impacts arising from the uncontrolled struvite formation within a typical large WWTP. For this aim,
74 the objectives were to:

- 75 i. Establish a mass balance for the nutrients present in the system. This is to enable the specific
76 locations within the operational system that present higher possibility for struvite
77 precipitation to be identified (Jaffer et al, 2002; Marti et al, 2008).
- 78 ii. Create a profile for struvite that incorporates the potential operational hotspots for
79 uncontrolled struvite precipitation and other factors that can affect struvite formation.
- 80 iii. Identify the operational and maintenance costs and the environmental impacts arising from
81 struvite precipitation at the WWTP.

82 The secondary aim of this study was select the most appropriate monitoring pathway for the
83 uncontrolled struvite precipitation based on the characteristics of the studied WWTP. For this aim, the
84 objectives were to:

- 85 i. Identify and evaluate current technologies regarding nutrient removal and/or controlled
86 struvite formation.

- 87 ii. Evaluate the economic costs and benefits of the controlled struvite formation.
- 88 iii. Develop an integrated cost benefit analysis for the proposed struvite monitoring technology.

89 We critically discuss findings in the context of enabling wastewater treatment processes to
90 recover more value from wastewater (resources), reducing treatment and maintenance costs and
91 enabling circular economy (CE) thinking to be operationalized.

93 **2.0 Methodology**

94 **2.1 WWTP characteristics**

95 Budds Farm wastewater treatment plant (BF-WWTP), owned by Southern Water (SW) in
96 England, treats the domestic wastewater of Portsmouth, Havant, Hayling Island, Cosham, Paulsgrove,
97 Waterlooville, Horndean and Hambledon. It has a general capacity of 109,000 m³ of wastewater per
98 day. Before its establishment, untreated wastewater arising from Hampshire was discharging to
99 Langstone Harbour causing significant environmental impact at local and national level. (Smith et al,
100 1999; Doyle & Parsons, 2002). Indeed, SW has admitted deliberately and illegally dumping untreated
101 wastewater into this harbour, resulting in a huge fine (BBC News, 2021a) and damaging publicity
102 (BBC News, 2021b).

103 BF-WWTP is responsible for a population equivalent (PE) of approximately 410,000. It
104 presents an outfall of an average 2000 L/s and it operates for 24/7 for 365 days per year. It has one of
105 the biggest BNR facilities in UK with 3 main operational units. BF-WWTP handles indigenous and
106 imported sludge with its anaerobic digesters to treat 800 m³ of activated sludge on 14 day cycle. The
107 site is under tight nutrient consents, restricting discharges into the harbour to 10mg/L total nitrogen or
108 less. Figure 1 illustrates the main operational units associated with the wastewater treatment process
109 within the BF-WWTP.

110

111 Insert Figure 1

112

113 **2.2 Sampling and analysis**

114 Operational units and locations (hot spots) within WWTPs that have historically presented P
115 precipitation in the form of struvite are summarised in Table 1 (Le Corre et al, 2009). A sampling
116 strategy was created to determine concentrations for the three struvite ions ($Mg:NH_4:PO_4^{2-}$) or MAP.
117 External factors such temperature (T) and pH were determined to evaluate struvite behaviour within
118 the system (Bouropoulos et al, 2000; Doyle & Parsons, 2002; Jaffer et al, 2002; Fattah, 2012).

119

120 Insert Table 1

121

122 Wastewater samples were professionally collected by an operational engineer employed at
123 BF-WWTP. The samples were processed and analysed on-site at BF-WWTP's engineering
124 laboratory. All samples were filtered via Advantec Grade No.1 filter paper or cellulose acetate syringe
125 filter. Because of the high density of the sludge samples, filtration was necessary in order to remove
126 coarse particles and prepare samples for qualitative analysis. Temperature (T) and pH were measured
127 potentiometrically in the undiluted liquid wastewater sample after filtration and in less than one hour
128 from sample collection. The DO700 analyser provided automatic measurements for dissolved oxygen,
129 T, pH, conductivity and total dissolved solids (TDS) (Pass, Extech DO700 Portable Dissolved
130 Oxygen Meter).

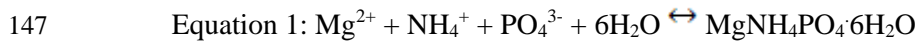
131 Ammonia concentrations were determined via a QUANTOFIX test kit that provides a
132 detection range between 10-400 mg/L NH_4^+ (Macherey-Nagel, Quantofix test strips). Phosphate
133 concentrations were determined via a QUANTOFIX test kit that only detected ortho-phosphate. This
134 method provides a detection range between 3-100 mg/L PO_4^{3-} (Macherey-Nagel, Quantofix test
135 strips). Magnesium concentration was determined via a viscolar ECO total hardness test kit that
136 provides a detection range between 10-100 mg/L CaO. (Macherey-Nagel, *VISOCOLOR*® *ECO*
137 Hardness, total). Dilutions of 1:4 or 1:10 (based upon previous experience) of wastewater samples to
138 double-distilled deionised water were required based on the colour indication of the test kits.

139

140 **2.3 Creation of the struvite precipitation profile within BF-WWTP**

141 Struvite precipitation generally correlates with the degree of supersaturation (Ohlinger, 1999;
 142 Bouropoulos et al. 2000; Kofina, A. 2005), magnesium to phosphorus molar ratio (Mg:P) (Barr &
 143 Münch 2001), pH (Barr & Münch 2001; Doyle et al. 2002), temperature (Doyle et al. 2001), crystal
 144 retention time, recycle ratio (Ohlinger 1999; Bouropoulos et al. 2000), turbulence and mixing
 145 (Ohlinger, 1999; Bhuiyan, 2007). Equation 1 summarises the kinetics of struvite formation:

146



148

149 The struvite profile (behaviour within the WWTP system) arose from the concentrations of
 150 the main chemical components of MAP and the struvite supersaturation rate (SSR) for each sampling
 151 point in correlation with pH and T. This correlation indicated which locations present higher potential
 152 for uncontrolled struvite precipitation (Doyle & Parsons 2002; Le Corre et al, 2009; Fattah et al, 2010;
 153 Fattah, 2012). In general, uncontrolled formation can occur when the concentrations of Mg^{2+} , NH_4^+
 154 and PO_4^{3-} exceed the K_{sp} of struvite and precipitates in a 1:1:1 molar ratio following Equation 1 (Le
 155 Corre et al, 2009). If the general equation of soluble salt in water is assumed then Equation 2 follows:

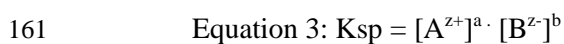
156



158

159 and the constant solubility product K_{sp} can be expressed as:

160



162

Where:

163

$[\text{A}^{z^+}]$ and $[\text{B}^{z^-}]$ are the total concentrations of ions in solution

164

z^+ and z^- are the valencies of the considered ions.

