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1   **Greening the global phosphorus cycle: How green chemistry can help achieve planetary**

2   **P sustainability**

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27 The sustainability of global phosphorus (P) use is emerging as a major societal goal to secure

28 future food, energy, and water security for a growing population. Phosphate rock (PR) is a

29 critical raw material whose inefficiency of use is leading to widespread eutrophication and

30 uncertainties about supplies of affordable fertilizers. Green chemistry and green engineering

31 can be applied to help close the global P cycle by addressing three sustainability challenges:

32 (1) consume less PR and with greater efficiency, (2) minimise P losses and generation of

33 waste P that can no longer be re-used, and (3) set economically, socially and environmentally

34 acceptable P sustainability targets to lower P demand. Greater precision in P use by the

35 agriculture sector (the main P flow) supported by smarter PR mining and processing

36 technology could greatly improve global P use efficiency. Emerging bio-based and green

37 chemical technologies could be more widely applied to enhance first- and second-generation

38 valorization of low-grade PR ores, manures, by-products and residues to provide renewable

39 secondary sources of P and other essential elements and compounds. All sectors of society

40 have the potential to lower their P demands, and all production systems could be redesigned

41 to facilitate recovery and recycling of P. Collectively these 'green engineering' actions at

42 sector and regional level can help achieve planetary P sustainability.

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46   **1. Introduction**

47   "This is no way to run a biogeochemical cycle."

48   (J. Elser quoted in Lougheed (2011)).[1]

49   Phosphorus (P) is a critical element for our food production systems, manufacturing

50   industries, and general economic growth whose long-term security of supply is of major

51   concern for regional and national economies. Phosphate rock (PR) is mined for processing

52   into P derivates, such as phosphoric acid (PA, H_3PO_4) and white phosphorus (P_4), for final

53   use in various products that society uses ranging from fertilizers to toothpaste to car batteries.

54   The mineable reserves of PR are essentially finite for the human era because of the geological

55   timescales over which the natural cycling and therefore renewability of P occurs. Current

56   high rates of P consumption (over 20 Tg P yr^{-1})[2] driven largely by fertilizer use are putting

57   increasing pressure on the global supplies of this vital resource, leading to rising and volatile

58   prices.[3] Estimates of how long global PR reserves will last are uncertain and currently vary

59   from <100 up to 400 years, but their accessibility and cost are a major concern for many

60   countries with no PR reserves, such as Europe.[4,5] Future demand for P in emerging

61   economies, notable in Africa and Asia, is anticipated to be very high, while rising demands

62   are also imposed by expanding biofuel production.[6] Ironically, a more immediate

63   environmental problem is the widespread leakage of P to waterbodies where it causes

64   nuisance algal blooms, loss of aquatic biodiversity, and increased risk to human health.[7]

65   These pressing problems have been evidenced quite tangibly in the bloom-induced drinking

66   water crises that have emerged in recent years in Lake Taihu (China)[8] and Lake Erie

67   (USA/Canada).[9] Phosphorus is therefore both a critical element and a pollutant and must be

68   used more efficiently and sustainably in the future to help safeguard future food, energy and

69   water security.[5,10-12]

70   Phosphorus has no substitute, but can be continually re-used, and is thus a prime example

71   of a critical resource that could be utilized more efficiently in a circular economy to support

72   sustainable growth with less pollution.[13,14] The current P cycle is inherently inefficient

73   because the vast majority of the P that is mined each year becomes dissipated in low-grade

74   PR ores, manures, by-products and residues that are not fully re-used or re-used uniformly,

75   and in surface waters and seas. Actual rates of P re-use will clearly vary considerably

76   between sectors and countries, but a recent review of P budgets across different geographical

77   scales suggests it is <20 % of total P inflows.[15,16] This is a low percentage and there

78   continues to be large scale disposal of P to landfill in developed countries. A large proportion

79   of dissipated P (wrongly termed waste) could potentially be re-used as secondary P resources

80   subject to technological and financial constraints.[17-19] A distinction has been made between

81   strategies that enhance P re-use through more uniform recycling directly back to land, and

82   those that first require recovery through innovation in bio- and chemical engineering.[5] True

83   wastage occurs when P is dissipated to the oceans. These permanent P losses have

84   quadrupled due to anthropogenic activity in the 20th century and must also be reduced.[20]

85   Achieving long-term sustainability of P use in society will require insights from a variety

86   of emerging approaches, including "green chemistry" and "green engineering".[21,22] In the

87   context of P, these two concepts adopt the same core principles of (a) the development of

88   benign products and processes, (b) the elimination of waste, (c) the use of renewable

89   (secondary) resources, and (d) the design of output-driven production systems with minimum

90   requirements and maximum efficiency.[23] These green principles will be critical in developing

91   new strategies for how we use P in the technosphere and how products can be designed in the

92   future with a focus on recycling. For example, an immediate green chemistry challenge is to

93   remove and re-use the potentially harmful elements naturally present in PR, such Cadmium

94   (Cd), Uranium (U) and Lead (Pb), that might persist in the environment or through the food

95 chain.[24] The cradle-to-cradle philosophy implicit in green chemistry has yet to be fully

96 adopted by sectors in the P cycle, although the conceptual basis for achieving this transition

97 exists through P accounting and recent drivers towards industry sustainability and a circular

98 economy.[13,25-27] This probably relates to the relatively recent recognition of P as a critical

99 resource by government and industry, and P sustainability as a serious societal problem. For

100 example, RP has only just been recognized in Europe as a critical raw material.[28] Considering

101 the environmental impact of the whole life cycle, and afterlife, of products and not just the

102 impact of their initial manufacture will also require a large paradigm shift in attitude by all

103 stakeholders and actors in defining societal needs and how systems can be best designed to

104 meet them.[29-31]

105 This paper outlines a variety of avenues for the application of green chemistry principles

106 and practice to transform P use in society. We describe a variety of existing and emerging

107 technologies and strategies for elemental re-use in the P cycle. If not constrained by cost,

108 their adoption will help deliver a sustainable P system that can sustain future generations with

109 abundant food, feed, fibre, fuel, clean water and other essential P products society relies on.

110 After a synopsis of global P use, we consider sustainability and green chemistry challenges in

111 recycling and recovery technologies within different sectors and then system design with

112 some regional examples of progress. Our ultimate objective is to inspire green chemists and

113 engineers to take a major role in developing and implementing a more efficient and

114 sustainable P cycle.

115

116 **2. Phosphorus distribution in the technosphere**

117 Information on how mined PR is dispersed in the technosphere is needed to identify where

118 opportunities for green chemistry and engineering are most likely to occur in the P cycle (Fig.

119 1). Numerous attempts at global P budgets have been made, but they are all simplified to

120   some degree or another, and contain large errors because accurate data for all the stores and

121   flows are very difficult to obtain or estimate. However some important general trends

122   emerge. Anthropogenic flows of P are much greater than in natural systems, but are still

123   relatively small (<50 Tg yr^{-1}) compared to the very large global stores of P present in the

124   pedosphere, (40,000-200,000 Tg), biosphere (550-3050 Tg) and hydrosphere (8300 –

125   123,000 Tg).[20,33] They are also very widely dispersed because PR derivates have a very wide

126   range of uses in industrialized society and are therefore traded globally: for example in

127   fertilizers, feeds, foods, pesticides, plastics, computer chips, lubricants, chemical extractants,

128   detergents, toothpaste, car batteries and flame retardants. This P becomes further dispersed in

129   industrial and municipal wastewater, solid waste, livestock manures and crop residues after

130   its first use. Variation in demography, agricultural intensity and industrial activity in different

131   regions, countries and catchments will therefore lead to different priorities for improving P

132   resource use efficiency, choosing the most economic recycling and recovery options and

133   reducing environmental impacts.[15,34] This regional variation is an important aspect regarding

134   achieving progress in global P sustainability.

135   Two major issues emerge from global P budgeting. The first is that food consumption

136   patterns and global trade in food, feed and livestock products have a major impact on P flows

137   and their global distribution.[35] In particular, increasing demand for meat is a major driver of

138   fertilizer and feed P consumption and a major cause of global inefficiency of P use.[36] This is

139   because large areas of agricultural land are needed to grow the fodder and grain to feed

140   animals, and 70-80% of the P consumed by animals is excreted and must be handled. The

141   second issue is that the amount of new PR mined each year is currently about 30 Tg of P,

142   whilst the actual incremental demand for new P by a growing world population is estimated

143   at only 1 Tg P yr^{-1}.[2,37] This highlights the gross inefficiency of the global P cycle and the

144   necessary infrastructure and societal costs of handling of dissipated P. Sheldon introduced the

145   E Factor (or Environmental Factor) to describe the ratio of the amounts of waste generated

146   per unit of product processed.[23] Although not strictly comparable, PR production has an E

147   factor of *at least* 30 making it comparable to the fine chemical industry in terms of waste

148   generation.

