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5

Evaluation of hydrothermal carbonization in urban mining for the recovery of phosphorus from the organic fraction of municipal solid waste

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Abstract

The organic fraction of municipal solid waste was identified as an alternative phosphorus resource: hydrothermal carbonization provided phosphorus-rich hydrochar. Two alternative valorization pathways can be considered for the latter: the use as a fertilizer or as solid fuel after phosphorus extraction. By means of life cycle assessment (LCA) the environmental impact of extracting phosphorus and using the hydrochar as solid fuel was evaluated. Therefore, in a first step, phosphorus extraction with nitric acid, hydrochloric acid and sulfuric acid was experimentally investigated on laboratory scale. Nitric acid proved to be the most suitable because it offered high extraction efficiency and improved solid fuel properties such as lower ash content and lower levels of chlorine and sulfur. In contrast, hydrochloric acid increased the chlorine content and sulfuric acid only replaced phosphate by sulfate, but did not reduce the ash content of hydrochar. Then phosphorus can be precipitated and used as fertilizer.

Although technically feasible, LCA points out that the separate use of hydrochar and phosphorus represents an overall environmental burden for wide range of impact categories, including climate change and resource depletion. Therefore, other applications for phosphorus-rich hydrochars, like agriculture and horticulture, should be considered.

Keywords

Advanced hydrochar, low-ash solid fuel, phosphorus extraction, phosphorus fertilizer,

Graphical Abstract

42

43

44 Introduction

45 Phosphorus is an essential element for all life on earth, and the European Commission (EC) has
46 identified phosphate rock as a critical raw material in 2017 with a nonexistent recycling
47 rate.(European Commission, 2017) Approximately 95% of the world's phosphate production is
48 used in the fertilizer industry.(Desmidt et al., 2015) This figure makes it clear that phosphate
49 consumption is strongly related to nutrition and population growth.

50 Phosphorus is a chemical element whose use does not make it disappear, but spreads it out on
51 the planet. Therefore, the recovery of phosphorus from alternative sources is urgently needed.
52 A promising approach is to perform a fixation step for the phosphorus, a type of
53 homogenization and concentration. For example, sewage sludge is a plant nutrient rich
54 resource(Zhang et al., 2018, 2017) and when sewage sludge is incinerated, phosphorus is
55 concentrated in the ash and the liquid phase is then absent.(Cieřlik and Konieczka, 2017; Melia
56 et al., 2017) The ashes can directly be used as fertilizers but phosphorus extraction with
57 mineral acid and precipitation increases its bioavailability.(Cieřlik and Konieczka, 2017)

58 The present study was initiated when elevated phosphorus concentrations were determined
59 for hydrochar originating from the organic fraction of municipal solid waste (OFMSW). It
60 became evident that hydrothermal carbonization (HTC) can be part of a novel process for
61 phosphorus concentration from this undervalorized resource. The HTC process is an emerging
62 technology and produces hydrochar, a solid carbonaceous material, as main product from wet
63 lignocellulosic biomass such as the OFMSW.(Funke and Ziegler, 2010; Hu et al., 2010; Titirici et
64 al., 2012; Maria M Titirici et al., 2007) The wet conditions during the process make the
65 previous drying superfluous, which is a significant advantage over alternative thermochemical
66 processes (torrefaction, pyrolysis, and gasification), considering the economics for wet
67 feedstocks.(Cha et al., 2016; Kambo and Dutta, 2015)

68 In terms of valorization and commercialization of phosphorous-containing hydrochar, two
69 main pathways can compete with each other: application of phosphorus-containing hydrochar
70 to soil(Lang et al., 2019) or phosphorus extraction for its use in agriculture and the use of the
71 depleted hydrochar as solid fuel.

72 For the use of hydrochar in agriculture, a post-treatment is required as pristine hydrochar may
73 involve phytotoxicity. Therefore, several options are known(Busch et al., 2013, 2012; Dalias et
74 al., 2018; Fornes and Belda, 2017) and a by-product-free treatment is to desorb the undesired
75 compounds and to use them directly for heat generation for the HTC process.(Hitzl et al., 2018)
76 In the latter case, the product is referred to as advanced hydrochar, which is suitable for
77 agriculture, to distinguish it clearly from pristine hydrochar. The use of pristine hydrochar in
78 agriculture, e.g. in Spain, involves climate change benefits,(Owsianiak et al., 2018) and a rough
79 estimation confirmed that this also applies to advanced hydrochars.(Hitzl et al., 2018)

80 When hydrochar is considered a solid fuel and phosphorus should be destined to agriculture,
81 then phosphorus should be extracted at the production site and, thereby, further
82 concentrated. The reason for this is that burning of hydrochar as solid fuel is foreseen in
83 smaller units such as domestic or district heating systems. This leads again to a territorial
84 spread of the phosphorus-rich ash, which would cause again logistic costs for its collection.

85 An additional economic benefit of this approach is the improvement in the fuel quality of
86 hydrochar.(Wang et al., 2018) Phosphorus forms part of the ashes of hydrochar, and its
87 removal reduces the ash content. This is relevant because carbonaceous materials are
88 classified as solid fuels in terms of their ash content.(International Organization for

89 Standardization, n.d.) Improving the product quality of hydrochar as a solid fuel increases its
90 value and contributes positively to the economic balance of the production process.