165

166 By applying Equation 3 on Equation 1, Equation 4 is produced (Michałowski & Pietrzyk, 2006):

167

168 Equation 4: $K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$ or $c^* = (K_{sp} / 1)^{1/3}$

169

170 Based on Equation 4, if the product of the concentration of Mg^{2+} , NH_4^+ , and PO_4^{3-} is greater
 171 than the value of K_{sp} , then the solution is supersaturated in terms of struvite and precipitation
 172 potentially will occur (Bhuiyan, 2007; Le Corre et al, 2009). This can also be described as the
 173 supersaturation ratio (SSR) and can be expressed as Equation 5 (Le Corre et al, 2009):

174

175 Equation 5: $SSR = \frac{S-sample}{K_{sp}}$

176

177 **2.4 Cost benefit analysis of P recovery via struvite precipitation**

178 An economic feasibility study of P recovery was established using a cost-benefit analysis
 179 (CBA). The net profit (NP) is the difference between benefits and costs (i.e. $NP = IB + EB$ where net
 180 profit [$NP = \text{total income} - \text{total costs}$]; internal benefit [$IB = \text{internal income} - \text{internal costs}$]; and
 181 external benefit [$EB = \text{positive impact} - \text{negative impact}$]). Through a CBA, a project is only
 182 economically feasible only if $NP > 0$ (Molinos et al. 2011).

183 The term internal income includes the sale of recovered P and treated water, as well as
 184 savings from reduced WWTP operating costs arising from chemical utilisation for the chemical
 185 precipitation of phosphorus; reduced sludge generation and associated management cost and reduced
 186 pipe and tube cleaning due to less uncontrolled struvite scaling (Molinos et al, 2011).

187 Internal costs include investment cost, civil works (equipment, machinery, and auxiliary
 188 facilities); operating and maintenance costs (reagents for chemical precipitation and pH value
 189 maintenance); and financial costs. (Molinos et al, 2011).

190 Investment costs depend largely on the size of the WWTP (Molinos et al, 2011). Operating
 191 and maintenance cost proposed values depend on the concentration of P in the waste streams and the
 192 reagents used to operate the plant. The cost depends on the people equivalent covered from the plant
 193 and the operational streams the P is be extracted. Thus, considering these incomes and costs, the
 194 internal benefit can be expressed as Equation 6 (Molinos et al, 2011):

195

196 Equation 6:

$$197 \quad IB = \sum_{t=0}^T [(ASR \times SPP) + (ASR \times CSM) + (ARR \times CR) + (APR \times CCD) - (IC + OMC + FC)]$$

198 Where:

199 IB = internal benefit (\$)

200 ASR = annual volume of struvite recovered (kg)

201 SPP = present selling price of struvite (\$/kg)

202 ASR = annual volume of sludge generation reduction (kg)

203 CSM = cost of sludge management (\$/kg)

204 ARR = annual volume reduction of reagents (kg)

205 CR = cost of reagents (\$/kg)

206 APR = annual volume reduction of uncontrolled struvite precipitation (kg)

207 CCD = cost of cleaning struvite deposit (\$/kg)

208 IC = investment cost (\$)

209 OMC = operational and maintenance cost (\$)

210 FC = financial costs (\$)

211

212 External benefits (EB) refer to any positive or negative impact that derives from a proposal
 213 and effects on people without economic value. P recovery from waste streams is regarded as having
 214 positive EB, such as an increase in the availability of a non-renewable resource and important
 215 environmental benefits, because if phosphorus discharge is prevented, then its level in water bodies is
 216 reduced and, consequently, there are fewer eutrophication problems. The external benefits can be
 217 expressed as Equation 7 (Molinos et al, 2011):

218

$$219 \quad \text{Equation 7: } EB = \sum_{t=0}^T (PI - NI)$$

220 Where:

221 PI = positive impact (\$)

222 NI = negative impact (\$)

223

224 In general, IB can be estimated directly as monetary units while the EB is difficult to estimate
225 as marketable price. In order to give a comparable value for the EB, the term shadow price may be
226 used (Molinos et al, 2011). Given the volatility of markets during the COVID19 pandemic, pre-
227 COVID monetary values have been used to establish order-of-magnitude indicative costs/prices.

228

229 **2.5 Integrated evaluation of chosen struvite monitoring technology**

230 Except for the financial elements, the integrated evaluation (IE) took into consideration the
231 environmental (shadow indicator) and social impacts that a proposal can cause at a national and
232 international level. The CBA determined if a technology can be viable from an economic perspective.
233 The IE demonstrated the sustainable trends of the modern industrial models and aimed to present a
234 holistic approach regarding the P monitoring pathway. (Molinos et al, 2011; Molinos et al, 2012; Bird,
235 2015).

236

237 **3.0 Results**

238 **3.1 Operational diagram and struvite precipitation**

239 Based on the BF-WWTP operational diagram as well as the locations shown in Table 1, the
240 sampling map was established in consultation with the BF-WWTP management team. Figure 2
241 illustrates the sludge treatment process within the plant focusing on the areas that present higher
242 possibility for uncontrolled struvite precipitation.

243

244 Insert Figure 2

245

246 Table 2 presents data arising from the determination of the main factors that affect the struvite
247 formation at the different operational hot-spots.

248

249 Insert Table 2

250

251 Several struvite K_{sp} values have been proposed in the literature. The most widely accepted
252 value was found to be $10^{-12.6}$ (Snoeyink, V. & Jenkins, D. 1980; Michałowski & Pietrzyk 2006). At
253 full-scale wastewater treatment processes, the K_{sp} value was determined as $10^{-13.26}$ (Ohlinger et al.
254 1998), thus struvite estimated to be less soluble than presented to be based on other researches. Table
255 3 presents the concentrations of the tested locations of BF-WWTP in M (mol/L) and the SSR.

256

257 Insert Table 3

258

259 The SSR for the selected locations indicates that the influent that reaches BF-WWTP presents
260 extremely high concentrations of the three ions of MAP. Thus there is high possibility of uncontrolled
261 struvite formation in the majority of the operational system; this is regularly observed on-site.
262 However, a positive SSR does not ensure that struvite is necessarily formed (Fattah, 2012). This is
263 mainly because the kinetics of P precipitation (how fast P is precipitated) and the competing reactions
264 must be taken into consideration. Furthermore, ions such as Ca^{2+} , K^+ , CO_3^{2-} , etc., can influence the
265 saturation of struvite by reacting with Mg^{2+} , PO_4^{3-} , and NH_4^+ . It is therefore necessary to evaluate the
266 availability of free ions (i.e. the ionic activity) for a given pH in order to accurately estimate the
267 precipitation rates (Snoeyink & Jenkins, 1980; Ohlinger et al, 1998; Barr & Münch, 2001). Figure 3
268 presents the variation of pH in the different operational hot spots at BF-WWTP.

269

270 Insert Figure 3

271

272 Struvite can potentially be formed at locations that present positive SSR and a pH range
273 between 7 and 10.7 (Tables 2 & 3, Figure 3) (Snoeyink & Jenkins, 1980; Ohlinger et al, 1998; Barr &
274 Münch, 2001). In general, the digester recirculation pumps, PDST, centrifuge feed, centrate and SAS
275 storage tank demonstrate suitable conditions for P precipitation in the form of struvite. The correlation
276 between K_{sp} and pH indicates that struvite solubility decreases with increasing pH which in turn leads

277 to an increase in the precipitation potential of a solution (Booram et al, 1975; Ohlinger et al, 1998;
278 Musvoto et al, 1999b; Doyle & Parsons, 2002).