149   The first stage of waste generation is in the mining operation and subsequent processing to

150   PA, with global estimates of unrecovered P amounting to 7-11 Tg P yr^{-1}.[2] Over 80% of mined

151   PR is used to manufacture fertilizers (chiefly through PA), with the remainder used in feed

152   and food additives mainly as calcium and sodium phosphates (through PA), and in the

153   chemical industry as white phosphorus (from PR).[38] The majority of fertilizer P accumulates

154   in the soil from where crops take up their P requirements to be harvested or grazed into food

155   for animals and humans. Excreted P is either recycled back to the land, incinerated, taken to

156   landfill after treatment or discharged to water (Fig. 1). Fluxes of P through animals are

157   similar in size to those through crops (arable crops and managed grass, *ca.* 20-25 Tg yr^{-1}, and

158   dominate the technosphere P budget.[33,39] Globally there is more P in animal excreta than in

159   manufactured fertilizers, but both grazing returns and collected manure are not recycled

160   uniformly. Animal slaughter also leads to significant amounts of slaughter waste which is

161   often co-incinerated for its fuel value in cement works and power stations. Global estimates

162   of P in slaughterhouse waste suggest it could be 10-15% of total P imports and therefore

163   significant.[40] For example, for Europe it represents about 70% of the P imported into the

164   livestock sector.[15]

165   High animal stocking rates in some areas lead to an oversupply of collected manure P for

166   the available land area. This misplacement of P, together with its intrinsically high P content,

167   is both a source of localized P surplus, P accumulation in soil and P loss in land runoff

168   causing a high eutrophication risk.[41,42] Surpluses of P in soil also arise due to excessive

169   fertilizer use.[43,44] Global surpluses of P accumulating in agricultural soils are estimated at 11-

170 16 Tg P yr^{-1}.[45,46] The legacy soil P associated with cumulative past P surpluses therefore

171 represents a considerable P resource base to reduce P fertilizer use.[5,47] For example, Ringeval

172 et al. recently estimated that over 80% of the total P in French soils (0-35 cm) was of

173 anthropogenic origin.[48] Estimates of global P losses in land runoff to water associated with

174 erosion and direct losses from the fertilizers and manures applied are typically quoted at 13-

175 24 Tg yr^{-1}. [2,33,46] Although there is large uncertainty around these runoff losses, there is

176 clearly potential to reduce them.

177 The flux of P associated with consumed food, with smaller contributions from detergents

178 and other materials is ca. 5 Tg yr^{-1}.[45,49] The majority of this P input ends up in wastewater, or

179 in solid (largely food) waste. Wastewater P is either discharged directly to watercourses, or

180 treated in a septic tank or collectively at a treatment centre. Wastewater treatment plants

181 (WWTPs) are estimated to receive about 4 Tg P yr^{-1}, of which up to 90% is removed in the

182 form of sewage sludge depending on local effluent regulations. Of this P rich sludge, ca. 50%

183 is returned to the land as biosolids, but this figure can vary considerably; for example in

184 Europe between 0 and 80%.[15] The remainder of sewage P, i.e. that is not captured in the

185 sludge, is discharged to water as treated sewage effluent amounting to ca. 1.5 Tg P yr^{-1}.[51]

186 Globally consumer waste is increasingly being recycled, but the majority is still disposed of

187 in landfill or incinerated.[52] Total amounts of household and industrial P that are disposed of

188 to landfill, or incinerated are estimated at 2-3 Tg P yr^{-1}.[2] The total amounts of P potentially

189 recoverable from wastewater effluent, landfill and incineration are therefore only ca. 5 Tg P

190 yr^{-1}, and much lower than the larger global fluxes of P retrievable from agricultural systems.

191 Global usage of P in the chemical industry is estimated at only 1-3 Tg yr^{-1}, but there are

192 still opportunities to recycle industrial residues containing P.[18,49,52] The use of P in

193 applications that might be considered non-essential are also relatively minor (1 Tg P yr^{-1}), but

194 still contribute to the P cycle.[2] This evidently raises debate on which applications of P are

195   considered unnecessary and what the consequences of replacement would be. Detergent P is

196   one example of unnecessary P that is now being phased out in the USA and Europe.[2,5]

197

198   **3. Greening the phosphorus cycle**

199   The wide dispersal of P in the technosphere and the large variability in P flows across

200   sectors in the P cycle suggests that P sustainability targets are best set and met at the sector

201   and regional level.[15,34,53] A large proportion of dissipated P is contained in mined ores that do

202   not pass the bone phosphate of lime standard for processing (BPL <68), and in sector wastes,

203   by-products, residues and wastewaters. These secondary materials provide a range of

204   accessible resources from which P could be recovered by green chemical and bio-

205   technologies into safe, renewable P sources for re-use, and for substitution of primary PR,

206   with minimum waste (Fig. 2). Many technologies are still in their infancy (i.e. pilot stage),

207   whilst others have been already implemented.[18,55,56] These secondary sources are also

208   increasingly being considered as sources for other essential elements and compounds that

209   society uses. For example, Westerhoff et al.[57] recently identified a range of valuable metals in

210   municipal sludge and suggested that the 13 most lucrative (Ag, Cu, Au, P, Fe, Pd, Mn, Zn, Ir,

211   Al, Cd, Ti, Ga, and Cr) had a value of US $280 per tonne of sludge. Wastes and wastewaters

212   generated in the food chain are also renewable sources of energy (electricity and fuel), and a

213   number of essential 'functionalized' compounds that society needs including flavonoids,

214   waxes, fatty acids and biopolymers (Fig. 3).[58-60] This raises the question over whether first

215   generation valorization of secondary bioresources from the food chain through recycling P to

216   land is the most sustainable route.

217

218   **3.1 The mining sector**

219   The first stage in the P cycle for progress in sustainability is in the PR mining operation.

220   A recent green chemistry development by the fertilizer industry has been a renewed interest

221   in comprehensive extraction (CX), Table 1. CX sees PR not just as a source of P, but as an

222   ore "which can contain the entire periodic table". Since PR contains U and a number of rare

223   earths essential to society, the co-extraction U and rare earths from PR and PA is a prime

224   example of how the mining industry can gain added value from PR processing.[62]

225   Technologies for co-extraction of P and U from lower grade ores by adding solvent

226   extraction circuits to existing wet process technology for PA manufacture, or though ion

227   exchange, are now being revisited with commercial-scale projects starting in Brazil and India

228   in 2017.[63] Simpler, gravity separation techniques (shaking table) have been shown to work for

229   extracting both heavy and light rare earths from flotation tailings (heavy) and from

230   phosphogypsum (light). Thorium (Th) is another metal in PR ores and PA that could also be

231   potentially recovered to provide a long-term supply of safe nuclear energy, with pioneering

232   plants in China, India and Brazil.[63] Co-extraction technologies also help to remove the

233   environmental hazards associated with PR–derived products making them more benign for

234   future P re-use; a clear green chemistry goal. A future challenge for these technologies is to

235   remain economic.

236   The challenge of recovery of P from low-grade PR ores (BPL values of 50 or above) is

237   stimulating innovation in an industry that has been very change averse. Ecophos and the

238   Improved Hard process (IHP) are typical examples of such innovation. The Ecophos process

239   expands on the well-known hydrochloric acid route to dissolve phosphate from rock

240   (www.ecophos.com). This serves as an alternative to the standard sulphuric acid method (wet

241   process), which is applied worldwide. Unlike the latter, the hydrochloric acid route does not

242   create an insoluble stream of PG to separate the calcium oxide from the phosphoric acid, but

243   instead produces soluble calcium chloride which remains mixed with the PA product. This

244   poses a separation challenge which can be surmounted by solvent extraction of the PA, or

245   precipitation with lime. The latter route yields feed grade phosphates in the form of dicalcium

246   phosphate. This process has a marked operational cost advantage if hydrochloric acid waste

247   is locally available and is more sustainable than the market procurement of sulphur (S),

248   which is needed to produce sulphuric acid for the conventional wet process of PA

249   manufacture. The IHP uses the local formation of P_4 in a heated mixture of low-grade rock

250   and a low-cost reduction agent such as petcoke. The offgases are oxidized immediately,

251   giving off sufficient heat to keep the process going without significant external energy input.

252   The now-oxidized P is hydrolysed to PA which is used in fertilizer and industrial phosphates

253   manufacture. The process is eminently suited to use low-grade rocks, being competitive in

254   variable cost for these, and might use other locally available P-rich waste also as input. This

255   process has seen a very long development phase and is now at pilot stage near Fort Meade,

256   Florida. The operator anticipates this will become commercially viable sometime in the

257   coming years based on a 200,000 t yr^{-1} plant.[64]

258   Another sustainable development within the mining industry has been the focus on

259   registering mine and PA processing wastes, reducing their volume and re-using them. The

260   efficiency of P extraction from PR ore is very variable, with estimates of P losses and

261   wastage during mining, beneficiation, chemical processing and handling of between 15 and

262   50% (average 30%) depending on PR quality and the methods deployed.[38,49,63] This wastage

263   could be substantially reduced by optimising the PR extraction process and recovering P from

264   mine tailings and the by-product phosphogypsum (PG) produced during PA manufacture.[19]

265   About 20 Tg (dry weight) of mine tailings equivalent to 1 Tg P yr^{-1}, and about 160-170 Tg of

266   PG (dry weight) equivalent to 0.5 Tg P yr^{-1} are produced each year.[63] Reducing ore waste at

267   the mine face is being explored through laser technology to improve ore quality detection,

268   and mine tailings can be flocculated and thickened using polymers and re-used to strengthen

269 concrete.[63] As a result of an evidence-based review by the International Atomic Energy

270 Agency,[65] PG is also no longer classed as a hazardous waste (it contains the radionuclide

271 Radium, Ra), but as a co-product, encouraging its re-use rather than indefinite disposal to

272 stacks. By 2015, annualised re-use of PG as a soil amendment and fertilizer in agriculture, as

273 a building and road base material in the construction industry and as a source of ammonium

274 sulphate (through the Merseburg process) will be at least 30 Tg yr^{-1} from a near zero base in

275 2008. However, although their re-use has increased, the recovery of P from mine tailings and

276 PG remains a challenge and one potentially for green chemistry to tackle.

277

278 **3.2 The agricultural sector**

279 The agricultural sector generates the largest amounts of potentially recoverable and

280 recyclable P. Most of the dissipated P from past fertilizer and recycled manure inputs has