91 Here we show that the phosphorus extraction from hydrochar is generally possible with
92 mineral acid. By simply neutralizing the extract, phosphorus is recovered and can then be
93 marketed as a solid fertilizer from secondary phosphate sources. Based on these data, we
94 performed the Life Cycle Assessment (LCA) of the developed process, considering the
95 extracted hydrochar as solid fuel and the consequences of its combustion.

96 [Materials and Methods](#)

97 [Hydrothermal carbonization](#)

98 All residual biomass was processed at Ingelia's pilot plant.(Hitzl et al., 2015) The production of
99 hydrochar from the OFMSW has been described elsewhere.(Hitzl et al., 2018) The organic
100 fraction was obtained from households in Guipúzcoa (The Basque Country, Spain) by separate
101 collection which was operated by Gipuzkoako Hondakinen Kudeaketa SAU. It contained
102 biodegradable plastic bags, glass and plastic bottles as "impurities" in low amount and a water
103 content of 75%. For the trial, 9.24 t of this resource were transformed into 1.05 t of dry
104 hydrochar with an ash content of 12.9% (determined by calcination at 815 °C).(Hitzl et al.,
105 2018) Details on the processing of green waste can be found in literature,(Hitzl et al., 2015) as
106 well as for the transformation of orange peel waste (OPW).(Burguete et al., 2016) Hydrochar
107 from sewage sludge was also produced at Ingelia's pilot plant during the FP7 NEWAPP
108 project.("New technological applications for wet biomass waste stream products," n.d.)

109 [Phosphorus extraction](#)

110 In a round-bottom flask, 4.00 g of hydrochar was placed together with 15 mL of acid solution.
111 The latter was prepared from HTC process water obtained from Ingelia, adding the amount of
112 the corresponding concentrated acid to reach the desired concentration. The final
113 concentration of sulfuric acid was 5 wt%, of nitric acid 6 wt%, and of hydrochloric acid 4 – 5
114 wt%. During the acidification of the process water, a solid precipitated which was removed by
115 filtration and discarded. The hydrochar suspension was stirred for four hours at different
116 temperatures, namely at 40, 60 , 80, and 100 °C (see also , Figure S2, ESI). The solid was
117 collected by filtration, washed with 100 mL of deionized water and dried overnight at 100 °C.
118 Phosphorus content in hydrochar was calculated from ash content and ash composition, the
119 latter determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on a
120 Varian 715 ES spectrometer. Phosphorus recovered was calculated from the amounts and
121 concentrations of the acid extract and the washing water. Their phosphorus content was
122 determined directly by ICP-OES. Higher heating values (HHV) were determined following the
123 analytical standard UNE-EN 14918:2011.

124 [Phosphorus precipitation](#)

125 For phosphorus precipitation the pH of the acid extract was adjusted to 8 to 9.5 adding calcium
126 hydroxide. The solid was collected by filtration and dried in an oven at 100 °C overnight.

127 [LCA modelling part](#)

128 Environmental performance of phosphorus removal was assessed using environmental LCA. It
129 was conducted in accordance with the requirements of the ISO 14044 standard and the
130 guidelines of the EU Commission's International Reference Life Cycle Data System (ILCD)
131 Handbook.(*ILCD Handbook: General guide for Life Cycle Assessment - Detailed guidance*, 2010,

132 *ISO 14044:2006 Environmental management -- Life cycle assessment -- Requirements and*
133 *guidelines, 2006)*

134 *Goal and scope*

135 Because hydrothermal carbonization is a waste treatment option, the functional unit was
136 defined as “hydrothermal carbonization of 1 kg of wet biowaste with 100% content of biogenic
137 carbon of total carbon”. This definition allows for a fair comparison between biowaste with
138 varying phosphorus content and with hydrothermal carbonization of biowaste without
139 phosphorus recovery. The most likely use of hydrochar is as solid fuel for domestic heating.
140 Nitrogen and sulfur content of the hydrochar were taken into account for emissions, whereas
141 a complete elimination of the mineral acids during the washing process was assumed.

142 The current study is considered a micro-level decision support (type A) situation according to
143 ILCD guidelines, and the assessment applies an attributional approach where average Spanish
144 data are used. System boundaries specifying the processes included have been described
145 before.(Owsianiak et al., 2016) We included replaced the conventional waste management
146 system (composting), replaced combustion of fossil coal, construction of a HTC plant,
147 production of the hydrochar and HTC process water and transportation of the hydrochar. In
148 addition, production of acids and base for recovery of P was included. System expansion was
149 performed for processes with recovery of commodities; recycled steel substitutes the
150 production of virgin steel and the HTC process water (concentrated at the HTC plant using
151 reverse osmosis) substitutes the production of inorganic fertilizers. Likewise, impact offsets
152 (also known as credits) are given to recovered phosphorus (replacing phosphorus from
153 phosphate rock), to avoided conventional treatment of biowaste, and to energy recovery when
154 hydrochar is used for domestic heating (replacing combustion of fossil coal), in accordance
155 with the recommendations of the ILCD guidelines for this decision support type.