279 Generally, in digestion of BNR sludge, the stabilising counter ions of polyphosphate produce
280 Mg in a molar ration of ~ 0.3 mol Mg / mol P. Thus, it can be assumed that all the removed Mg
281 potentially can be precipitated as struvite (Wild et al, 1996; Doyle & Parsons, 2002). Moreover, in the
282 presence of high influent P concentrations (>200 mg/L) struvite crystals may demonstrate a growth
283 rate up to 0.177 mm/d (Abe, 1995). If it is assumed that BF-WWTP uses 3.94 in (100 mm) sludge
284 lines, then based on these struvite growth rates, an operational hot spot in the optimum pH range (>7)
285 can potentially present a full blockage in less than $(100/0.177 \text{ mm/d} = 564.97/365 \text{ days/year} \Rightarrow) 1.55$
286 years (Doyle & Parsons, 2002).

287 BNR sludge contains a higher concentration of Mg than activated sludge, thus more struvite
288 can be formed (Table 3). Mg is taken up with polyphosphate formation, at a molar ratio of 0.34 mol
289 Mg / mole of P and the amount of Mg released during polyphosphate hydrolysis is reported as 0.25 g
290 of Mg per g of P (Wild et al, 1996).

291 Figure 4 demonstrates the T variations between the different hot-spots; K_{sp} is linearly
292 correlated with T. A low T reduces the solubility of $MgNH_4PO_4$ causing uncontrolled struvite
293 formation. Specifically, reduction of T from one operational hotspot to another in combination with
294 an optimum pH range is a significant indicator for potential struvite formation (Parsons & Doyle,
295 2002).

296

297 Insert Figure 4

298

299 The T presents significant fluctuations between the different operational hotspots. If all the data
300 provided are taken into account then the locations with the higher possibility to present uncontrolled
301 struvite formation are: digester feed, digester recirculation pump and PDST. More specifically, it
302 seems that anaerobic digester facilities and associated pumps are the most energetic hot spots mainly
303 because they meet all the criteria regarding struvite uncontrolled formation.

304

3.2 Current and upcoming phosphorus removal techniques

There are a wide range of technologies to remove and recover P from wastewater, including chemical precipitation, biological phosphorus removal, crystallisation, novel chemical precipitation approaches. Phosphorus in wastewater represents a significant renewable resource and there is no environmental or technical reason why phosphorus cannot be recycled (Morse et al, 1998; de-Bashan & Bashan, 2004; Xie, 2016). Morse et al. (1998) summarises applied technologies focusing on the main inputs, auxiliary inputs, main output as well as the form that the P is recovered, industrial and agriculture value, associated advantages and limitations.

It was reported that chemical precipitation can achieve an average of 0.6 mg/L of total P in the effluent with an average Alum dose of 45 g/L. (Patoczka 2005). In real operational conditions, crystallization via chemical precipitation can remove 45 mg/L of P to 6 mg/L of P within a pH of 8.7 (Dhakal, 2008). BNR can reduce mean influent total P concentration from 6 mg/L to 1.5 mg/L (Dhakal, 2008). Egle et al (2016) categorised the most industrial applied and robust technologies in three categories; aqueous phase (digester supernatant, dissolved P in anaerobically digested sludge and effluent), sewage sludge and sewage sludge ash.

4.0 Discussion

4.1 Decision-making for struvite monitoring

Based on the finding regarding the availability of the main ions that constitute struvite as well as the external factors that can affect the uncontrolled formation, large plants such as BF-WWTP demonstrate a high potential for the application of an economically-viable struvite controlled-recovery technology. Within a typical operational system, locations such as digester feed, digester recirculation pump, PDST and centrate are likely to be highly suitable for struvite formation and hence extraction.

In general, monitoring technologies target: the disruption of solubility or alteration of the growth mechanisms of crystals or promotion of controlled struvite formation for recovery. (Barr & Münch, 2001; Le Corre et al, 2009; Fattah, 2012; Egle et al, 2016). Since struvite precipitation is mainly based upon the equilibria of the main chemical components, most previous case studies tried

332 to overcome this problem by either forming other phosphate based salts or by reducing the pH under
333 the optimum formation range (Egle et al, 2016). This is mainly because once one of the P, Mg or NH₃
334 ions are removed, this automatically leads inhibition of struvite formation (Le Corre et al, 2009).

335 Acid washing with mainly CH₃COOH or H₂SO₄ has been used by many WWTPs in order to
336 overcome blockage problems within their operating systems (Williams, 1999; Doyle & Parsons,
337 2002). The use of FeCl₃ is the most dominant option for struvite inhibition. However, it can produce
338 large quantities of sludge mainly because of the poor molar removal of P per mole of Fe added. A
339 ratio between 0.38 and 0.48 molar removal of phosphate per mole Fe added has been reported
340 (Mamais et al, 1994). Na₂HPO₄ has also been described as a struvite inhibitor.

341 The REM-NUT®, Ostara®, PRISA, Gifhorn, Stuttgart and LOPROX technologies produce
342 struvite as final product with P content in the range of 10–12%. This final product typically presents
343 similar plant uptake efficiency as commercial fertilizers in acidic soils and partially in alkaline soils
344 (Kratz et al, 2010; Wilken et al, 2015). In general, except from MgNH₄PO₄·6H₂O (the most dominant
345 form), P can be precipitated as magnesium hydrogen phosphate trihydrate or newberyite
346 (MgHPO₄·3H₂O) at pH < 6 or trimagnesium phosphate (Mg₃(PO₄)₂·22H₂O / Mg₃(PO₄)₂·8H₂O) at pH
347 between 6 - 9 (Musvoto et al, 1999b; Michałowski & Pietrzyk, 2006).

348 The REM-NUT technology is the most expensive (2017) with >€42 per kg P produced at full
349 operational scale (pre-COVID value), because of the tremendous requirements for resins and
350 chemicals (Egle et al, 2016). Ostara®, DHV®, PRISA and P-RoC®, present an annual cost of
351 approximately €6-10 per kg P produced or €0.8-2 per PE per year (for BFWWTP = 0.8 + 2 = €2.8 /
352 PE / 2 = €1.4 / PE * 410,000 PE/year = €574,000 /year). The cost of 1 kg of P recovered via wet-
353 chemical processes is €9–16 (Gifhorn & Stuttgart processes). The high requirements regarding
354 chemicals, including acids, caustics and precipitation agents set the recovery costs at relatively high
355 levels. The cost of wet-oxidation processes, such as Aqua Reci®, PHOXNAN and MEPHREC®, is
356 approximately between €23–27 per kg Prec, which makes them economically unattractive (Egle,
357 2016).

358 DHV Crystalactor® is not economically viable, even with maximum revenues, maximum
359 savings and an up-scaling of the plant to 500,000 PE due to the high operational resources demand.

360 (Egle et al, 2016). High annual costs have also been reported for the Aqua Reci® and the
361 MEPHREC® processes.