281 accumulated in farmed topsoil (50,000 Tg)[53], and in some cases subsoil.[66] Progress in the

282 recovery of this legacy soil P in-situ is largely dependent on improving its accessibility to

283 plants through bio-engineering based on the inherent traits present in plants and

284 microorganisms for soil P acquisition.[67,68] A more accessible regional source of secondary P

285 in agriculture is livestock manure. Although livestock manure is a multifunctional fertilizer,

286 containing organic matter and essential major nutrients and trace elements, its nutrient

287 composition is not ideally balanced for many crops. In areas with intensive livestock farming

288 and limited land area (e.g. large pig and poultry units), uniform spreading of manure on fields

289 is limited by its P content and costly transport over longer distances, or treatment, is

290 needed.[69] Due to the necessity for local disposal, spreading allowances quickly exceed crop P

291 requirement due to their low N:P ratio. In such cases, manure application becomes diffuse

292 landfilling (push model) rather than a demand-driven application. A selective technology for

293 partial chemical removal of P from manure through acidulation and solid/liquid separation

294   may remedy this and enable more demand-driven application of P-poor solid fraction of

295   manure as organic fertilizer, and the separate re-use of a precipitated P-rich concentrate (*e.g.*

296   struvite or calcium phosphates) elsewhere as an inorganic P fertilizer (Fig. 4). The recoveries

297   of P from manure and liquid manure fractions by struvite and calcium phosphate precipitation

298   can be high (50-90%).[55] For example, Suzuki recovered 171 g of 95% pure struvite from 1

299   m^3 of pig slurry in a crystallization plant.[70] Potential alternative technologies for partial

300   removal of P from manures to decrease their N:P ratio for land application and reduce the

301   need for costly manure export pose a challenge for green chemistry. One green engineering

302   option might be to use simple micro-filtration of animal slurries to manipulate their N:P

303   ratios since a significant proportion P in manures and slurries is water-soluble.[71,72]

304   Drying, or prior separation before drying and pelletizing may pose an environmentally

305   acceptable solution, allowing the dried manure (nutrient concentrate) to be transported over

306   longer distances to crop producing areas with P demand. Separation of the P-poor liquid

307   fraction to allow more efficient drying of the P-rich solid fraction requires separate treatment

308   and /or disposal of the liquid which increases cost. Green chemistry techniques to combust

309   whole (wet) manures without separation by supercritical and sub-critical oxidation or and

310   water gasification for energy production could provide a solution, but are still in their

311   infancy.[55] Alternatively, bulky manures or separated solids can be anaerobically digested,

312   incinerated or pyrolysed to provide energy (Fig. 4). Pyrolysis can promote the conversion of

313   animal manure into charcoal (*i.e.* biochar) by heating to 300-550 °C in the absence of

314   oxygen, thereby reducing the solid volume. Biochar is proving a useful soil amendment and

315   fertilizer with low greenhouse gas emissions.[73] Pyrolysis has also been used as a pre-

316   treatment for raw biomass which is not suitable for direct combustion because of a low

317   energy density and high moisture content.[74] Gasification heats manure at higher temperatures

318   (800-1000°C) but loses more of the carbon as CO_2.[55] Incineration of animal manure is an

319 attractive option in regions with a high animal density, particularly for handling chicken

320 manure, and the incineration ash, contains a considerable amount of P and can be processed

321 into fertilizers (see wastewater sector below).[75]

322

323 3.3 The food processing sector

324 After leaving the farm considerable amounts of P are dissipated in slaughter wastes, food

325 processing waste and wastewater. After various steps aiming at recovery of valuable by-

326 products such as animal fats, gelatine and proteins, livestock slaughter waste becomes Meat

327 and Bone Meal (MBM). This is a mixture of calcium phosphate (bones) and proteins (meat)

328 potentially usable as a fertilizer or feed. Various streams of MBM occur worldwide with

329 different protein/bone phosphate ratios, and generally have the highest P concentrations of

330 waste flows suitable to substitute PR. After the Bovine Spongiform Encephalopathy (BSE)

331 crisis, Europe required a BSE-sensitive fraction MBM, Category I, to be thermally destroyed

332 instead of being used as feed ingredients for proteins and minerals.[40,76] Currently, these

333 materials with high calorific value are often used as bio-co-fuel in power plants, to give

334 carbon dioxide (CO_2) credits. This unfortunately dilutes their considerable P content beyond

335 recovery. MBM mono-incineration and smart development to recover P from the ashes (as

336 for other incinerated wastes) needs to be implemented to avoid this P wastage. In one

337 process, MBM is incinerated with alkaline earth compounds at 1000 °C in a rotary kiln to

338 improve P availability in the ash and marketed for use in agriculture (ULOPHOS®).[77]

339 Wastewater from the vegetable industry has been conventionally treated with iron salts to

340 remove P to allow discharge to rivers, but alternative green chemistry approaches are now

341 being explored. In the potato industry after anaerobic digestion of the organic matter to

342 produce biogas, P is recovered from the P-rich wastewater as struvite by adjusting pH and

343 adding magnesium chloride in the NuReSyS-P process (www.nuresys.com).[56] The process is

14

344   suitable for any anaerobic digestate or P-rich wastewater (>55 mg PO_4-P L^{-1}) with up to 80%

345   P recovery and produces a crystalline struvite product suitable for re-use as fertilizer. Another

346   process used in the potato industry uses a fluid-bed crystallizer partially filled with sand or

347   mineral to seed the crystallization process to struvite or calcium phosphate (Crystalactor®).[78]

348   The process is accurately controlled to limit the growth of the crystals to approximately 1mm

349   which then move to the bottom of the bed for removal and drying. The advantage of this

350   process is that there is no residual waste because the nearly dry phosphate pellets are fully

351   recovered and useable. However, the pH adjustments necessary before entry to the bed is

352   quite demanding in terms of energy (CO_2 stripping) and chemicals (acids/bases).[56] A

353   comparable approach currently under investigation is recovering P from vegetable

354   wastewater as calcium phosphate for subsequent conversion to PA for use in the chemical

355   industry (www.biorefine.eu).

356   Food waste contains non-negligible amounts of P, not least because society wastes at least

357   a third of its food, whilst in rich countries it can be up to 40%.[79,80] As food waste has by

358   definition been safe for consumption before its expiry, it is suited for composting (provided

359   packaging can be separated) and the small amount of P in the ensuing compost contributes to

360   its wider agricultural value. As such, it may not be necessary to selectively extract P from

361   food waste, but rather see it as an essential if minor part of its wider agricultural value as a

362   soil amendment, or as a source of other second generation critical compounds.[81]

363

364   3.4 The wastewater sector

365   Phosphorus recovery from human sewage (*e.g.* excreta, detergents and food washings) has

366   generated most P recovery research not least because accessibility is already guaranteed.

367   WWTP need to remove P to reduce effluent P concentrations discharged to water, most

368   commonly by conventional anaerobic digestion and Fe/Al dosing. The remaining P-rich

369   sludge (biosolid) can be directly recycled to land as another multifunctional fertilizer, but the

370   presence of pathogens, pharmaceuticals and hormone residues and heavy metals are a

371   continual cause for concern.[82] The plant availability of recycled Fe-bound P to agricultural

372   crops can also be low.[83] Urine diversion from human excreta via a specially designed toilet is

373   an option for improving the direct re-cycling of human waste to agriculture, especially in

374   developing countries where the majority of households are not already directly connected to

375   WWTP.[84,85] Mihelcic et al.[86] suggested there is 1.7 Tg P in global urine, and recycling urine

376   as a fertilizer seems to be socially acceptable.[87]

377   To avoid potential environmental and human health risks, there is an increasing global

378   trend towards sludge incineration with the ashes offering an entry point for P recovery and

379   metal removal to produce fertilizers that are safer to store, handle and apply.[88,89] The green

380   chemistry advantage of this route is the near-complete collection of sewage P provided

381   WWTPs are well-designed and meet operational criteria. There is also potential to recover

382   other non-renewable elements of value to society (e.g. K, Zn, Cu, Se).[57] While P recovery

383   from liquid phases at WWTP is only 40-50% at most, recovery of P from ashes is up to

384   90%.[56] Thermo-chemical and wet chemistry technologies using acid or caustic digestion of

385   these ashes can produce P products with high P-availability suitable for animal feed or

386   fertilizers, or as elemental P, whilst also removing any heavy metal contamination that might

387   otherwise reduce the recycling value.[52,55] For example an innovative refinement of the

388   hydrochloric acid technology used in the Ecophos process to produce feed phosphate from

389   sewage sludge ashes is currently being investigated and may achieve full scale in 2017

390   (www.ecophos.com). Two full-scale plants have been implemented in Japan to recover P

391   from incinerated sludge ash using the alkaline (NaOH) leaching technology to minimize the

392   leaching of heavy metals from the ash that would otherwise contaminate the recovered

393   product.[18] The relatively low level of Ca (typically less than 10 % CaO by weight) in the ash

394 makes the alkaline leaching sufficiently efficient. Such routes are economical wherever a

395 local source of attractively priced NaOH (e.g. as by-product) is available.

