

1 **Elemental composition and phosphorus availability in hydrochars from seaweed**  
2 **and organic waste digestate**

3 **Abstract**

4 By hydrothermal liquefaction (HTL) of organic matter, hydrochars are produced which  
5 may be applied to soil for carbon sequestration. From substrates of wild seaweed and  
6 organic waste digestate, we measured the distribution of solids (hydrochars) and liquids  
7 after HTL at 150 and 200 °C, 50 bar for 1 hour. The output of liquids and solids was  
8 recorded. Elemental analysis was conducted for essential plant nutrients, potentially  
9 toxic elements (PTEs) and silicon in the hydrochars. Sequential extraction of  
10 phosphorous (P) was conducted to assess the P availability for plants. About 20% of the  
11 initial dry matter dissolved during HTL of digestate, and 55% for seaweed. More dry  
12 matter was dissolved by increased temperature. Except from arsenic in seaweed chars,  
13 the concentrations of PTEs were below quality compost thresholds. About 85% of P  
14 was recovered in chars for digestate. For seaweed, the recovery was 97 % at 150 °C,  
15 decreasing to 84% at 200°C. The solubility of P in chars decreased by HTL, and more  
16 with higher temperature. Reduced P availability, especially by higher temperature, is  
17 negative for the immediate fertilization effect. However, for soil sequestration of  
18 carbon, reduced P availability in hydrochars may expand the area where application  
19 may occur without negative environmental effects of eutrophication of water bodies.

20

21 **Keywords:** sequential extraction; marine algae, hydrothermal liquefaction,  
22 carbonization, potential toxic elements, carbon sequestration

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25

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31

## 32 **Introduction**

### 33 Making hydrochars from organic matter

34 Hydrothermal liquefaction (HTL) is a technology used to produce organic compounds  
35 (liquids, solids or gases) from moist organic matter, with moderately low temperature  
36 conditions (150-300 °C) and a pressure of 50 bar. The process is also referred to as wet  
37 pyrolysis (Libra et al. 2011), or hydrothermal carbonization (HTC), depending on what  
38 is the primary purpose of the process. The products from HTL of biomass comprise a  
39 liquid biocrude consisting of an immiscible oil fraction and dissolved organic  
40 components in an aqueous solvent, a gas phase rich in carbon dioxide, and a solid phase  
41 mainly in the form of a char (Kambo & Dutta 2015). The solid phase is commonly  
42 termed hydrochar to be distinguished from biochars produced by torrefaction  
43 (pyrolysis) at higher temperatures (Libra et al. 2011). The process was introduced  
44 (Bergius 1913) to simulate a natural formation of coal, and has received increased  
45 attention in later years as a technology to treat various organic materials and change  
46 their characteristics. One purpose may be transformation of high moisture biomass to  
47 biofuels or hydrochars, another to stabilize moist organic substrates. HTL takes place in  
48 water under subcritical conditions, where the water behaves as solvent, reactant and  
49 catalyst. The kinetic pathways during HTL involve de-polymerization of the main  
50 biomass constituents, decomposition of monomers by cleavage, dehydration,  
51 decarboxylation and deamination, and recombination of the reactive fragments. The  
52 distribution of product yields, the chemical composition and the physical properties of  
53 the different products vary widely depending on the composition and physical  
54 properties of the biomass feedstock and solvent, and the process conditions. HTL of  
55 biomass exhibits several remaining challenges for commercialization of the process,

56 including automatic feeding of slurries into a pressurized reactor, corrosion, and salt  
57 precipitation. The upgraded oil product may be in the diesel fuel range while chemicals,  
58 e.g. sugars, may be extracted both from the liquid phase and the char. Where hydrochars  
59 are not produced for special applications, they should be utilized as fertilizers or soil  
60 amendments, possibly combined with carbon sequestration. Mineable phosphorous (P)  
61 is a scarce resource (Cordell & White 2011), and the fate of P during technical treatment  
62 or organic materials deserves special attention. Will P be contained in the solid or liquid  
63 phase by HTL, and will the P availability be affected, as compared with the raw  
64 materials?