362 A P controlled crystallization process appears to be a suitable method to recover P in the form
363 of struvite (Battistoni et al, 1997, 2000, 2004, 2005; Barr & Münch, 2001; Parsons & Doyle, 2002;
364 Pastor et al, 2008). Thus an Ostara fluidised bed crystallisation reactor seems to be a very promising
365 option regarding the sustainable management of the struvite precipitation problem (Merlo R. 2011;
366 Bird et al, 2015; Egle et al, 2016).

367

368 **4.2 P recovery and recycling through struvite crystallization**

369 The operational design of BF-WWTP is likely to enhance struvite formation at specific
370 operational hotspots when the optimum conditions are met. Consequently, a controlled struvite
371 recovery can potentially be viable. Controlled struvite precipitation process via crystallisation can
372 recover struvite at rates of 80 to 90% from reject waters. (Shu et al, 2006; Petzet et al, 2011; Xavier et
373 al, 2014). This system can reduce ammonia concentrations by 29% (Shu et al, 2006; Xavier et al,
374 2014).

375 A struvite crystallizer reactor incorporates reverse gravitational flows of reject waters from
376 anaerobic digesters and solids dewatering facilities (Britton et al, 2005; Fattah et al, 2010; Cullen et
377 al, 2013). Struvite crystals are separated by density and size as result of the upward flow through
378 increasingly larger reactor chambers. Spherical pellets or beads (known as prills) remain in the upper
379 chamber until enough minerals accumulate, increasing the size and density while the smaller particles
380 drop down into the smaller reactor chamber in the lower section. Each reactor zone has a reduced
381 liquid retention time. The larger diameter area at the top of the reactor has the smallest struvite
382 particles with higher retention time to allow for crystal growth (Cullen et al, 2013). The largest prills
383 present in the lowest and smallest reactor chamber are harvested, dried and bagged.

384 Precipitation of struvite requires a molar ratio of $1(\text{Mg}^{2+}):1(\text{NH}_4^+):1(\text{PO}_4^{3-})$ (de-Bashan &
385 Bashan, 2004; Le Corre et al, 2009). It has been estimated that 95% of P can be precipitated as
386 struvite from the centrifuge supernatant, by the addition of 1.05 – 1.3 or 1:1 molar ratio of Mg to P,

387 i.e. a Mg dose of about 210 mg/L (if P concentrations 200 mg/L be assumed) (Fujimoto et al, 1991;
388 Siegrist et al, 1992).

389 Supernatants and reject water pH levels are often unsuitable for struvite formation. Thus, pH
390 levels must be regulated (Barak & Stafford, 2006; Rahaman et al, 2014). Sodium hydroxide is mainly
391 used for pH regulation within a crystallizer reactor (Jaffer et al, 2002; Britton et al, 2005; Rahaman et
392 al, 2014; Xavier et al, 2014). In general, recovery cannot be viable in mainstream activated sludge,
393 trickling filter and anaerobic processes mainly because of low of P and NH_4 concentrations (Williams,
394 1999). However, based on the results arising from this study, plants such as BF-WWTP produce high
395 concentrations of MgNH_4PO_4 at a variety of operational locations. Anaerobic digestion supernatants
396 as well as centrate from sludge filter can be potential locations, because of the high decomposition of
397 microbial mass due the microbial bio-activities and the release of optimum P and NH_4 concentrations
398 (Bhuiyan, 2007).

399

400 4.3 Cost benefit analysis

401 For the CBA of a WWTP the following (pre-COVID) data are considered (Molinos et al, 2010
402 & 2011):

403 For a given data set of 22 WWTP with treated water volume between 1,000,000 and 8,000,000
404 m^3/year the average operational cost is as follow: energy = 0.0392 €/m³, staff = 0.0712 €/m³, regents =
405 0.0301 €/m³, waste management = ~0.0342 €/m³, maintenance = 0.0453 €/m³ (Molinos et al. 2010 &
406 2011). Based on these data, the overall (pre-COVID) operating cost of WWTPs are in the range
407 0.1158 €/m³ and 0.7491 €/m³. Based on the treating capacity the weighted average is approximately
408 0.2200 €/m³. Considering that Budds Farm WWTP presents treating capacity (109,000 m³/day * 365
409 days/year = 39,785,000 m³/year =) 4.97 times higher than the proposed, then the overall operational
410 cost can be estimated approximately as (4.97 * 0.22 €/m³ =) 1.09 €/m³. Because of the incorporation
411 of BNR in the BFWWTP operational system, the annual cost for chemical struvite precipitation is
412 estimated as (1.09 €/m³ * 109000 m³/day * 365 days/year =) **43,365,650 €/year**.

413 Environmental benefits reflect the value of the environmental damage resulting from the
414 uncontrolled management and dumping of the undesirable outputs (known as shadow price). By

415 taking into account the volume of pollutants removed in the treatment process (kg/year), the volume
 416 of treated wastewater (m^3/year), and the prices obtained for each pollutant, the overall environmental
 417 benefit resulting from wastewater treatment is calculated between 0.0099 €/m^3 and 1.0039 €/m^3
 418 (Molinos et al. 2010 & 2011). Based on the treating capacity of the WWTPs that have been examined
 419 the weighted average is 0.3609 €/m^3 . For Budds Farm WWTP this value can be expressed as $(0.3609$
 420 $\text{€/m}^3 * 4.97 =) 1.79 \text{ €/m}^3 * 109,000 \text{ m}^3/\text{day} * 365 \text{ days / year} = \mathbf{71,215,150 \text{ €/year}}$.

421 The price of treated water is estimated to be 0.345 €/m^3 (Molinos-Senante et al. 2010). If the
 422 WWTP proceeds to sale of the treated water, then assuming 50% and 100% of the treated water is
 423 sold, the mean net profit is increased by ~55% ($= 0.3138 \text{ €/m}^3$) and 71% ($= 0.4863 \text{ €/m}^3$), respectively
 424 (Molinos-Senante et al. 2010). If the 50% water sale scenario is applied to BF-WWTP, the (pre-
 425 COVID) income is estimated as $(0.3138 \text{ €/m}^3 * 109,000 \text{ m}^3 / \text{day} * 365 \text{ days / year} =) \mathbf{12,484,533}$
 426 €/year .

427 Regarding a full-scale pilot plant with treating capacity $400 \text{ m}^3/\text{d}$ of homogeneous liquors, the
 428 NaOH addition costs range from 0.0014 to 0.51 €/m^3 , which can be responsible for the 97% of the
 429 chemical expenses (Barr & Münch 2001; Jaffer et al. 2002; Battistoni et al. 2005a). For BF-WWTP
 430 this estimation can be calculated as $(0.51+0.014 = 0.5114/2 = 0.2557 * 109,000 \text{ m}^3 / \text{day} = 27,871 \text{ €/}$
 431 day . An alternative to NaOH addition was examined by Battistoni (2004) with use of air stripping to
 432 adjust the pH of struvite precipitation. The addition of $\text{Mg}(\text{OH})_2$, which is cheaper than MgCl_2 and
 433 simultaneously helps to increase the pH, is a possible option (Barr & Münch 2001). A further
 434 potential option is the incorporation of sea water as an alternative source of magnesium. This proposal
 435 can reach 95% P removal compared to 97% removal with MgCl_2 . BF-WWTP could utilise saline
 436 water from the nearby Langstone Harbour and because of its location the transportation cost
 437 associated will be minimal (Shin & Lee, 1997). Furthermore, Battistoni et al. (2005a) indicated that
 438 the cost associated with struvite recovery can be reduced from 0.28€ to 0.19€ per m^3 ($0.28 - 0.19 =$
 439 $0.09 * 100 = 9\%$). For BF-WWTW this reduction can be estimated as $(1.09 \text{ €/m}^3 * 0.09 = 0.0981 \text{ €/m}^3,$
 440 $1.09 \text{ €/m}^3 - 0.0981 \text{ €/m}^3 = 0.99 \text{ €/m}^3 * 109,000 \text{ m}^3 / \text{day} * 365 \text{ days / year} =) \mathbf{39,462,741.2 \text{ €/year}}$ by
 441 using sand as auto-nucleation media.