396 An alternative green engineering approach to P removal in WWTPs is by biological

397 treatment, a setup where little or no further chemical P removal is needed.[54] In enhanced

398 biological P removal (EBPR), alternate anaerobic and aerobic cycles facilitate polyphosphate

399 accumulation in microorganisms.[90] Inorganic P (P_i) can be released from EBPR sludge in a

400 more concentrated form by various technologies, including heat treatment,[91] anaerobiosis,[92]

401 anaerobic digestion,[93] and incineration followed by chemical leaching.[94,95] P can also be

402 recovered from P_i-rich solution using precipitation technologies with inorganic cations such

403 as Ca^{2+} or Mg^{2+}, producing either calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), or struvite

404 ($MgNH_4PO_4 \cdot 6H_2O$).[96,97] Struvite poses a scaling issue in EBPR plants, and its targeted

405 precipitation therefore offers considerable operational cost savings. The recovered product

406 has so far proved a useful slow-release fertilizer, but recovery of struvite from liquid phases

407 is applicable in WWTP with EBPR.[55] Recovery of struvite directly from the digested sludge

408 is also in full-scale operation (e.g. Airprex, and Seaborne processes), but not on a large scale

409 due to economic feasibility and national legislation.[56] In the Seaborne process, P and metals

410 are recovered separately. Digested sludge is first acidified with sulphuric acid to mobilise P

411 and heavy metals, the metals are removed with sulphur-rich digester gas and the P is

412 precipitated as struvite by addition of sodium hydroxide. Both struvite and ammonium

413 sulphate produced from the process can be re-used in agriculture. A more green chemistry

414 approach at the pilot stage is the Budenheim process which uses carbon dioxide rather than

415 acid to dissolve the P in the sludge before precipitating the P as calcium phosphate.[77] The

416 CO_2 extractions are very efficient at mobilising the P with 60-70% recovery and the used

417 CO_2 is recycled in the process (www.budenheim.com).

418 A number of potential green and bio-engineering solutions to recover P from dilute

419   wastewaters are at the pilot scale. Amorphous calcium silicate hydrates (A-CSHs)

420   synthesized using natural and low cost materials, such as siliceous shale and calcium

421   hydroxide ($Ca(OH)_2$) have proved an effective option to recover P from aqueous solutions by

422   simple adsorption.[98] Similar suitable materials can even be obtained from construction

423   material production waste. The lack of any need for pH adjustment and the high settling rates,

424   filterability, and dewaterability of recovered P are the advantages of A-CSHs over

425   conventional $CaCl_2$ and $Ca(OH)_2$ chemistry.[99] No chemical coagulants are required for P

426   recovery by ACSHs, and, unlike $Ca(OH)_2$, no significant carbonate inhibition occurs with P

427   recovery with A-CSHs. Other novel phosphate-binding materials for treating wastewater

428   have included polymeric hydrogels synthesized by chemically crosslinking linear PAA · HCl

429   chains with epichlorohydrin, and ion-exchangeable ceramic beads (0.55 mm diameter and

430   85% porosity) which exhibit a high specificity for fast phosphate adsorption over a wide pH

431   range (pH 2 to 14), and can be used more than 100 times.[100,101] With an increasing need to

432   further lower WWTP effluent P concentrations for eutrophication control, sorption and ion

433   exchange may become more attractive green engineering approaches for enhanced

434   wastewater P recovery in the future.[102,103] Microfiltration (0.2 µm) and nanofiltration

435   technology together with various pre-treatment steps also have the potential to produce

436   recovered products with specific N:P ratios from wastewaters.[60,71] Microalgal recovery of

437   wastewater P for re-use in biodiesel production is another bio-based technology, but the

438   economics of this route still remain unfavourable.[104,105]

439

440   **3.5 The industrial sector**

441   The waste-based production of white P, a key intermediate for many industrial products

442   (flame retardants, plasticizers, battery ingredients, catalyst ligands, pharmaceuticals, lubricant

443   additives, specialty fertilizers, herbicides and metals and electronics etchants) has been

444   pioneered by Thermphos International and is subsequently being developed by the Recophos

445   consortium (www.recophos.org). The raw material is sewage sludge ash (or other P-rich

446   waste), which is converted to white phosphorus in a novel, lean manufacturing setup which

447   shows a clear departure from the classical large scale furnace design practised for over a

448   century. The process will be entering pilot stage in 2015. The processing route involves

449   reduction of phosphates by means of coke to the element (P_4), with carbon monoxide and a

450   calcium silicate slag as sellable/usable by-product.

451   Elemental P from this process, or the classical production route, serves as the base for a

452   large number of derivatives. Processing routes include the intermediate product phosphorus

453   trichloride (PCl_3), the workhorse for organic P chemistry. The chlorine in this case merely

454   serves as a means to activate the P atom and does not turn up in most - if not all - final

455   products. Therefore, more direct and green routes to such derivatives are needed. Chlorine

456   free routes have been pioneered by CNR-ICCOM, Thermphos International and are now

457   being pursued by the SusPhos project, aimed at green non-phosphate (i.e. white P) based

458   chemistry especially in fine chemistry applications (www.susphos.eu). For example,

459   triphenylphosphine (TPP) is commonly used in the Wittig reaction for the industrial

460   production of Vitamin A, carotenoids and many other alkenes. Yet, the P-containing by-

461   product, triphenylphosphine oxide (TPPO), does not currently have a large-scale application,

462   which results in thousands of tonnes of solid P-containing waste.[106] SusPhos aims to achieve

463   an economic recycling protocol to create a P waste-free Wittig reaction, which can be applied

464   throughout a wide range of industrial processes. More generally, using white P in an atom

465   efficient way remains a challenge for the non-fertilizer P industry. Designing products to

466   allow re-use over and over again is also a goal for such industries.

467   High-grade PA is widely used in the chemical and manufacturing industries and a

468   considerable portion could be recovered and recycled from different industrial wastes.[11] In

469   terms of quantity, P emitted into steel-making slag is a particularly important secondary P

470   resource and is an input to the P cycle outside the usual PR-based inputs. Coal and iron ore,

471   which are essential raw materials for the manufacture of iron and steel, contain small

472   amounts of P (typically less than 0.03 % P_2O_5 by weight). Since P has detrimental effects on

473   the mechanical properties of steel, it is removed into dephosphorizing slag at concentrations

474   as high as 2-10 % P_2O_5 by weight.[107] The global production of iron ore is approximately

475   2,000 Tg yr^{-1}. Steel slags therefore contain approximately 0.6 Tg P yr^{-1}, which is equivalent

476   to one-fifth of the annual world industrial P demand (2.8 Tg P yr^{-1}). Removing P from these

477   slags would allow their iron content to be recovered in the process, adding economic benefits

478   to this P recovery route. As elemental P is reported in some of these cases as a nuisance, its

479   targeted recovery poses a challenge for green chemistry. The separation of iron and other

480   metals from the product (P_4 or PA) may be difficult to achieve.

481

482   3.6 Losses in the P cycle

483   Dissolved and particulate P transfer in land (urban and agricultural) runoff represents a

484   significant loss of P from the cycle. Whilst improvement in land management practices can

485   help reduce these losses, by-product chemical amendments are increasingly viewed as a

486   potential green chemistry strategy for prevention and/or control.[108] Applications of moderate-

487   charge-density anionic polyacrylamide (co-polymerised with sodium acrylate) to the soil

488   surface, or in irrigation water, have been highly effective (up to 90%) at reducing sediment

489   and nutrient losses in land runoff from agricultural land and from construction sites.[109] The

490   water-soluble polymer works by flocculating soil particles through co-bridging with divalent

491   cations already present in the soil or co-applied. Stabilizing the soil in this way prevents

492   surface crusting, increases water infiltration rates and reduces the risk of soil erosion, which

493   is the main process of P loss in many situations. High P solubility in over-fertilized soils is

494   also a significant eutrophication risk, which can be reduced by application of by-product

495   chemical amendments that bind P. For example, coal combustion by-products from

496   technologies to improve air quality, such as fluidized bed combustion fly ash and flue gas

497   desulfurization gypsum, have been shown to be effective (20-40%) at reducing soluble P

498   concentrations in soils without affecting plant P availability, or increasing soil or runoff

499   contamination from heavy metals and arsenic.[110] When targeted at the small critical source

500   areas in catchments that generate the majority of the P loss, by-product re-use provides a

501   cost-effective green chemistry approach to preventing P release to runoff. Similarly a range

502   of natural materials (e.g. Fe-rich sand), synthetic filtration materials (e.g. calcinated clay) and

503   industrial by-products (e.g. steel slag, gypsum, red mud) with high P binding capacity can be

504   used to remove P in land runoff, providing the runoff can be channelled, the flow velocity is

505   not too high and is sufficiently P-rich.[102,108] For example from livestock hard standing

506   areas.[111] The recovered P is either directly suitable for re-use as a fertilizer, or the P is

507   stripped from the binding agent using acid-base technology and the binding agent re-used.

508   However, the amounts of recoverable P at each site are usually very small. Direct recovery of

509   P from eutrophic waters using algae or aquatic plants, has also been considered with the

510   advantage of also lowering eutrophication risk.[112] Whether this is a feasible and worthwhile P

511   recovery route in itself still needs to be established. The synergy between P removal and

512   potentially using the harvested material as P source is the main advantage here.

513

514   **4. Designing a new food system**

515   Progress towards greening the global P cycle also requires consideration of sector or process

516   design, and utilization efficiency.[22] Food and industry production systems could be better

517   designed for maximum efficiency and allow maximum recovery of secondary P as a

518   substitute for primary PR; a key green chemistry goal. Agriculture dominates regional and

519   global P flows, but it is an input-driven rather than a demand-led sector that overuses P

520   unnecessarily because the P demands of the food chain have no governance. This leads to

521   unsustainable P surpluses, continued P accumulation in soils and increased eutrophication

522   risk, as is currently being evidenced most dramatically in China.[113] Animal product

523   consumption accounts for 72% of global dietary P demand and P demands could be reduced,

524   and P efficiency substantially increased, by reducing meat consumption.[36,114] For example, in

525   Europe and the USA average dietary P intake is double actual P requirements due to a high

526   proportion of meat in the diet.[15,115] It may also be possible to reduce crop P requirements by

527   20-30% through breeding more P efficient plants.[116,117] Reducing the intake and improving

528   the utilization of P in animal feeds, for example through precision (phase) feeding, phytase

529   addition and feeding low phytate crops, could reduce both P inputs and excretion rates by up

530   to a third.[118,119] The addition of the phytase enzyme allows the phytate in crops to be more

531   effectively utilized by monogastrics without the need for inputs of highly-soluble feed P

532   supplements. Refining livestock (and human) feeds to improve digestibility through other

533   green biotechnologies could also help to reduce the volumes of livestock (and municipal)

534   manure that requires recovery and recycling. For example the use of biorefinery to separate

535   out the main constituents of feeds (proteins, enzymes and phosphates) to increase their

536   digestibility and absorption.[55] The microfiltration of liquid feeds to manipulate their P content

537   might be one green chemistry option.