156 Product systems were modelled in SimaPro, version 8.3.0.0 (PRe Consultants bv, the
157 Netherlands). Parameters and data underlying the modeling of HTC plant are documented in
158 literature.(Owsianiak et al., 2016) Data for foreground processes in the HTC system, are based
159 on primary data measured at a HTC plant at Ingelia S.L. (Valencia, Spain). Data for generic
160 processes, such as electricity production and waste management processes, are based on
161 those available in the ecoinvent database, version 3.2.(Weidema et al., 2013)

162 ILCD’s method was used in the life cycle impact assessment phase (ILCD 2011 Midpoint+,
163 version 1.05),(Hauschild et al., 2013) as implemented in the LCA modeling software SimaPro,
164 version 8.3.0.0 (PRe Consultants bv, the Netherlands). All ILCD impact categories were used,
165 except ionizing radiation impacts on ecosystems which is considered not sufficiently
166 representative for this type of impact.

167 *Scenarios*

168 In total, twelve scenarios were considered (Table 1). Overall, three different acids (HNO_3 ,
169 H_2SO_4 and HCl) in two concentrations applied to phosphorus extraction from hydrochar made
170 from the OFMSW and a hypothetical one with the double phosphorus amount. In detail, for
171 the first three scenarios (1–3) the same acid (and base) concentrations and amounts were
172 used as in the experiments. Initial phosphorus content in the hydrochar for these scenarios
173 was the content measured for hydrochar made from the OFMSW (1.25%; 22.1% of the ashes),
174 which is in a higher range than values measured for hydrochars made from other biowaste
175 types. Assuming that amounts of acids and bases can be optimized during up-scaling, further
176 three scenarios were considered with amounts of acids and base reduced 10 times (scenarios

177 4–6). In addition, as starting material for the extractions, in six scenarios hydrochar was
 178 considered to involve the double amount of phosphorus, compared to the current one.
 179 Hereby, extraction efficiency was maintained. In the first group, acid amount was maintained
 180 as in the experimental procedures (scenarios 7–9) and in the second group (scenarios 10–12)
 181 reduced acid amounts and concentrations were used. Sensitivity of the results to the
 182 parameters presented in Table 1 was done by simply comparing impact scores between
 183 scenarios.

184

Scenario	Sensitivity parameter	Acid type	Acid concentration	P content
1	Baseline	HNO ₃	High (6%)	High (1.25%)
2, 3	Acid type	HCl; H ₂ SO ₄	High (4%; 6%)	High (1.25%)
4–6	Acid concentration	HNO ₃ ; HCl; H ₂ SO ₄	Optimized (1/10 of initial)	High (1.25%)
7–9	P content	HNO ₃ ; HCl; H ₂ SO ₄	High (4%; 6%)	Very high (2.50%)
10–12	All potential improvements	HNO ₃ ; HCl; H ₂ SO ₄	Optimized (1/10 of initial)	Very high (2.50%)

185

186 *Table 1. Overview of scenarios used in the scenario analysis.*

187

188 Results and discussion

189 Phosphorus extraction

190 As previously reported, the organic fraction of municipal solid waste has been converted into
191 hydrochar on a ton scale.(Hitzl et al., 2018) In a nutshell, 9.24 t of wet starting material gave
192 1.05 t of dry hydrochar, which corresponded to a mass yield of 45% (based on dry matter). The
193 total ash content of the hydrochar was 13% and the concentrations of its major components
194 are shown in Figure S1. From these data a total phosphorus content in the hydrochar of 1.25%
195 (as P) was calculated. This high concentration was relatively surprising as the phosphorus
196 content was generally neglected in the analysis of hydrochar. When it was reported, it was
197 significantly lower at 0.42% for food waste.(Idowu et al., 2017)

198 The second HTC product, the process water, generally contains a low phosphorus
199 concentration of less than 5 ppm. Therefore, it can be concluded that phosphorus is fixed in
200 hydrochar, i.e. all phosphorus present in the wet raw material is recovered in dry hydrochar
201 and, its concentration is increased by a factor of nearly nine in the present case.

202 Nevertheless, the phosphorus concentration in the solid hydrochar was still an order of
203 magnitude lower than in the phosphate rock, in which its concentration is typically between 13
204 and 17%. However, hydrochar offers advantages over the rock for the extraction process. In
205 particular, hydrochar already has a small particle size (<5 cm) and a high grindability index (the
206 particle size is further reduced easily by milling).(Kempegowda et al., 2017; Smith et al., 2018)
207 In addition, the chemical transformation during the HTC, that is, the dehydration, breaks up
208 the plant structure(Hitzl et al., 2015) and the hard biomass is “perforated by a spongy,
209 continuous system of nanopores”.(M M Titirici et al., 2007) Therefore, it should be easy for an
210 extracting liquid to completely penetrate the carbonaceous material and access all phosphorus
211 domains.