442 The feasibility of controlled recovery of struvite via crystallisation is heavily dependent on the
443 profits generated from struvite sales as fertilizer. The revenue produced from the struvite sales is
444 difficult to estimate because of the differences in regional demand and rates of production (Le Corre
445 et al. 2009). It should be noted that currently (2022) there are concerns about the increasing costs of
446 energy used for ammonia production for fertiliser and the associated greenhouse gas emissions; the
447 process of making ammonia is not a “green” process as it is most commonly made from methane,
448 water and air, using steam methane reforming and the Haber process. In Japan, struvite was
449 historically sold as fertiliser for agricultural purposes for approximately 250 €/t (Kohler 2004). For a
450 process treating 400 m³/d of centrate liquors incorporating an activated sludge handling system and a
451 BNR, the potential revenue regarding the struvite recovery and sale has historically been estimated as
452 ~25,000 €/month (= 300,000 €/year) with a 90% P removal (Barr & Münch 2001; Jaffer et al. 2002).
453 It reported that 1 kg of struvite can be recovered from 100 m³. Based on the Budds Farm outfall
454 [(2000 L/s * 1 kg) / 100,000 L = 0.01 kg/s * 3600 s/hour * 24 hours/day * 365 day/year =] 315 tonnes /
455 year can be produced (Barr & Münch 2001). Based on historical data, the average marketable price of
456 struvite is estimated as 200 - 1,885 \$/tonne. Assuming an average price of 1042.5 \$/tonne (Barr &
457 Münch 2001; Doyel & Parson 2002) then an annual income of (1042.5 \$/tonne * 315 tonnes / year =)
458 \$328,387 / year can be estimated. The income from this activity will cover only ~33% of the chemical
459 cost requirements (amount of NaOH and Mg needed for 90% P recovery). For BF-WWTP this is
460 (109,000 / 400 = 272.05 * 25,000 = **6,812,500 €/year**) with a chemical cost 20,643,939.39 €/year; thus
461 based on historical data and assuming all values change over time at the same rate, the proposal is
462 financially unviable (-20,643,939.39 €/year + 6,812,500 €/year = - 13,831,439.39) (Benisch et al.
463 2002; Neethling & Benisch 2004; Le Corre et al. 2009).

464 Currently the fertiliser market is dominated by phosphate rock, with 2020 price ~65 €/ t (i.e.
465 much cheaper than the assumption used). Hence rock P fertiliser is by far more economic. However, if
466 the sludge handling optimisation is taken into consideration, the reduction of sludge disposal can
467 significantly impact the feasibility of controlled struvite recovery. The recovery of phosphorus can
468 reduce the volume of sludge generated by 49% (Benisch et al. 2002). For WWTPs treating 100 m³/d,
469 1,000 m³/d, and 55,000 m³/d of wastewaters, the sludge disposal cost reduction would be significant

470 (Shu et al. 2006). For BF-WWTP, overall cost of cake disposal pre-COVID was ~ €880 k with a total
 471 sludge production of 48,000 tonnes. Based on historical data, an annual saving of $(374\text{€} / \text{d} * 2 = 748\text{€}$
 472 $/ \text{d} * 365\text{ days/year} =)$ **273,020 €/year** could be achieved.

473 An Ostara reactor presents an annual operational cost of **574,000 €/year** (Egle, L. et al. 2016).
 474 In general, the cost arising from struvite precipitation problems within a medium size WWTP (25
 475 MGD = 25×10^6 gallon/day * 4.54 L/gallon = 113,500,000 L/day) has historically exceeded **US \$100**
 476 **000 or 83,366.68 €/year** (Benisch et al. 2002). By taking into account the savings arising from the
 477 reduction of operational and maintenance cost due of struvite scaling, including chemical addition for
 478 chemical struvite precipitation, manpower, and maintenance costs, the overall saving could range
 479 from 1,470€ to 7,350€ per 4,540 m³ depending on the size of the treatment plant (Neethling &
 480 Benisch 2004; Le Corre et al. 2009). If a mean price is assumed then the cost saving is estimated as
 481 $0.97\text{€} / \text{m}^3$ of waste water. For Budds Farm WWTP cost saving can be estimated as $(0.97$
 482 $\text{€} / \text{m}^3 * 109,000\text{ m}^3 / \text{day} * 365\text{ days/year} =)$ **38,591,450 €/year**.

483 The investment cost for a controlled crystallisation reactor depends on the size of the treatment
 484 facilities. Investment cost for the recovery of P from the effluent and sludge can be 3,732,549 € and
 485 1,417,739 € respectively, for a population of 100,000. BF-WWTP covers a total of 410,000 PE thus,
 486 investment cost can be up to 15,303,450.9 € and 5,812,729.9 € respectively (mean price =
 487 **10,558,089.95 €**) (Montag et al. 2009).

488 For the determination of the environmental benefits, according to the results that Molinos et al.
 489 (2011) presented, the average value of the P shadow price is approximately $-42.74\text{€} / \text{kg}$ (meaning
 490 that for every kg of phosphorus that is not dumped into the environment, the damage prevented, or the
 491 environmental benefit generated equals €42.74). Base on the data set tested, the weighted average
 492 shadow price, depending on the volume of treated wastewater and it is approximately $0.218\text{€} / \text{m}^3$. If
 493 it is considered that BF-WWTP presents an outfall of an average 2000 L/s and it operates for 24/7 for
 494 365 days per year, then the shadow price arising from its treating capacity is $(0.218\text{€} / \text{m}^3 * 2000\text{ L} / \text{s}$
 495 $* 3600\text{ s/min} * 60\text{ min/hour} * 24\text{ hours/day} * 365\text{ days} / \text{year} =)$ **824,981,760,000 €/ year**.

496 Table 4 summarises the integrated evaluation of the 3 proposed technologies by taking into
 497 account all the financial and environmental associated aspects.

498

499 Insert Table 4

500

501 Based on the data extracted from the CBA, struvite recovery via chemical precipitation is not
502 viable. This also applies for chemical precipitation in combination with saline water for Mg
503 requirements and sand as auto-nucleation media. However, a crystallisation reactor is potentially more
504 attractive. Considering a WWTP with treatment capacity 410,000 PE that recovers P in the form of
505 struvite from digested sludge and its wastewater volume is 110,000 m³/day with a phosphorus
506 concentration in the influent of 200 mg/ L, this proposal is potentially economically viable with pay-
507 back period of less than 10 years (assuming interest rate 6% and discount rate 3.5%).