538   Similarly fertilizer use efficiency could be increased at the field scale through improved

539   product formulation design and by more precise application methods targeting the crop rather

540   than the soil.[120,121] The synthesis of nano-particle P fertilizers that are able to supply P to

541   crops efficiently and with lower leaching risk represents a significant advance. Stable

542   hydroxyapatite nanoparticles (15.5 nm in diameter) have been successfully synthesized using

543   sodium carboxymethyl cellulose solution and used to fertilize soybean.[122] Fertilizer P

544   nanoparticles (28.2nm in diameter) have also been recently biosynthesized from tricalcium

545   phosphate using mycelium from the Aspergillus tubingensis fungus.[123] The green engineering

546   advantage of these nanoparticles is that they can be potentially be (bio)-synthesized from a

547   range of secondary P products, and engineered so that the particle size (and hence P uptake

548   rate) can be matched to the P uptake patterns of different crops, thereby improving P

549   efficiency.

550   It has been suggested that society could potentially substitute at least 50% of its PR

551   processing requirement based on recovered secondary P at the regional scale.[15,18,45,77] Such

552   predictions belie the huge financial and social challenges in developing and marketing

553   recovered products that have suitable physical and chemical consistency, good P availability,

554   are safe to use and are economically viable. In view of these constraints, progress in greening

555   the global P cycle will be more realistically achieved in the short term through sector and

556   regional level initiatives.[21,29,53] For example, green chemistry principles have already been

557   adopted in regional government policies towards circular and bio-based economies,[13] and in

558   sustainable food production initiatives such as Origin Green in Ireland.[124] New smarter, more

559   diversified and customer-focused business models are rapidly emerging in the mining

560   industries that take account of the their wider social responsibilities, the need to raise safety

561   and environmental standards and reduce wastage.[27] For example, under a government-

562   industry covenant, Amsterdam-based ICL has committed to substituting its entire PR

563   feedstock, amounting to 0.5 Tg yr[1] with secondary P, initially from human wastewater. Yet

564   more ambitious are the aspirations of leading edge Chinese producer Wengfu, who have

565   taken a top-down policy-led decision to reach zero waste by 2015, which includes 100% re-

566   use of PG as ammonium sulphate and calcium carbonate.[63] This has entailed restructuring the

567   company from being a fertilizer only company to having three divisions, fertilizers, chemical

568   products and construction materials. It has also started to recover a wide range of materials

569   from phosphate ores, including 100 t yr^{-1} of iodine.

570

571   **5. Conclusions**

572   Although it has taken at least one generation to realize the unintended consequences of PR

573   processing, there is compelling economic, environmental and ethical justification for more

574   efficient and sustainable use of P to safeguard PR resources and the environment for future

575   generations. We conclude that the potential opportunities for green chemistry in achieving

576   planetary P sustainability goals are large and fully consistent with societal migration to bio-

577   based and circular economies based on smart science, practical policies and innovative

578   technologies. We define three major areas for progress: (a) maximizing the economic and

579   resource value of PR in fertilizer and other uses (b) recover and recycle P from the vast array

580   of secondary P resources though innovative green technologies so that they can increasingly

581   be re-used as renewable materials in the future, and with minimum waste, and (c) provide P

582   governance in the food chain and define more precisely what societal (end user) P

583   requirements are to provide a firm foundation for designing and investing in new smarter

584   demand-driven production systems that use only what is needed and with maximum

585   efficiency and minimum P losses to the oceans.

586

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591

592   **References**

593   1 T. Lougheed, *Environ. Health Perspect.*, 2011, **119(5)**, A208–A213.

594   2 L. Reijnders, *Resourc. Conservat. Recycl.,* 2014, **93**, 32-49.

595   3. J. J. Elser, T. J. Elser, S. R. Carpenter and W. A. Brock. *PLoS One*, 2014, **9**: e93998.

596   4. J. Cooper, R. Lombardi, D. Boardman and C. Carliell-Marquet, *Resourc. Conservat.*

597   *Recycl.*, 2011, **57**, 78-86.

598   5 P. J. A. Withers, K. C. van Dijk, T-S.S. Neset, T. Nesme, O. Oenema, G. H. Rubæk, O. F.

599   Schoumans, A. L. Smit and S. Pellerin, *AMBIO*, 2015, 44 (Suppl. 2), S163-S179.

600   6 L. Hein and R. Leemans, *AMBIO*, 2012, **41**, 341-349.

601   7 V. H. Smith and D. W. Schindler, *Trends Ecol. Evolut.* 2009, **24**, 201–207.

602   8. B. Qin, G. Zhu, G. Gao, Y. Zhang, W. Li, H. W. Paerl and W. W. Carmichael, *Environ.*

603   *Manage.*, **45(1)**, 105-112.

604   9. D. F. Millie, G. L. Fahnenstiel, J. D. Bressie, Julianne Dyble; R. J. Pigg, R. R. Rediske, D.

605   M. Klarer, P. A. Tester and R. W. Litaker, Aquatic Ecology, 43(4), 915-934.

606   10. J. Elser and E. Bennett. *Nature*, 2011, **478**: 29-31.

607   11. W. Schipper, *Eur. J. Inorg. Chem.*, 2014, 1567-1571.

608   12 R. W. Scholz, A. H. Roy, F. S. Brand, D. T. Hellums and A. E. Ulrich, *Sustainable*

609   *Phosphorus Management: A Global Transdisciplinary Roadmap*, Springer, Dordrecht,

610   2014.

611   13 E. C., Memo 14/377, http://europa.eu/rapid/press-release_IP-14-599_en.htm, 2014.

612   14 M. A. Sutton, A. Bleeker, C. M. Howard, M. Bekunda, B. Grizzetti, W. de Vries, et al.,

613   *Our Nutrient World: The challenge to produce more food and energy with less pollution*,

614   The Centre for Ecology and Hydrology, Edinburgh, U. K., 2013.

615   15 K. C. Van Dijk, J. P. Lesschen and O. Oenema, *Sci. Tot. Environ.*, In press.

616   16 R. B. Chowdhury, G. A. Moore, A. J. Weatherley and M. Arora, *Resourc. Conservat.*

617   *Recycl.,* 2014, **83**, 213-228.

618 17 D. Cordell, A. Rosemarin, J.J. Schroder and A.L. Smit, *Chemosphere* 2011, **84**, 747-758.

619 18 H. Ohtake and K. Okano, *Global Environ. Change*, 2015, **19(1)**, 1-30.

620 19 J. Hilton and C. Dawson, *Waste Resourc. Manage.*, 2012, **165(4)**, 179-189.

621 20 V. Smil, *Ann. Rev. Energy Environ.*, 2000, **25**, 25-53.

622 21 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice,* Oxford

623   University Press, Oxford, U. K., 1998.

624 22 P. T. Anastas and J. B. Zimmerman, *Environ. Sci. Technol.,* 2003, **37**, 94A.

625 23 R. A. Sheldon, *Chem. Commun.,* 2008, 3352-3365.

626 24 W. Jiao, W. Chen, A. C. Chang and A. L. Page, *Environ. Pollut.*, 2012, **168**, 44-53.

627 25 K. Syers, A. E. Johnston and D. Curtin, FAO Fertilizer and Plant Nutrition Bulletin 18:

628   Food and Agriculture Organization of the United Nations, Rome, Italy, 2008.

629 26 D. Seyhan, *Resourc. Conservat. Recycl.*, 2009, **53(12)**, 698–709.

630 27 R. Batterham, *Procedia Engineering*, 2014, **83**, 8-15.

631 28 E. C., COM/2014/0398, http://eur-lex.europa.eu/legal

632   content/EN/TXT/?uri=CELEX:52014DC0398, 2014.

633 29 J. Voorthuis and C. Gijbels, *Sustainability*, 2010, **2**, 371-382.

634 30 J. Hilton, A.E. Johnston and C. J. Dawson, *The Phosphate Life-Cycle: Rethinking the*

635   *options for a finite resource.* Proceedings 668, International Fertiliser Society, York, U.

636   K., 2010.

637 31 J. S. Guest, S. J. Skerlos, J. L. Barnard, M. B. Beck, G. T. Daigger, H. Hilger, et al.,

638   *Environ. Sci. Technol.*, 2009, **43(16)**, 6126−6130.

639 32 R. Sylvester-Bradley and P. J. A. Withers, *Innovation in Crop Nutrition*. Proceedings

640   700, International Fertiliser Society No. 700, Leek, U. K., 2013.

641 33 J. Peñuelas, B. Poulter, J. Sardans, P. Ciais, M. van der Velde, L. Bopp, O. et al., *Nature*

642   *Commun.,* 2013, **4**, 2934, doi: 10.1038/ncomms3934.

643   34 K. Senthilkumar, T. Nesme, A. Mollier and S. Pellerin, *Nutr. Cycl. Agroecosyst*, 2012,

644   **92**, 145-159.