212 With the aim to proof this hypothesis, the hydrochar derived from OFMSW was extracted with
213 three different mineral acids, sulfuric acid, hydrochloric acid and nitric acid. In fact, Figure S2
214 shows that all three acids were able to remove the phosphorus almost quantitatively with an
215 efficiency of more than 96%. In addition, the extraction was independent of the reaction
216 temperature: In the temperature range from 40 ° C to 100 ° C, no significant change in the
217 efficiency was observed. This is relevant because in the industrial HTC process a hot hydrochar
218 water slurry exits the reactor and cools down during the downstream processing. The results
219 of the extraction indicated that the temperature of the carbonaceous material could be
220 neglected and the extraction could be carried out after excess process water had been
221 removed in the filter press (to a humidity of approximately 50%).

222 Phosphorus extraction worked well with all three mineral acids, but the effect on ash content
223 was not the same in the three cases. For sulfuric acid, the ash content did not vary
224 significantly, whereas for nitric acid and hydrochloric acid, the ash content after extraction
225 decreased from 13% to approximately 4% (Figure 1a). Analysis of the ash components showed
226 that calcium and phosphorus are significantly reduced in the latter cases, whereas with sulfuric
227 acid the calcium concentration was still similar to the initial one (Figure 1b). In view of the low
228 solubility of calcium sulfate, this was a predictable observation: calcium phosphate in the
229 hydrochar is replaced by calcium sulfate. The sulfate content is included in the “other” fraction
230 in Figure 1b. From these results it was concluded that sulfuric acid was suitable for phosphorus
231 extraction. However, with high calcium hydrochars, the ash content did not decrease when

phosphorus was removed. If a lower ash content was desired, sulfuric acid was not a valuable choice and hydrochloric acid or nitric acid should be used.

When mineral acids were used for phosphorus extraction from sewage sludge ashes, sulfuric acid was the reagent of choice for economic reasons, although it increased the amounts of inorganic residues.(Ottosen et al., 2013) In contrast, in the present case the organic nature of the by-product was a game changer: sulfate deposits deteriorated the product properties.

When using nitric acid and hydrochloric acid ash contents were clearly reduced (Figure 1a), and in particular calcium and phosphorus concentration in the acids (Figure 1b). Therefore, it can be concluded that these two mineral acids were very efficient in dissolving of calcium phosphate from hydrochar.

242

243 a)

b)

244

245 *Figure 1. Ash content (a) and concentration of different metal oxides (b) in hydrochar, in the original sample and*
 246 *after extractions with different mineral acids.*

247

248 Phosphorus extraction of different hydrochar samples

249 Phosphorus extraction and ash reduction were successful with hydrochar from the OFMSW.
 250 With the aim to evaluate the scope of the process, it was applied to several hydrochar samples
 251 from the FP-7 NEWAPP project. In the latter, organic residual feedstocks were processed by
 252 HTC on industrial scale, namely sewage sludge, orange peel waste (OPW) and green and
 253 garden prunings. ("Industrial Scale Hydrothermal Carbonization: new applications for wet
 254 biomass waste," 2016) The hydrochar samples had a different ash content, from high ash (27%
 255 sewage sludge and 18% garden-pruning) to lower ash (OPW 7%, Figure 2a). In addition, ash
 256 compositions were significantly different since hydrochar originating from sewage sludge
 257 contained the expected increased phosphorus content, while for the other two samples the
 258 concentration of this element was rather low (Figure 2b).

259

260

261 a)

262

263 b)

264

265 *Figure 2. Ash content (a) and concentration of different metal oxides (b) in hydrochar, measured for the original*
 266 *sample and after extractions with hydrochloric acid (4%, 60 °C, 4 h). Hydrochars were prepared from the organic*
 267 *fraction of municipal solid waste (OFMSW), sewage sludge, orange peel waste (OPW), and garden prunings.*

268

269 The hydrochloric acid extraction process (4%, 60 °C, 4 h) was able to reduce the phosphorus
 270 content to almost zero in all cases (Figure 2b). When the phosphorus content was high (for
 271 example, in the sample obtained from sewage sludge), the ash content was also significantly
 272 reduced from 27% to 15%. At low phosphorus content (OPW, garden prunings), the gain in ash
 273 reduction was rather low (Figure 2a). It was remarkable that calcium was almost completely
 274 removed in the sewage sludge-derived hydrochar (initially 7%), as well as in the OFMSW
 275 derived hydrochar, but not in the garden-pruning derived one (originally 5%). In the latter
 276 case, the calcium content was reduced by only half. Therefore, these data showed that calcium
 277 reduction was more efficient when phosphate was present at the same time. Therefore, it was
 278 concluded that the present extraction method generally worked well for the phosphorus
 279 extraction and was effective for reducing the ashes when both elements, calcium and
 280 phosphorus, were present in significant amounts.

281 Performance of the extracted hydrochar as solid fuel

282 It has already been shown that phosphorus extraction can be carried out with the aim to
283 achieve two goals simultaneously: the recovery of phosphorus and the ash reduction. The
284 latter purpose is interesting when hydrochar is commercialized as solid fuel. Therefore,
285 relevant properties of the material after extraction were analyzed and evaluated. Only samples
286 produced with nitric acid and hydrochloric acid were considered since sulfuric acid was
287 previously discarded for improving fuel quality.