65 Substrates used: Seaweed and digestate

66 For the present study, HTL was conducted with wild seaweed, and solid digestate from  
67 a biogas plant. Harvesting seaweed grown nearby fish farming plants may be one means  
68 to close nutrient gaps (Chopin et al. 2001), since increasing proportions of fish feed are  
69 derived from agriculture (Gaylord et al. 2010) and significant amounts of terrestrial P  
70 are lost into the sea. The P load from Norwegian fish farming is estimated to 9.8 kilo  
71 tons annually (Taranger et al. 2014), which is more than is used as mineral P fertilizer in  
72 Norwegian agriculture; 7.9 kilo tons annually (Hanserud et al. 2016). Seaweeds produce  
73 biomass rapidly, and have the capacity to produce energy-rich oils (Hannon et al. 2010;  
74 Marinho et al. 2015). The species used here, sugar kelp (*Saccharina latissima*) is suited  
75 for cultivation, and contain 40-70 % carbohydrates depending on season (Skjermo et al.  
76 2014).

77 Anaerobic digestion of organic waste was used to treat about 10 % of the organic waste  
78 in Norway by 2013 (Statistics Norway 2013), with food waste, sewage effluent and

79 production water, animal manure, fish sludge and other organic materials used as  
80 substrates. Iron (Fe) and aluminum (Al) salts are often used in sewage sludge treatment  
81 to fixate P, which may reduce the P availability of digestate. The digestate studied here  
82 was obtained by a decanting procedure and is referred to as solid digestate. Seaweed  
83 and digestates may be directly applied as fertilizers. For instance, residuals after alginate  
84 extraction increased crop yields (Riley (2002), with additional positive effects on soil  
85 physical characteristics. Solid digestates, which usually have a dry matter (DM) content  
86 of about 30%, contain a majority of the digestate P (Bachmann et al. 2016), whereas  
87 much of the nitrogen (N) remains in the liquid phase. Even if the P may be of low  
88 availability to plants, especially in the case of digestates from sewage sludge treated  
89 with iron and aluminum salts, the total P content of the soil will be increased, and the  
90 organic matter is usually valuable for mineral soils. However, both seaweed and solid  
91 digestate have a low content of dry matter and are not biologically stable, which  
92 hampers a broad utilization. Treatment by HTL may transform these substrates to  
93 stable, easily stored chars that may be more applicable as soil amendments than the raw  
94 substrates.

#### 95 P contents and effect of HTL on P availability

96 The P content of biochars and hydrochars is closely related to the P content of the  
97 substrate (Novak et al. 2014). Whereas solid digestate may contain significant  
98 proportions of P (0.93-1.13% of DM; Bachmann et al. 2016), seaweed contains less, but  
99 with significant variations over time. For instance, the P content varied between 0.1 and  
100 0.3% of DM for a common temperate species of brown algae, bladderwrack (*Fucus*  
101 *vesiculosus*), during two years (Perini & Bracken 2014). A high degree of plant  
102 availability of P is usually an important target for organic fertilizers and soil

103 amendments. For carbon sequestration, high P availability in hydrochars is not  
104 necessarily positive, since this may cause P losses to water bodies. If P becomes  
105 available over longer time periods, P uptake in crops may balance the P release. During  
106 incineration of organic materials, inorganic P tends to bind with basic oxides in the ash,  
107 forming more crystalline and less soluble P such as hydroxy apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$   
108 which decreases the P availability for plants (Ulery et al. 1993; Gray & Dighton 2006).  
109 Increasing the temperature from 400 to 700 °C reduced the P availability for plants by  
110 about 50% in ash from animal manure (Thygesen et al. 2011). A negative relation  
111 between plant availability of P, and crystallinity of the P-containing compound, was  
112 shown by Frossard et al. (2002) and Nanzer et al. (2014). Since the temperature regime  
113 used for HTL is well below 400 °C, the negative effect on P availability for plants may  
114 possibly be lower than by incineration, but this has been little studied until now.

115

116 Sequential fractionation is a well-known procedure to assess the ability of a soil to  
117 supply plants with P, by quantifying the distribution of P in inorganic and organic forms  
118 with different solubility (Hedley et al. 1982). The method is also well suited to assess  
119 the plant availability of P in various organic fertilizers, as shown by Brod et al. (2015).  
120 Sequential fractionation does not give a precise picture of the actual chemical speciation  
121 of P in the analyzed compound, but is relevant for the actual behavior of the compound  
122 when used as fertilizers or soil amendment (Frossard et al. 1994; Traore et al. 1999;  
123 Frossard et al. 2002). A recent study of sewage ashes treated thermo-chemically with  
124 chlorine to remove heavy metals (Nanzer et al. 2014) showed that the molecular  
125 speciation actually agrees well with the operational speciation measured by sequential  
126 fractionation. The effect of hydrothermal carbonization (HTC) on speciation of P in