645   35 M. E. Schipanski and E. M. Bennett, *Ecosyst.*, 2012, **15**, 256-268.

646   36 G. S. Metson, E. M. Bennett and J. J. Elser. *Environ. Res. Lett.,* 2012*,* **7**, 044024.

647   37 C. J. Dawson and J. Hilton, *Food Policy*, 2011, **36**, S14-S22.

648   38 M. Prud'Homme, *World Phosphate Rock Flows, Losses and Uses*, in Proceedings of

649   Phosphate 2010 International Conference, Brussels, 2010.

650   39 L. Bouwman, K. K. Goldewijka, K. W. Van Der Hoekc, A. H. W. Beusena, D. P. Van

651   Vuurena, J. Willemsa, M. C. Rufinoe and E. Stehfesta, *Proc. Natl. Acad. Sci.,* 2011,

652   **110(52)**, 20882-20887.

653   40 H. Lamprecht, D. J. Lang, C. Binder, R. Scholz and W. Roland, GAIA, 2011, **20**(2), 112-

654   121.

655   41 A. C. Edwards and P. J. A. Withers, *Soil Use Manage.*, 1998, **14(Suppl. 1)**, 124-130.

656   42 A. Sharpley, H. P. Jarvie, A. Buda, L. May, B. Spears, and P. Kleinman. *J. Environ.*

657   *Qual.,* 2013*,* **42**, 1308-1326.

658   43 G. K. MacDonald, E. M. Bennett, P. A. Potterc and N. Ramankuttyd, *Proc. Natl. Acad.*

659   *Sci.*, 2011, **108(7)**: 3086-3091.

660   44 H. Li, G. Huang, Q. Meng, L. Ma, L. Yuan, F. Wang, W. Zhang, Z. Cui, J. Shen, X.

661   Chen, R. Jiang and F. Zhang, *Plant Soil*, 2011, **349**, 157-167.

662   45 R. H. E. M. Koppelaar and H. P. Weikard, *Global Environ. Change*, 2013, **23**, 1454-

663   1466.

664   46 E. M. Bennett, S. R. Carpenter and N. F. Caraco, *Bioscience*, 2001, **51(3)**, 227-234

665   47 S. Sattari, A. Bouwman, K.E. Giller and M. van Ittersum, *Proc. Natl. Acad. Sci.*, 2012,

666   **109**, 6348–53.

667   48 B. Ringeval, B. Nowak, T. Nesme, M. Delmas and S. Pellerin, *Global Biogeochem.*

668   *Cycles,* 2014, **28**, 743–756.

669   49   G. Villalba, Y. Liu, H. Schroder and R. U. Ayres, *J. Ind. Ecol.*, 2008, **12(4),** 557-569.

670   50   G. van Drecht, A.F. Bouwman, J. Harrison and J. M. Knoop. *Global Biogeochem.*

671   *Cycles,* 2009, **23**, Gb0a03. doi:10.1029/2009GB003458

672   51   T. Karak, R. M. Bhagat and P. Bhattacharyya, *Crit. Rev. Environ. Sci. Technol.*, 2011,

673   **42(15)**, 1509-1630

674   52   W. J. Schipper, A. Klapwijk, B. Potjer, W. H. Rulkens, B. G. Temmink, F. D. G. Kiestra,

675   and A. C. M. Lijmbach, *Environ. Technol.,* 2001, **22**, 1337-1345.

676   53   O. Oenema, W. Chardon, P. Ehlert, K. van Dijk and O. Schoumans. *Phosphorus*

677   *Fertilizers from By-Products and Wastes*, Proceedings 717, International Fertiliser

678   Society, Leek, U. K., 2012.

679   54   H. Ohtake, *in Biochemical Engineering and Bioprocessing,* Vol. 3, Wiley, 2015, pp. 1-

680   15.

681   55   O. F. Schoumans, F. Bouraoui, C. Kabbe, O. Oenema, and K. van Dijk, *AMBIO*, 2015,

682   **44(Suppl. 2)**, 180-192.

683   56   E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. van der Bruggen, W. Verstraete, K.

684   Rabaey and B. Meesschaert, *Crit. Rev. Environ. Sci. Technol.*, 2015, **45**, 336-384.

685   57   P. Westerhoff, S. Lee, Y. Yang, G.W. Gordon, K. Hristovski, R. U. Halden and P.

686   Herckes, *Environ. Sci. Technol.*, 2015, DOI: 10.1021/es505329q.

687   58   J. H. Clark, L. A. Pfaltzgraff, V. L. Budarin, A. J. Hunt, M. Gronnow, A. S. Matharu, D.

688   J. Macquarrie, and J. R. Sherwood, *Pure Applied Chem.*, 2013, **85(8)**, 1625-1631.

689   59   C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon and M. Poliakoff, *Science*, 2012, **337**,

690   695–699.

691   60   M-P. Zacharof and R. W. Lovitt, *Waste Biomass Valor.*, 2013, **4**, 557-581.

692   61 J. Hilton, B. K. Birky and M. Moussaid, *Comprehensive Extraction, a Key Requirement*

693   *for Social Licensing of NORM Industries?,* Proceedings, NORM 7, Beijing, China, 2013.

694   62 P. Christmann, *Procedia Engineering*, 2014, **83**, 19-26.

695   63 P. Zhang, *Procedia Engineering*, 2014, **83**, 37-51.

696   64 Anon. *JDCPhosphate starts hot operations*, *Fert. Internat.* 2014, **458**, 40-41.

697   65 IAEA, *Radiation Protection and Management of NORM Residues in the Phosphate*

698   *Industry*, Safety Reports Series No. 78, International Atomic Energy Agency, Vienna,

699   Austria, 2013.

700   66 G. H. Rubaek, K. Kristensen, S. E. Olesen, H. S. Østergaard and G. Heckrath,

701   *Geoderma,* 2013, **209–210**, 241–250.

702   67 A. R. Richardson and R. J. Simpson, *Plant Physiol.*, 2011, **156**, 989–996.

703   68 L. Ramaekers, R. Remans, I. M. Rao, M. W. Blaier and J. Vanderleyden, *Field Crop*

704   *Res.*, 2010, **117**, 169-176.

705   69 A. Bateman, H. van der Horst, D. Boardman, A. Kansal, and C. Carlliel-Marquet,

706   *Resourc. Conservat. Recycl.,* 2011, **55**, 1146-1153

707   70 K. Suzuki, Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto, T. Yasuda and M. Waki,

708   *Bioresource Technol.*, 2007, **98**, 1573–1578.

709   71 M. L. Gerardo, M. P. Zacharof and R. W. Lovitt, *Water Res.*, 2013, **47**, 4833-4842.

710   72 P. J. A. Kleinman, A. N. Sharpley, A. M. Wolf, D. B. Beegle and P.A. Moore,

711   Jr. *Soil Sci. Soc. Am. J.*, 2002, **66**, 2009–2015.

712   73 T.Wang, M. Camps-Arbestain and M. Hedley, *Plant and Soil*, 2014, **375**, 61-74.

713   74 Z. Liu and R. Balasubramanian, *Applied Energy*, 2014, **114**, 857-864.

714   75 K. S. Ro, K. B. Cantrell, P. G. Hunt, T. F. Ducey, M. B. Vanotti and A. A. Szogi, *Biores.*

715   *Technol.*, 2009, **100**, 5466-5471.

716   76 C. J. De Vos and L. Heres, *Risk Analysis,* 2009, **29(4)**, 541-557.

717   77   C. Kabbe, *in Factor X. Re-source – Designing the Recycling Society, Eco-Efficiency in*

718   *Industry and Science,* eds, M. Angrich, A. Burger and H. Lehmann, Springer, Dordrecht,

719   The Netherlands, vol 30, pp. 261-273.

720   78   A. Giesen, *Environ. Technol.*, 1999, **20(7)**, 769-775.

721   79   D. Gunders, *Wasted: How America is Losing Up to 40 Percent of Its Food from Farm to*

722   *Fork to Landfill*, NRDC, Washington, U.S.A., 2012.

723   80   J. Parfitt, M. Barthel, and S. Macnaughton, *Phil. Trans. Royal Soc. B.*, 2010, **365**, 3065-

724   3081.

725   81   L. A. Pfaltzgraff, M. de Bruyn, E. C. Cooper, V. Budarin and J. H. Clark, *Green Chem.,*

726   2013, **15**, 307-314.

727   82   S. R, Smith, *Phil. Trans, Roy. Soc. A.*, 2009, **367**, 4005-4041.

728   83   H. A. Elliott and G. A. O'Connor, *Soil. Biol. Biochem.*, 2007, **39**, 1318-1327.

729   84   W. Pronk and D. Kone, *Desalination*, 2009, **248(1-3)**, 360-368.

730   85   B. Etter, B., et al. (2011). *Water Research* **45(2)**, 852-862.

731   86   J. R. Mihelcic, L. M. Fry and R. Shaw, <u>Chemosphere, 2011</u> **84(6)**, 832-839.

732   87   J. Lienert and T. A. Larsen, *Environ. Sci. Technol.*, 2009, **44(2)**, 556-566.

733   88   C. Adam, B. Peplinski, M. Michaelis, G. Kley and F. G. Simon, *Waste Manage*., 2009,

734   **29**, 1122-1128.

735   89   Z. Tan, Z. and A. Lagerkvist. *Renew. Sustain. Energy Rev.,* 2011, **15**, 3588-3602.

736   90   R. Hirota, A. Kuroda, J. Kato and H. Ohtake, *J. Biosc. Bioeng.*, 2010, **109**, 423-432.