288 The first and most important feature of a solid fuel is its energy content, quantified as higher
289 heating value (HHV). Table 2 shows that the HHV for various hydrochar samples increased by
290 up to ten percent through the extraction process. This was due to two different facts: First, the
291 HHV calculated on dry and ash-free base was not significantly affected by the extraction
292 process, and, secondly, the ash content decreased. Since the latter did not contribute to total
293 HHV (on a dry basis), the intrinsic energy was less diluted in the solid when it was removed.

294 The removal of the ash also affects the mass yield, which was reduced (Table 2). This was the
295 penalty for the higher energy concentration in the extracted hydrochar. Therefore, the energy
296 concentration compensates the mass loss and the balance for the amount of energy involved
297 in a given amount of material was the same before and after the extraction process.

298 For environmental purposes, chlorine and sulfur are worrying elements in fuels. For the
299 present treatments, extraction with hydrochloric acid increased the chlorine content by more
300 than a factor of two (from 0.085% to 0.261%). This indicated that washing the hydrochar
301 sample (approx. 4 g) with 100 mL of water, after treatment with 15 mL of dilute acid was not
302 sufficient. However, higher water consumption was discarded as this would further worsen the
303 economic and environmental balance. Clearly, the better option was to change the extracting
304 agent to nitric acid. In this case, the chlorine content was halved (from 0.085% to 0.043%).

305 A positive effect was also detected for the sulfur content. The latter decreased for both cases,
306 hydrochloric acid and nitric acid treatment, by 20 and 65%, respectively. However, the initial
307 value was relatively high at 0.494%, which was reduced to 0.169%. After treatment, hydrochar
308 complied with the requirements of international standard ISO 17225-8: 2016.(International
309 Organization for Standardization, n.d.) For the TA2 specification, the sulfur content must be
310 less than 0.2%. With respect to the chlorine content, both the original and the nitric acid-
311 treated sample satisfied the requirement of 0.1% or less.

312 In summary, it can be stated that the phosphorus extraction with nitric acid improved the
313 hydrochar characteristics as a solid fuel. Not only was the ash content reduced below 5%, but
314 also element concentrations critical for combustion such as chlorine and sulfur were reduced.
315 By this, the requirements of ISO 17225-8 are fulfilled.

316 Recovery of phosphorus as a solid

317 In general, phosphorus precipitation is undergraduate chemistry and does not require much
318 attention. In the present case, however, HTC process water was employed for the preparation
319 of the extraction liquids. Since dissolved material can affect both the precipitation process and
320 the solids properties, these issues were also studied in detail, and related information is
321 included in the Electronic Supplementary Information (ESI).

322 X-ray powder diffraction (Figure S3) and FTIR spectroscopy (Figure S5) showed the formation
323 of calcium hydrogen phosphate (brushite) by neutralization of the extraction liquid. From this
324 solid, phosphorus is available to plants as it is dissolved by neutral water (Figure S8), while

calcination (or combustion) converted it into less soluble species. In summary, the results confirmed that the OFMSW can provide a solid phosphorus fertilizer together with a high quality solid fuel.

Environmental performance – Impact scores for laboratory-scale phosphorus extraction

The LCA was carried out considering twelve scenarios, starting from experimental conditions and real phosphorus content and adding potential optimization events to the study (for more details, see the Materials and Methods section).

Table 3 shows the environmental impact scores modelled for the baseline scenario (scenario 1 in Table 3; nitric acid) and two other scenarios with different acids (scenarios 2 and 3 in Table 3; hydrochloric acid and sulfuric acid) expressed in category-specific units. Overall, three major observations are seen. First, impact scores are positive in most impact categories, suggesting that the treatment of biowaste with phosphorus recovery through hydrothermal carbonization is expected to result in environmental burden. This environmental burden is mainly due to the need to produce relatively large amounts of acids and bases for P recovery. Secondly, negative impact scores are seen for three impact categories, namely particulate matter formation, acidification (in scenarios 2 and 3) and water resource depletion. This suggests that environmental benefits are expected for these impact categories when biowaste is treated hydrothermally with recovery of phosphorus. Our analysis shows that these benefits are mainly due to the avoidance of fossil coal heat generation when using hydrochar as a solid fuel (in terms of particulate matter and acidification impacts). Negative scores for water resource depletion, however, are due to the avoided use of water in the upstream processes for the production of base (potassium hydroxide as example of a base from the ecoinvent database). The third finding is that phosphorus extraction with H_2SO_4 is environmentally friendly in twelve out of 15 impact categories (excluding particulate matter, water resource depletion and, in some cases, acidification) compared to extraction with HNO_3 or HCl . This is due to lower amounts of sulfuric acid (on a mass basis) needed for extraction per treated waste unit.