508 However, when the average value of the EB is taken into account, phosphorus recovery is
509 economically feasible even for the chemical struvite precipitation. Note that for the estimation of EB,
510 only environmental benefits have been estimated, and not the increase in resource availability; if this
511 impact was incorporated into the feasibility analysis, the results would be even more favourable.

512

513 **6.0 Conclusions**

514 Uncontrolled struvite formation is a significant operational problem that many WWTPs,
515 especially those incorporating secondary treatment and anaerobic sludge digestion facilities, are
516 required to overcome. Although uncontrolled formation of struvite can be a nuisance, controlled
517 production and recovery of struvite can be beneficial for WWTPs. This study has demonstrated for
518 the first time that struvite recovery from wastewater treatment is an economically viable circular
519 economy opportunity.

520 Plants such as BF-WWTP provide an example that could potentially deliver a sustainable
521 solution to this problem around the world due to its particular design and operational characteristics.
522 Operational hotspots such as digester recirculation pumps, PDST, centrifuge feed, centrate and SAS
523 storage tank demonstrate suitable conditions for P precipitation in the form of struvite. These

524 locations present a positive SSR, optimum pH ran between 7 and 10.7 and a significant T variation
525 indicating, based on the literature, potential struvite precipitation.

526 Controlled crystallisation process is one of the most promising P recovery technologies in the
527 form of struvite. Using a fluidised bed reactor, this technology discharges the WWTP operational
528 system from $Mg:NH_4:PO_4^{2-}$ by creating optimum formation conditions. A crystallisation reactor seems
529 to be the most robust technology for this process. Considering the great environmental and recovery
530 performance of this proposal, a CBA based on the characteristics of BF-WWTP indicates that the pay-
531 back period would be less than 10 years, especially given the likely increasing future energy costs and
532 greenhouse gas emissions associated with fertiliser production. Of course, economic viability and
533 payback periods will vary according to circumstances, but we recommend that WWTP operators
534 globally consider fitting a crystallisation reactor to appropriate plants, The outcomes and
535 recommendation from this study are particularly timely given the global fertiliser shortage (2022) that
536 is driving up food prices and reducing crop sizes.

537

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- 683

Tables and Figures

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Table 1. Hot spots of struvite precipitation and their operational impact (adapted from Le Corre et al. 2009).

Operational hotspots	Effects	Type of plant	References
Pipes carrying supernatants of AD.	2.5 cm accumulation.	WWTP (USA)	Rawn et al. (1937)
Activated sludge process - pump onto separating screen.	Diameter reduction from 310 mm to 150 mm.	Hyperion WWTP (USA)	Borgerding (1972)
Anaerobic supernatant: pump impellers, pipes, etc.	-	Livestock WWTP (USA)	Booram et al. (1975)
Outfall pipelines, waste pumps, pipelines.	Accumulation: from 5.88 up to 14.44 mm in aerators; from 8 up to 28 mm in pipes carrying digester effluents.	Pig waste treatment plant (Singapore)	Mohajit et al. (1989)
Pipes from sludge supernatant system.	Accumulation along 5.6 km of pipes.	WWTP (USA)	Ohlinger et al. (1998)
Precipitation in pipelines - sludge holding tank to the centrifuges.	Pipes bore reduction from 100 to 50 mm.	WWTP (UK)	Williams (1999)
Pipes of centrate liquors.	Pipe diameter reduction from 150 to 60 mm in 12 weeks.	Sludge treatment plant (UK)	Doyle et al. (2000)
Pipes of anaerobic supernatants.	Pipe diameter reduction.	Pilot fluidised bed reactor plant, WWTP (Italy)	Battistoni et al. (2004)
Streaming pipes.	Two-month build up in a rubber lined 90° elbow.	WWTP (USA)	Neethling & Benisch (2004)

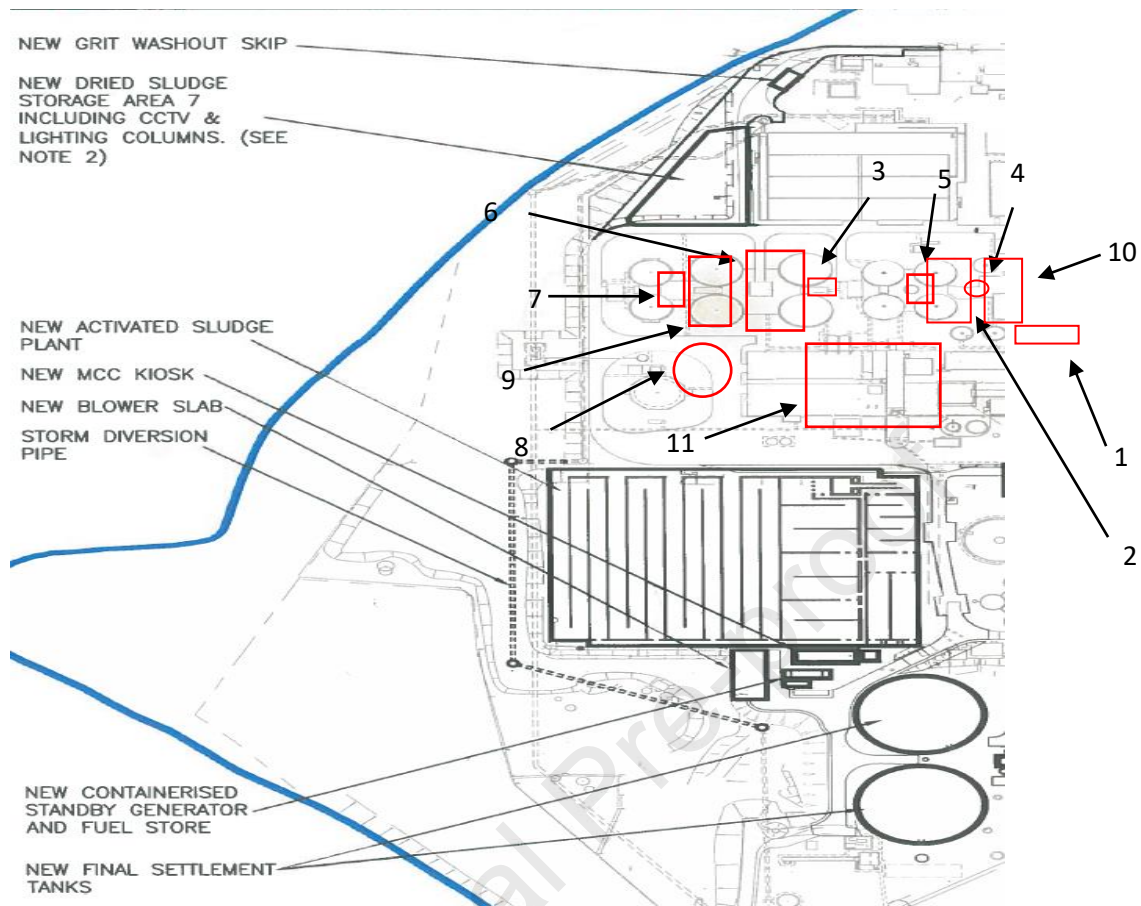


Figure 1: Part of Budds Farm operational diagram. 1) Screened sludge storage tank, 2) Thickened sludge storage tank, 3) SAS storage tank – Surplus Activated Sludge (SAS), 4) Blended cake, 5) Digester feed, 6) Digester recirculation pump, 7) PDST (digested sludge) – Post digested sludge treatment, 8) Centrifuge feed, 9) SAS filtrate, 10) Primary thickening filtrate, 11) Centrate SAS after thickened (figure provided by Southern Water).