737   91   A. Kuroda, N. Takiguchi, T. Gotanda, K. Nomura, J. Kato, T. Ikeda, and H. Ohtake,

738   *Biotechnol. Bioeng.*, 2002, **78**, 333-338.

739   92   P. L. Bond, L. Keller and L. L. Blackall, *Biotechnol. Bioeng.*, 1999, **63**, 507-515.

740   93   Y. Cao and A. Pawlowski, *Renew. Sustain. Energy Rev.*, 2012, **16**, 1657-1665.

741   94   A. Petterssona, L. E. Amand and B. M. Steenari, *Biomass Bioenergy*, 2008, **32**, 224-235.

742   95 S. Donatello and C. R. Cheeseman, *Waste Manage.*, 2013, **33**, 2328-2340.

743   96 Y. Song, P.G. Weidler, U. Berg, R. Nüesch and D. Donnert, *Chemosphere*, 2006, **63**,

744   236-243.

745   97 N. Marti, L. Pastor, A. Bouzas, J. Ferrer and A. Seco, *Water Res.*, 2010, **44**, 2371-2379.

746   98 K. Okano, M. Uemoto, J. Kagami, K. Miura, T. Aketo, M. Toda, K. Honda and H.

747   Ohtake, *Water Research*, 2013,**47**, 2251-2259.

748   99 K. Okano, S. Miyamaru, A. Kitao, H. Takano, T. Aketo, M. Toda, K. Honda, and H.

749   Ohtake. Sep. Prif. Technol., 2015, in press.

750   100 D. R. Kioussis , F. W. Wheaton, and P. Kofinas, *Agric. Eng.*, 2000, **23**, 315-332.

751   101 I. Midorikawa, H. Aoki, A. Ohmori, T. Shimizu, Y. Kawaguchi, K. Kassai and T.

752   Murakami, Proc.5th IWA Leading-Edge Conference on Water and Wastewater

753   Technologies, 2008.

754   102 P. Loganathan, S. Vigneswaran, J. Kandasamy, N. S. Bolan, *Crit. Rev. Environ. Sci.*

755   *Technol.*, 2014, **44**, 847-907.

756   103 B. E. Rittmann, B. Mayer, P. Westerhoff and M. Edwards, *Chemosphere*, 2011, **84**,

757   846–853.

758   104 J. K. Pittman, A. P. Dean, O. Osundeko, *Bioresour. Technol.*, 2011, **102**, 17–25.

759   105 W. Mulbry, S. Kondrad, C. Pizarro and E. Kebede-Westhead, *Bioresour. Technol.*,

760   2008, **99**, 8137-8142.

761   106 S. P. Marsden, *Nature Chemistry*, 2009, **1**, 685–687.

762   107 E. Yamasue, K. Matsubae, K. Nakajima, S. Hashimoto and T. Nagasaka, *J. Ind. Ecol.*,

763   2013, **17**, 722-730.

764   108 A. R. Buda, G. F. Koopmans, R. B. Bryant and W. J. Chardon, *J. Environ. Qual.*, 2012,

765   **41**, 621-627.

766   109 J. A. Entry and R.E. Sojka. *Trans. Am. Soc. Agric. Eng.*, 2003, **46**, 75-83.

767   110   W. L. Stout, A.N. Sharpley and J. Landa. *J. Environ. Qual.*, 2000, **29**, 1239-1244.

768   111   C. Penn, J. McGrath, J. Bowen, and S. Wilson, *J. Soil Water Conservat.*, 2014, **69(2)**,

769   51A-56A.

770   112   R. S. Quilliam, M.A. van Niekerk, D. R. Chadwick, P. Cross, N. Hanley, D. L. Jones,

771   A. J. A. Vinten, N. Willby and D. M. Oliver, *J. Environ. Manage.,*

772   http://dx.doi.org/10.1016/j.jenvman.2015.01.046

773   113   L. Ma, G. L. Velthof, F. H. Wang, W. Qin, W. F. Zhang, Z. Liu, Y. Zhang, J. Wei, J. P.

774   Lesschen, W. Q. Ma, O. Oenema and F. S. Zhang, *Sci. Tot. Environ.*, 2012, **434**, 51-61.

775   114   S. D. Donner, *Global Environ. Change*, 2007, **17**,105-113.

776   115   A. Flynn, T. Hirvonen, G. B. M. Mensink, M. C. Ocke, L. Serra-Majem, K. Stos, L.

777   Szponar, I. Tetens, et al. *Food Nutr. Res.*, 2009, **53**, 1-51.

778   116   T. J. Rose, J. Pariasca-Tanakaa, M. T. Rosea, Y. Fukutab and M. Wissuwaa, *Field*

779   *Crops Res.*, 2010, **119**, 154-160.

780   117   V. Raboy, *Plant Science*, 2009, **177**, 281–296.

781   118   R. O. Maguire, D. A. Crouse, and S. C. Hodges, *J. Environ. Qual.* 2007, **36**, 1235-

782   1240.

783   119   E. Kebreab, A. V. Hansen and A. B. Strathe, *Curr. Opin. Biotechnol.,* 2012, **23**, 872-

784   877.

785   120   P. J. A. Withers, R. Sylvester-Bradley, D. L. Jones, J. R. Healey, and P. J. Talboys.

786   *Environ. Sci. Technol.*, 2014, **48**, 6523-6530.

787   121   M. J. McLaughlin, T. M. McBeath, R. Smernik, S. P. Stacey, B. Ajiboye, and C.

788   Guppy. *Plant and Soil,* 2012, **349**, 69-87.

789   122   R. Q. Liu and R. Lal, *Sci. Rep.*, 2014, **4**, 5686; DOI:10.1038/srep05686.

790   123   J. C. Tarafdar, R. Raliya and I. Rathore, *J. Bionanosci.*, **6**, 1-6.

791   124   Origin Green, www.origingreen.ie, 2014.

792   Table 1. The operating principles of comprehensive extraction developed by the PR industry

793   have a number of similarities to those of green chemistry. Adapted from Hilton et al.[61].

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- address all available resources from a given site/ deposit in an integrated resource management strategy
- disturb the ground once
- construct regulation of naturally occurring radioactive materials (NORM) industries based on shared values between operators and regulators
- obtain and keep a social licence to operate, focused on equitable distribution of benefits between stakeholders and stockholders
- sequence extraction procedures and select extraction technologies to optimise deposit returns, *e.g.* by classifying and progressing resources on a whole "energetic basin" project management basis
- extract and store resources that would otherwise be wasted or dispersed for future use
- manage resources across the whole life-cycle seeking to conserve primary resources and substitute secondary resources for primary where feasible
- align to the waste hierarchy seeking all opportunities for re-use and recycling of by-products, residues and "wastes", resulting in a zero waste outcome
- promote new product development as strategic alternative to waste disposal (*e.g.* from recycling tailings or residues)
- ensure a net positive contribution to food, energy and water security as part of a wider commitment to sustainable development

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799 **Legends to Figures**
800
801 Figure 1. Phosphorus cycling in the technosphere showing thought bubbles suggesting where

802 green technologies and innovations could improve P sustainability by reducing P fluxes,

803 losses and wastage. Points of P loss are shown by dotted lines. Adapted from Sylvester-

804 Bradley and Withers.[32]

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806 Figure 2. The Phosphate Refinery for production of renewable secondary P sources in

807 agriculture and industry. After Ohtake.[18,54]

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809 Figure 3. Components present in food chain waste and their uses in common consumer

810 applications, highlighting sectors of the chemical industry that could benefit from the use of

811 such a renewable resource. After Clark et al.[58]

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813 Figure 4. Schematic overview of the main options to recover P from manures and biosolids.