352

353

entry	starting material	initial HHV ^a [MJ/kg]	final HHV ^b [MJ/kg]	HHV increase ^c [%DRY]	HHV change ^d [%DAF]	final ash content ^e [%]	mass yield ^f [%]	energy balance ^g [%]
1	OFMSW	27.9	30.6	9.6	-0.3	34	86	94.2
2	OPW	24.1	25.4	5.5	2.2	55	92	97.1
3	prunings	20.4	22.3	9.5	4.2	77	90	98.6

354 ^a HHV of hydrochar before extraction on dry base. ^b HHV of hydrochar after extraction on dry base. ^c Change in HHV caused
355 by the extraction procedure on dry base. ^d Change in HHV caused by the extraction procedure on dry and ash-free (DAF)
356 base. ^e Final ash content compared to the initial one. ^f Mass yield for hydrochar after the extraction procedure. ^g Energy
357 balance considering hydrochar as an energy carrier and comparing the final energy amount (mass x HHV) with the initial
358 one (Formula: energy balance = (final HHV x mass yield)/initial HHV).

359

360 *Table 2. Solid fuel properties of different hydrochars before and after applying an extraction procedure with HCl (4%, 60 °C, 4 h).*

361

362

363

364

Impact category	Unit	Impact score		
		HNO ₃	HCl	H ₂ SO ₄
Climate change (GWP)	kg CO ₂ eq	5.19E-01	2.91E-01	1.50E-01
Ozone depletion	kg CFC-11 eq	4.82E-08	8.85E-08	3.94E-08
Human toxicity, cancer effects	CTUh	1.88E-08	2.44E-08	1.61E-08
Human toxicity, non-cancer effects	CTUh	7.70E-08	1.30E-07	6.68E-08
Particulate matter	kg PM _{2.5} eq	-9.03E-05	-1.45E-04	-1.09E-04
Ionizing radiation HH	kBq U235 eq	9.33E-02	1.27E-01	8.67E-02
Photochemical ozone formation	kg NMVOC eq	1.70E-03	1.35E-03	1.09E-03
Acidification	molc H ⁺ eq	8.00E-04	-6.49E-05	-4.37E-04
Terrestrial eutrophication	molc N eq	6.97E-03	2.08E-03	1.14E-03
Freshwater eutrophication	kg P eq	8.56E-05	1.50E-04	5.88E-05
Marine eutrophication	kg N eq	7.61E-04	6.17E-04	5.14E-04
Freshwater ecotoxicity	CTUe	4.41E+00	5.48E+00	3.92E+00
Land use	kg C deficit	6.69E-01	6.46E-01	5.31E-01
Water resource depletion	m ³ water eq	-7.1E-04	-5.8E-04	-7.0E-04
Mineral, fossil and renewable resource depletion	kg Sb eq	3.01E-05	4.17E-05	4.47E-05

365

366 *Table 3. Impact scores in category-specific units for acid-based P extraction using HNO₃, HCl or H₂SO₄ (scenarios 1, 2*
 367 *and 3 in Table 1, respectively).*

368

369 [Can phosphorus extraction bring environmental benefits?](#)

370 Using the experimental conditions from the laboratory scale extractions, only limited
 371 environmental benefits were noted. It should be further examined if benefits were reinforced
 372 in optimized extraction conditions (lower acid level) or for more appropriate cases (higher
 373 phosphorus content in hydrochar).

374 A relatively large contribution of acid and base used for extraction for all impact scores
 375 indicates that there is significant potential for environmental optimization (eco-design):
 376 reduction of acid and base levels during upscaling. In fact, the results presented in Figure 3

show that if the amounts of acids and bases are reduced by a factor of 10, which is not unrealistic when scaling from the bench to the pilot scale, the impact scores are reduced. The largest decrease was observed for the impact category freshwater ecotoxicity (where impact scores decrease by a factor of 100). For other impact categories, a reduction by a factor of up to 10 applies. In some cases impact scores become negative when amount of acid and base is reduced. This suggests that the environmental benefits of avoiding the burning of fossil coal in combination with the environmental benefits of avoiding the compositing of biowaste outweigh the burden of hydrothermal treatment and phosphorus recovery. This is the case for a total of 9 out of 15 impact categories, including climate change. In 11 out of 15 impact categories, impact scores are comparable to the system without phosphorus extraction. They are higher for two impact categories (ionizing radiation and freshwater ecotoxicity) and lower for two impact categories (freshwater eutrophication and water resource depletion) than for systems without phosphorus extraction.

A comparison with systems in which hydrochar contained larger amounts of phosphorus (scenarios 7–9 in Table 3) showed that impact scores were comparable to scenarios 1–3, suggesting that the benefits of obtaining relatively large quantities of phosphorus were not sufficient to outweigh the environmental burden (Figure S9 and Figure S10). Even if the amounts of acids and bases were optimized, the environmental benefits of P extraction were relatively low compared to the system without phosphorus extraction.

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397

398 *Figure 3. Impact scores for scenarios 1–6 in Table 3; expressed in % and normalized internally to the “No phosphorus*
 399 *extraction” scenario, for which impacts are equal either 100% (for positive impact scores) or –100% (for negative*
 400 *impact scores).*

401

Conclusions

The OFMSW has been proposed as an alternative phosphorus reservoir for phosphorus recovery and solid fuel production. It has been shown that phosphorus can be extracted from hydrochar with mineral acid with high efficiency. At high phosphorus content, the ash content decreased accordingly when nitric acid or hydrochloric acid was used for the extraction. In terms of fuel properties, nitric acid was the preferred mineral acid for extraction as the chlorine and sulfur content of the hydrochar decreased. This further improved the fuel properties of hydrochar and the latter even met the standard requirements for good quality solid fuels.