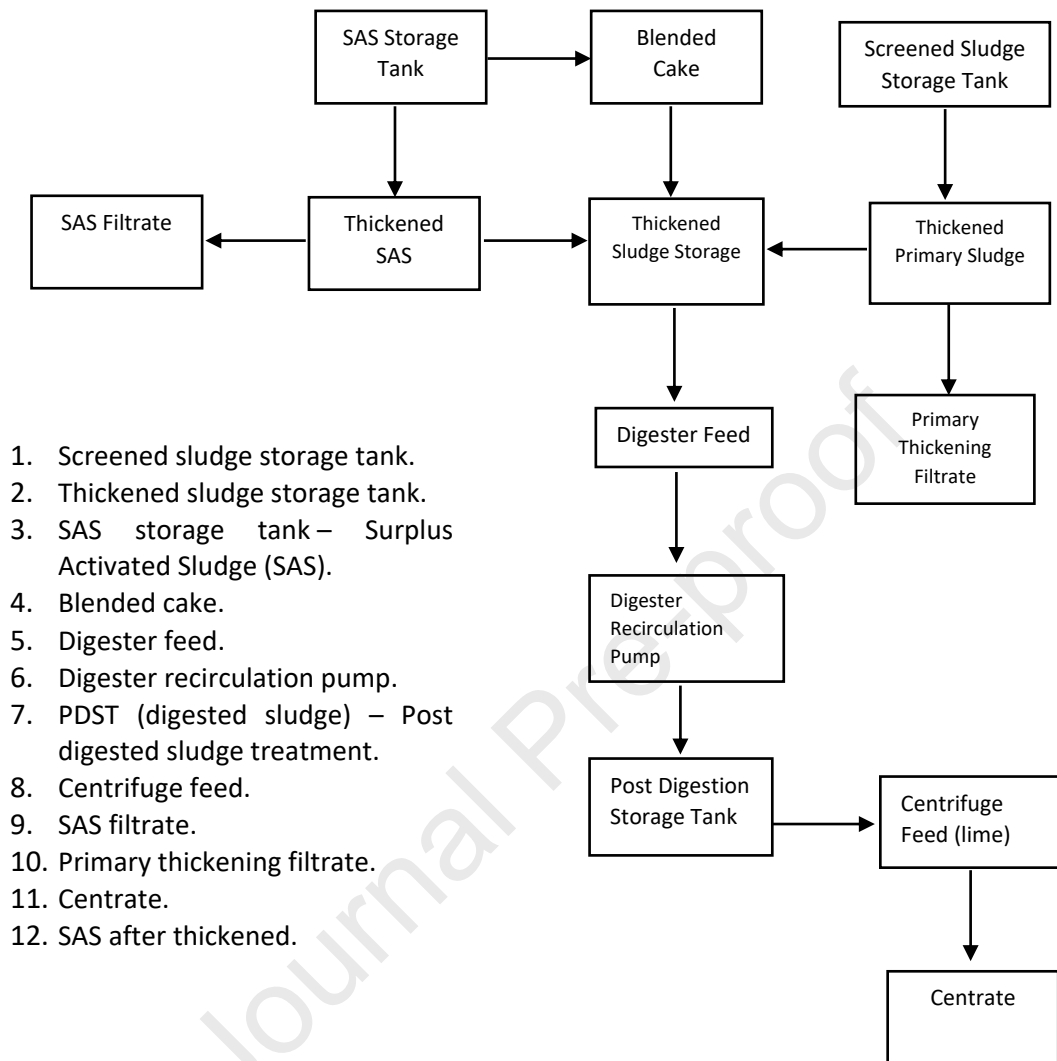


Figure. 2. Budds Farm WWTP sludge treatment process and sampling map. This diagram demonstrates the operational hotspots regarding the uncontrolled struvite formation.

Table 2. Data arising from the samples analysis of the most potential locations regarding the struvite formation within the operational system of Budds Farm WWTP. The locations that present the symbol * or ** indicate locations with the same sludge characteristics due to operational design. In addition, the brackets indicate the dilution of wastewater samples: double-distilled deionised water in order to reach the detection limits.

Hot-spots of struvite precipitation	pH	T (°C)	PO₄³⁻ (mg/L)	NH₄⁺ (mg/L)	Mg²⁺ (mg/L)
Screened sludge storage tank	6.5	20.8	100 (1:4)	400	390
Thickened sludge storage tank*	5.4	20.8	100 (1:4)	100	390
SAS storage tank	7.2	21.1	100	10	350
Blended cake	6.4	22.0	100	100	190
Digester feed*	5.9	20.8	100	100	390
Digester recirculation pump	8.4	21.2	40	100	150
PDST (digested sludge) **	8.4	20.8	200 (1:4)	200 (1:4)	190
Centrifuge feed**	8.4	20.8	200	200	190
SAS filtrate	7.1	20.3	100 (1:4)	10	380 (1:4)
Primary thickening filtrate	5.6	20.7	200 (1:4)	50	340
Centrate	8.1	21.5	40	200 (1:4)	230
SAS after thickened	7.0	20.5	100	10	260

Table 3. Concentrations of struvite ions in mol/L and the respective SSR.

Hot-spots of struvite precipitation	PO ₄ ³⁻ (mol/L)	NH ₄ ⁺ (mol/L)	Mg ²⁺ (mol/L)	Ksp	SSR
Screened sludge storage tank	0.0010	0.0200	0.0163	3.26 x 10 ⁻⁷	>1
Thickened sludge storage tank*	0.0010	0.0050	0.0163	8.15 x 10 ⁻⁸	>1
SAS storage tank	0.0010	0.0005	0.0146	7.3 x 10 ⁻⁹	>1
Blended cake	0.0010	0.0050	0.0079	3.95 x 10 ⁻⁸	>1
Digester feed*	0.0010	0.0050	0.0163	8.15 x 10 ⁻⁸	>1
Digester recirculation pump	0.0004	0.0050	0.0063	1.26 x 10 ⁻⁸	>1
PDST (digested sludge)**	0.0021	0.0100	0.0079	1.659 x 10 ⁻⁷	>1
Centrifuge feed**	0.0021	0.0100	0.0079	1.659 x 10 ⁻⁷	>1
SAS filtrate	0.0010	0.0005	0.0158	7.9 x 10 ⁻⁹	>1
Primary thickening filtrate	0.0021	0.0027	0.0142	8.0514 x 10 ⁻⁸	>1
Centrate	0.0004	0.0100	0.0096	3.84 x 10 ⁻⁸	>1
SAS after thickened	0.0010	0.0005	0.0110	5.5 x 10 ⁻⁹	>1