814 Adapted from Oenema et al.[53] and Schoumans et al.[55]

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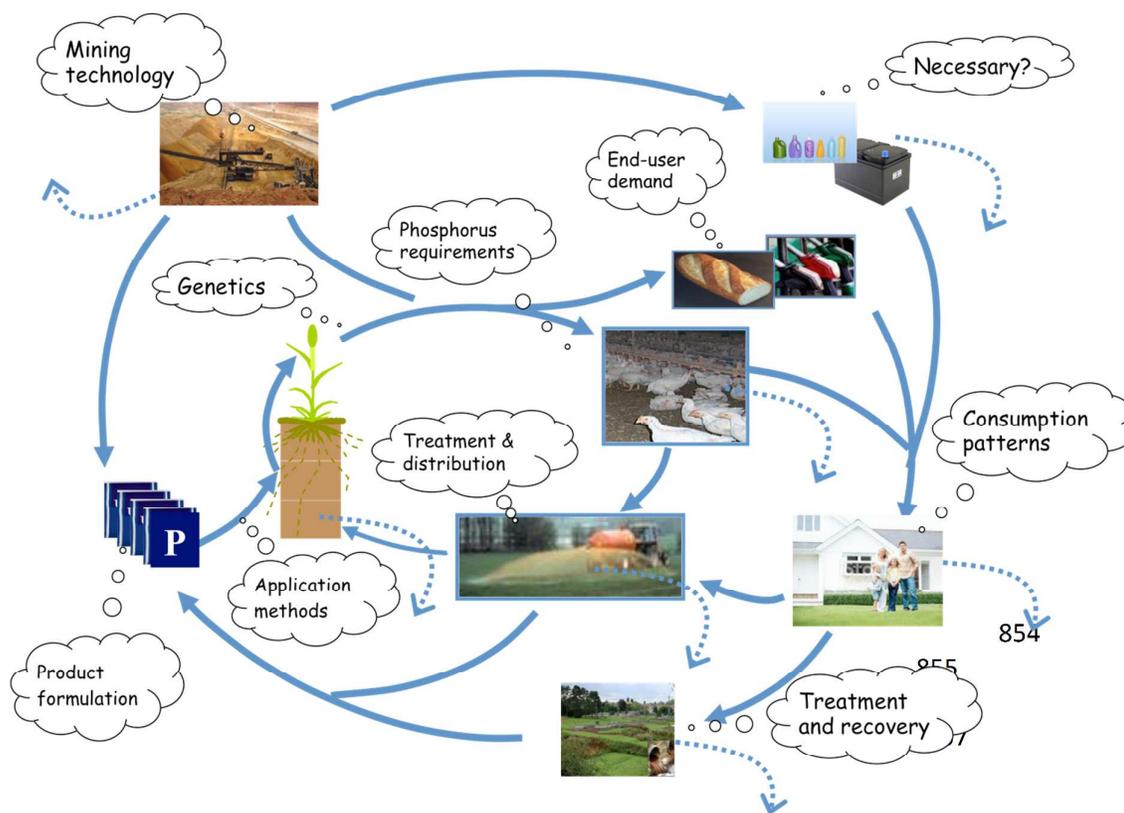835
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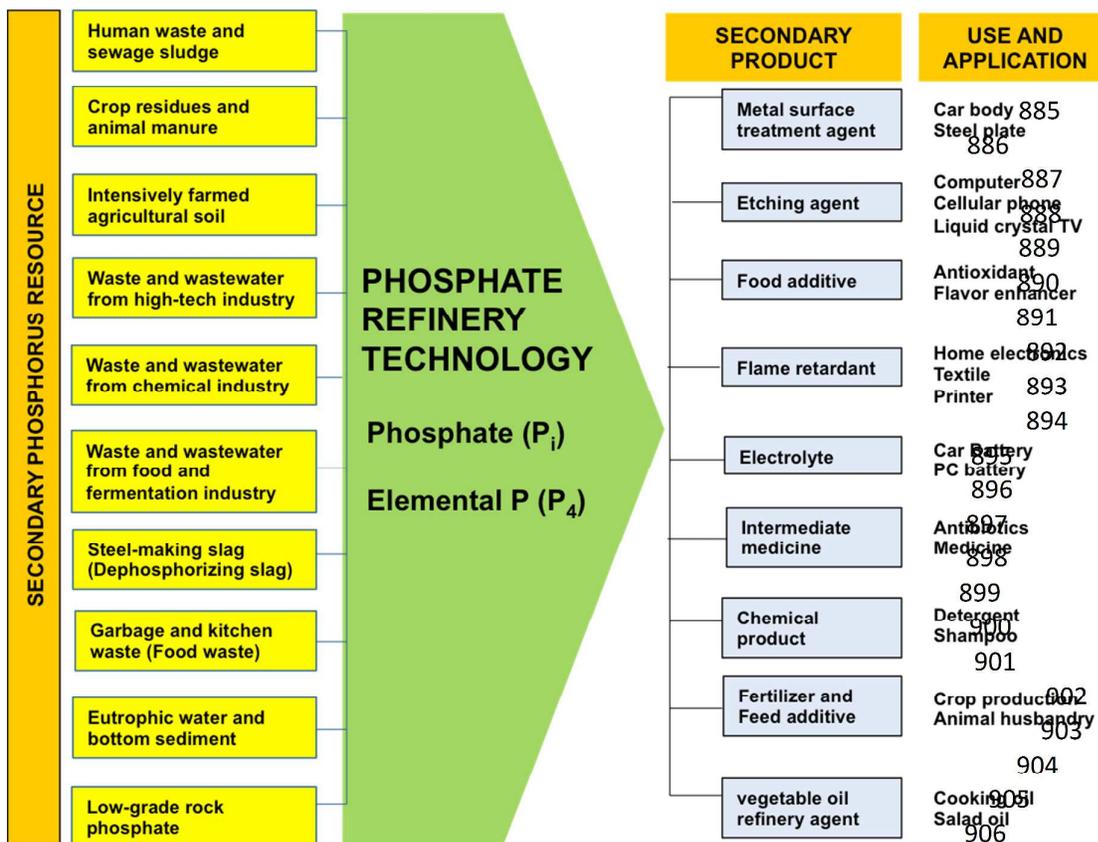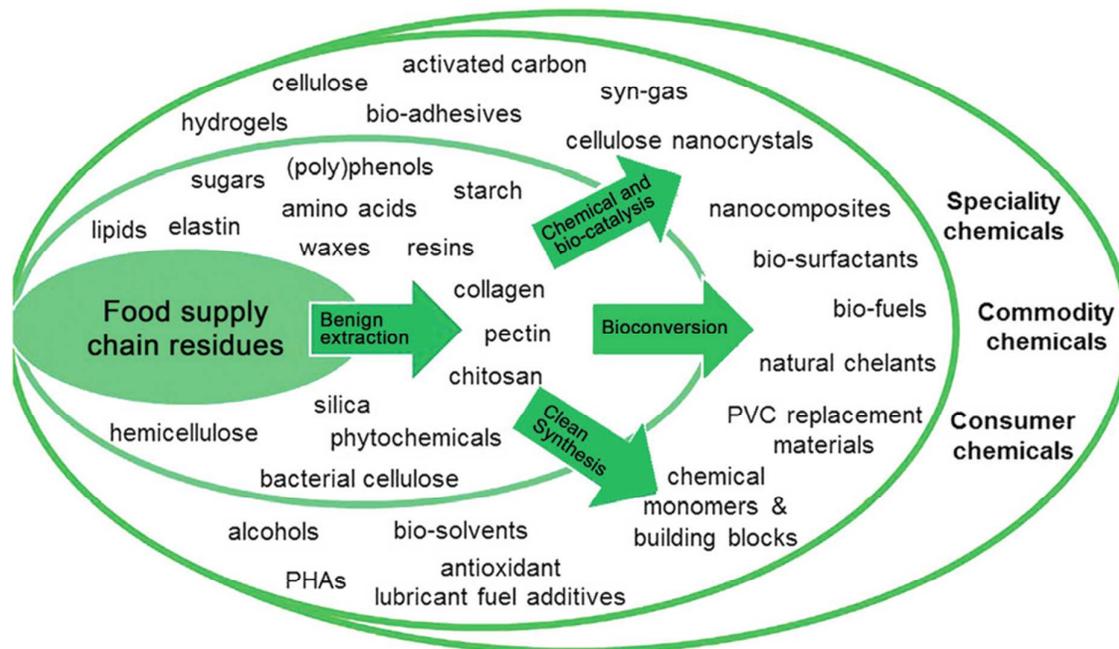870
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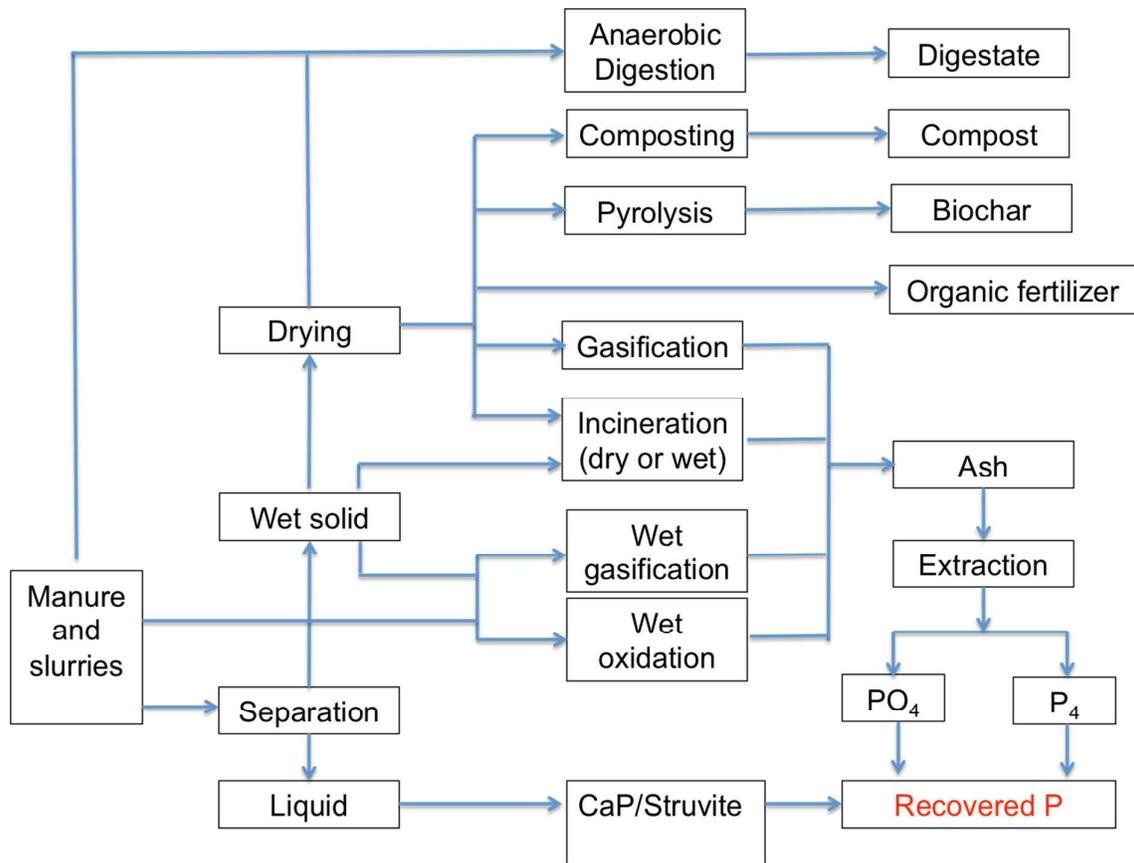
882   Figure 2

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929   Figure 3
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961   Figure 4
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