When phosphate was precipitated from the extraction solution, a solid phosphor material was obtained. The latter released phosphorus again in neutral water, so it was predicted that it was readily available to the plants and the solid is suitable as a phosphorus fertilizer. It was concluded that it was technically feasible to produce a solid fuel and a phosphorus fertilizer from phosphorus-rich OFMSW. However, the environmental benefits were limited, as the LCA of this concept showed. Phosphorus extraction was a burden in almost all fifteen-impact categories, including climate change and resource depletion. It is therefore recommended to study the application of phosphorus-containing advanced hydrochar in agriculture and horticulture, without intermediate concentration by extraction. It is predicted that carbon storage benefits are combined with fertilizing effects.(Hitzl et al., 2018; Owsianiak et al., 2018)

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Electronic supplementary information (ESI)

Evaluation of hydrothermal carbonization in urban mining for the recovery of phosphorus from the organic fraction of municipal solid waste

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Content

Experimental details on the recovery of phosphorus as a solid

Figure S1. Ash composition of hydrochar obtained from ICP-OES analysis. Amounts are expressed as weight% of the oxides of the elements. Initial ash content was 13 wt% on dry base.

Figure S2. Phosphorus extraction efficiency with different mineral acids at different temperatures.

Figure S3. XRD pattern of the precipitate (a) and of the precipitate after calcination (b).

Figure S4. XRD pattern of the hydrochar before extraction.

Figure S5. FTIR spectra a) of the precipitate and the precipitate after calcination and b) of the precipitate in comparison with brushite.

Figure S6. Thermogravimetric (TG) analysis of the precipitate under nitrogen atmosphere.

Figure S7. Composition of a) precipitate and b) precipitate after calcination, measured by ICP-OES.

Figure S8. Solubility of the two main components of the precipitate.

Figure S9. Impact scores for scenarios 1–3 and 7–9 in Table 3, expressed in %, normalized internally to “No phosphorus extraction” scenario, for which impacts are equal either 100% (for positive impact scores) or –100% (for negative impact scores).

Figure S10. Impact scores for scenarios 1–3 and 10–12 in Table 3, expressed in %, normalized internally to “No phosphorus extraction” scenario, for which impacts are equal either 100% (for positive impact scores) or –100% (for negative impact scores).

622 Recovery of phosphorus as a solid

623 For transportation means, solid phosphorus is preferred over dissolved and diluted
624 phosphorus. Therefore, the precipitation of the phosphorus from the extraction solution was
625 studied. By addition of lime ($\text{Ca}(\text{OH})_2$) pH was shifted to slightly alkaline (8–9.5) and up to
626 quantitative precipitation (99%) was achieved and the phosphor precipitate deeply analyzed.
627 Precipitation process and solid product characteristics might be influenced by components of
628 the HTC process water that was employed for the extraction (after adding concentrated
629 mineral acid) with the aim to simulate real world conditions.

630 By X-ray powder diffraction (XRD) calcium hydrogen phosphate (brushite) was identified in the
631 solid, contaminated by calcium carbonate (Figure S3a). As it was confirmed that calcium
632 carbonate was not present in the starting material, i.e. the hydrochar employed in the
633 extractions (Figure S4; at least not in crystalline form), it had to be concluded that the
634 carbonate was formed by incorporation of ambient carbon dioxide, probably during the
635 filtration processes in the laboratory. Hence, this might be avoided by changing the
636 experimental setup. The XRD pattern of the hydrochar indicated the presence of sand and
637 hydroxyapatite (Figure S4). The latter also reveals a potential origin of the phosphorus: up to
638 70% by weight of (human) bone is a modified form of hydroxyapatite, known as bone
639 mineral.(Straub, 2007)

640 The presence of both components in the precipitate, calcium hydrogen phosphate and
641 carbonate, was confirmed by IR spectroscopy (Figure S5). Calcium carbonate is evidenced by
642 bands at wavenumbers of 1430 cm^{-1} , 890 cm^{-1} and 710 cm^{-1} (green dashed lines), being the
643 first one the strongest and the most characteristic one.(Landi et al., 2003) Comparison of the
644 spectrum with the one of brushite (Figure S5b; blue dashed lines) permits to detect
645 characteristic bands such as 1645 cm^{-1} associated with water molecules in the lattice (Ucar et
646 al., 2017) and associated with the presence of the HPO_4^{2-} ion at 1135, 1060, 985, 575 and 525 cm^{-1} .(Ucar et al., 2017) The band observed at 1385 cm^{-1} (red dashed line) indicated
647 contamination with a small amount of nitrate from the extraction solution.(Lafon et al., 2008)

649 The presence of carbonate and nitrate species was further corroborated by their
650 decomposition by calcination at $815\text{ }^\circ\text{C}$. Hence, after calcination, the XRD pattern indicated the
651 presence of calcium hydroxyapatite and calcium phosphate (Figure S3b). In the FTIR spectrum,
652 the characteristic bands for carbonate and nitrate at 1430 and 1385 cm^{-1} were clearly
653 diminished (Figure S5a) whereas the characteristic phosphate band at 1030 cm^{-1} was clearly
654 evidenced.(Poinern et al., 2011; Singh and Purohit, 2011) Therefore, it can be stated that both
655 techniques confirmed a transformation of brushite and calcite during calcination.