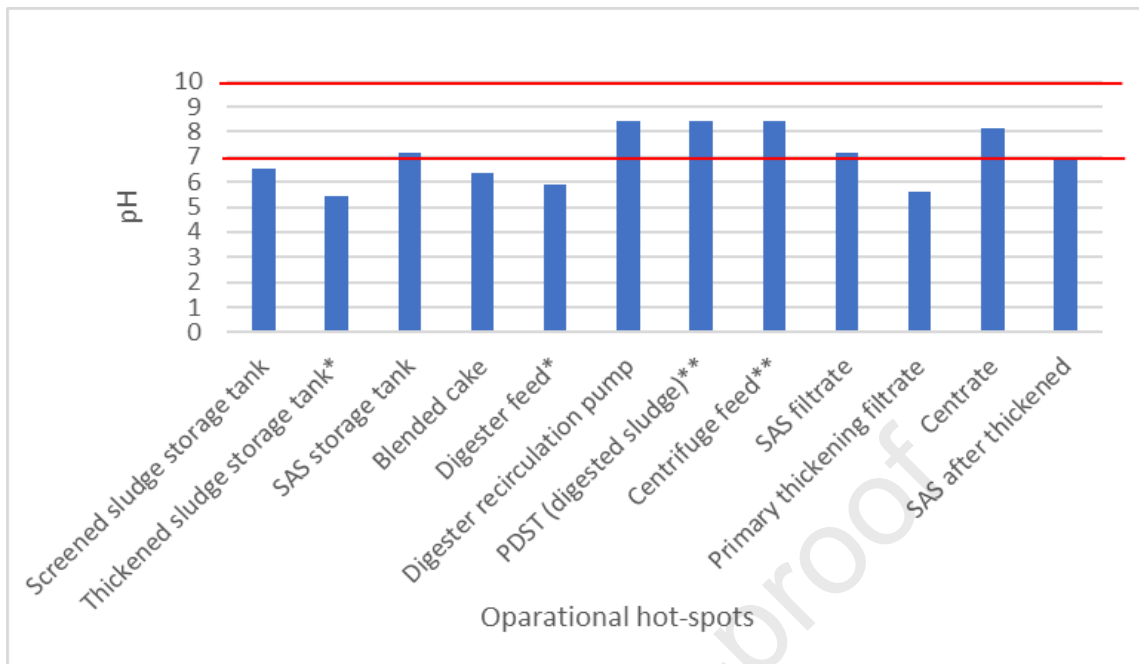


Figure 3. Operational pH variations for the proposed hot spots. The red lines indicate the thresholds for struvite precipitation. Values lower than 7 and higher than 10.7 present high solubility of struvite and thus less danger for operational problems arising from scaling.

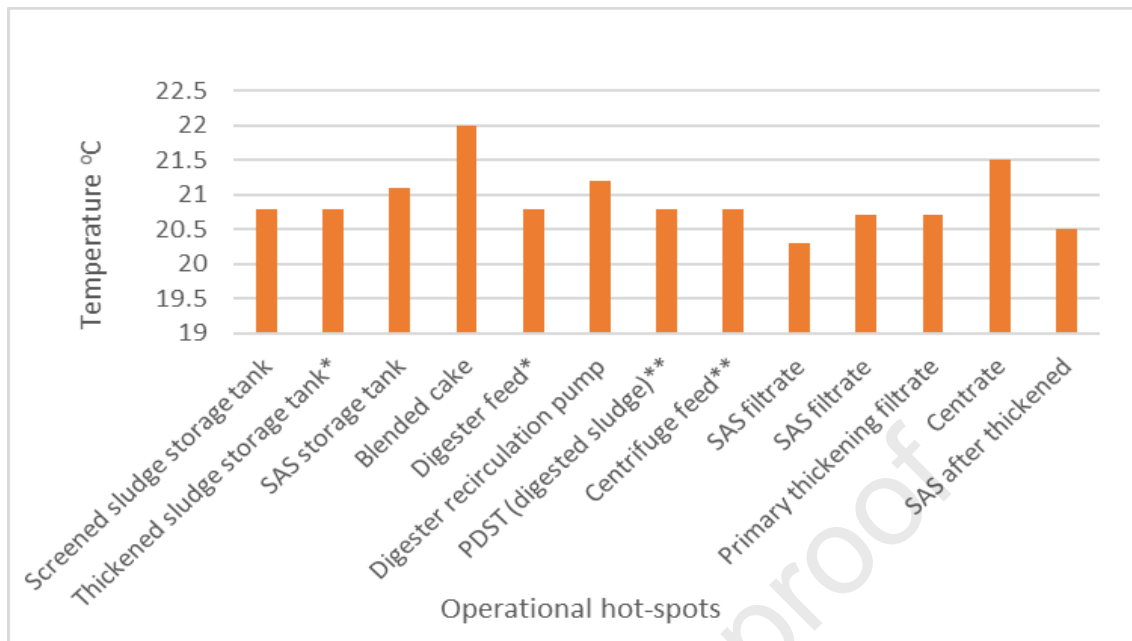


Figure 4. Temperature variations for the different operational hot-spots. T reduction is an indicator for uncontrolled struvite formation.

Table 4. Costs, benefits, and feasibility estimations for struvite chemical precipitation, utilisation of saline water and sand as auto-nucleation media in combination with chemical precipitation and Ostara controlled struvite recovery reactor.

Mean (€ year/L)	
Chemical precipitation of struvite	
General WWTP operation and maintenance cost including chemical requirements.	43,365,650
Chemical cost requirements.	20,643,939
Water sale.	12,484,533
Struvite sale.	6,812,500
Savings regarding struvite precipitation.	83,367
Environmental benefits.	71,215,150
Chemical precipitation in combination with saline water and sand usage	
General WWTP operation and maintenance.	39,462,741.2
Struvite sale.	6,812,500
Water sale.	12,484,533
Savings regarding struvite precipitation.	83,367
Environmental benefits.	> 71,215,150
Ostara crystallization reactor	
General WWTP operation and maintenance cost.	22,721,711
Reactor operational and maintenance cost.	574,000
Investment cost	10,558,090
Water sale.	12,484,533
Struvite sale.	6,812,500
Sludge disposal savings	273,020
Savings regarding struvite precipitation.	83,367
Saving in comparison with chemical precipitation of struvite	38,591,450
Environmental benefits	824,981,760,00

Highlights

- Biological P removal at wastewater treatment plants causes precipitation problems
- We evaluated if problem can be overcome by adopting circular economy thinking
- Mass balance estimates & struvite precipitation profiles used to identify hotspots
- Struvite recovery via a crystallization reactor demonstrated as economically viable
- Struvite recovery from wastewater treatment is viable circular economy opportunity

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Heliyon Author Contribution Statement

- 1 - Conceived and designed the experiments
- 2 - Performed the experiments
- 3 - Analyzed and interpreted the data
- 4 - Contributed reagents, materials, analysis tools or data
- 5 - Wrote the paper.

Panayiotis Achilleos – 2, 3, 4, 5

Ian D. Williams – 1, 3, 4, 5

Keiron Roberts – 1, 3, 5

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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