656 When the decomposition process was elucidated in detail by thermogravimetric (TG) analysis,
657 it was seen that two major weight losses occurred, namely up to $200\text{ }^\circ\text{C}$ and between 600 and
658 $900\text{ }^\circ\text{C}$ (Figure S6). Both losses were in accordance with literature reports for the involved
659 materials. Differential scanning calorimetry has determined 190 to $200\text{ }^\circ\text{C}$ as desorption
660 temperature of the crystal water molecules of dibasic calcium phosphate dihydrate.(Tamaki et
661 al., 2009) In addition, calcium carbonate is transformed into calcium oxide at temperatures of
662 $700\text{ }^\circ\text{C}$ to $850\text{ }^\circ\text{C}$ (Lu et al., 2006; Lysikov et al., 2007) and nitrate breakdown occurred almost in
663 the same interval ($680\text{ }^\circ\text{C}$) under dynamic rising temperature conditions.(Ettarh and Galwey,
664 1996) The second weight loss was also in accordance with the behavior of mixed materials.
665 Hence, thermal decomposition of carbonated apatite started at temperatures higher than $600\text{ }^\circ\text{C}$
666 $^\circ\text{C}$ in inert atmosphere:(Lafon et al., 2008) by IR measurements it has been confirmed that

667 after calcination in air at 600 °C decarbonatation had not occurred, whereas after the same
668 procedure at 800 °C only one third of the initial amount remained.

669 Chemical composition of the precipitate was further analyzed and quantified, namely
670 phosphorus by inductively coupled plasma – optical emission spectroscopy (ICP-OES) and
671 calcium by X ray fluorescence (XRF) spectroscopy. The combined results indicated a 41 wt%
672 content of $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ and a 47% content of CaCO_3 in the precipitate (Figure S7a). After
673 calcination, 64 wt% of the obtained solid consisted of $\text{Ca}_3(\text{PO}_4)_2$ and 30 wt% of CaO. There is a
674 small incoherency with the DRX pattern as CaO was not detected. However, this might be due
675 to an amorphous or nanocrystalline nature of the material.

676 For the suitability of a phosphorus-containing material as solid fertilizer, water solubility is
677 crucial. Plants absorb the inorganic phosphate either in the form of HPO_4^{2-} or of H_2PO_4^- from
678 the soil solution. (Yadav et al., 2012) However, brushite has been employed as a dicalcium
679 phosphate cement, suitable for bioceramics. (Tamimi et al., 2012) Therefore, it can be expected
680 that it possessed a low water solubility. In addition, hydroxyapatite is treated as a stable
681 mineral under surface Earth conditions and adopted as a proxy for paleo-environmental
682 reconstructions and in choice of remediation strategies. (Boudia et al., 2018) As a consequence,
683 it was mandatory to evaluate the solubility of the precipitate, so that it could be demonstrated
684 that the extracted and precipitated phosphorus fulfilled the minimum criteria as fertilizer.

685 From Figure S8 it can be seen that the phosphorus component dissolved well in neutral water,
686 whereas the calcite was only sparingly soluble. For the calcined precipitate solubility was the
687 contrary (not shown): calcium oxide dissolved readily whereas the phosphorus did not dissolve
688 at all. From this it can be concluded that calcination of the precipitate, or combustion of
689 hydrochar, is detrimental for phosphorus availability for plant growth. However, phosphorus
690 as precipitate should be readily available for the plants.

691

Figure S1. Ash composition of hydrochar obtained from ICP-OES analysis. Amounts are expressed as weight% of the oxides of the elements. Initial ash content was 13 wt% on dry base.

Figure S2. Phosphorus extraction efficiency with different mineral acids at different temperatures.

701

702 *Figure S3. XRD pattern of the precipitate (a) and of the precipitate after calcination (b).*

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706 *Figure S4. XRD pattern of the hydrochar before extraction.*

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710 *Figure S5. FTIR spectra a) of the precipitate and the precipitate after calcination and b) of the precipitate in*
711 *comparison with brushite.*

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721 *Figure S6. Thermogravimetric (TG) analysis of the precipitate under nitrogen atmosphere.*

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724 *Figure S7. Composition of a) precipitate and b) precipitate after calcination, measured by ICP-OES.*

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727 *Figure S8. Solubility of the two main components of the precipitate.*

728

729 Additional LCA results

730 Figure S9. Impact scores for scenarios 1–3 and 7–9 in Table 3, expressed in %, normalized internally to “No
 731 phosphorus extraction” scenario, for which impacts are equal either 100% (for positive impact scores) or –100% (for
 732 negative impact scores).

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734

735 Figure S10. Impact scores for scenarios 1–3 and 10–12 in Table 3, expressed in %, normalized internally to “No
 736 phosphorus extraction” scenario, for which impacts are equal either 100% (for positive impact scores) or –100% (for
 737 negative impact scores).

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