127 sewage sludge was studied by Huang and Tang (2015), and in further detail by Huang  
128 and Tang (2016). They used both sequential fractionation and spectroscopy to describe  
129 the molecular moieties of P (orthophosphate, polyphosphate etc.) as well as their  
130 chemical state (complexed with metal ions, adsorbed to surfaces etc.). Huang and Tang  
131 (2016), working further on the study published in 2015, found that HTC at 225 °C  
132 thoroughly homogenized and exposed P for interaction with various metals/minerals,  
133 with the final P speciation closely related to the composition/speciation of metals and  
134 their affinities to P. However, the study did not assess digestates made from mixed  
135 municipal organic waste, and only one temperature level was used. Further, the sewage  
136 sludge used by Huang and Tang (2015, 2016) was not treated by Fe or Al salts. HTL  
137 has been comprehensively studied as a treatment for seaweed e.g. by Smith et al.  
138 (2016), and studies of HTL of anaerobically digested food waste were nicely reviewed  
139 by Pham et al. (2015). For P speciation in hydrochars made from seaweed, one study  
140 was found (Gupta 2014), measuring total and plant available concentrations of P in one  
141 algae species grown on waste treatment water. However, the effect of temperature was  
142 not studied there.

143

144 The aim of the present paper is to study the effect of HTL treatment of seaweed and  
145 solid residues from anaerobically digested mixed municipal waste at two different  
146 temperatures, on morphology, elemental composition and P pools differing in solubility  
147 in the hydrochars. For this, scanning electron microscopy, elemental analysis and  
148 sequential fractionation were conducted on raw material and on the solid phases after  
149 HTL treatment. Our hypothesis was that the major part of P would be recovered in the

150 hydrochars. Further, we hypothesized that increased temperature during HTL would  
151 reduce the P solubility in hydrochars.

152

153 **Materials and Methods**

154 Substrates for HTL

155 Semi-solid residues from anaerobic digestion of organic waste were received from a  
156 Norwegian biogas company (Ecopro AS). The substrates for digestion at Ecopro are  
157 source-separated household wastes from 51 municipalities in the counties of Nordland  
158 and Nord-Trøndelag, Norway (about 50% by weight), sewage sludge from municipal  
159 plants in the same region (about 40 %), and animal by-products including fish (about  
160 10%). Upon decanting of the liquid digestate at the biogas plant, semi-solid residues  
161 were dried at 105 °C for at least 24 hours and milled, using a coffee grinder. The wild  
162 seaweed (*Saccharina latissima*) was collected fresh near Trondheim, Norway in  
163 October 2014. The seaweed was kept frozen, dried at 105 °C for at least 24 hours and  
164 milled using a coffee grinder. The powdered samples were kept in plastic bags during  
165 the experimental campaign.

166

167 Solid digestate had 28 % dry matter (DM), and 34 % of this DM was ash, measured by  
168 ignition loss at 550 °C. Wild seaweed had 20% DM, and 28 % of this DM was ash.

169

170 **HTL procedure**

171 For the hydrothermal liquefaction, a 250 ml Parr reactor model 4651 batch reactor was  
172 used. The experimental setup further consisted of a 4923EE bench-top ceramic heater  
173 and a Parr temperature controller model 4838. The system was connected to a nitrogen  
174 bottle for purging and pressurizing the reactor. Water was added to the dried and milled

175 samples in order to create a slurry that resembled the original moisture content, 72 % for  
176 the solid digestate and 80 % for the seaweed. 150 g slurry was added to the reactor,  
177 which was then sealed and tightened to avoid leakage. The slurry contained 42 g solid  
178 digestate, or 30 g seaweed (dry weights). The reactor was purged with nitrogen for 10  
179 minutes prior to pressurization to 50 bar using nitrogen. The pressure of 50 bar was  
180 chosen to ensure that water remained liquid throughout the whole experiment. The  
181 reactor was then heated using an electrically heated furnace to the preset temperature,  
182 which was 150 and 200 °C.

183

184 The residence time in the reactor was one hour. The heater was switched off and the  
185 reactor immediately transferred to an ice bucket and left to cool. Once the reactor was  
186 cooled down, the gases produced by the reaction were vented inside a fume hood  
187 followed by disassembly of the reactor. The reaction mixture (minus the gas product)  
188 was filtered by vacuum suction over a VWR filter paper at 5-13 µm particle retention  
189 size. The solid residue (hydrochar) was then oven dried at a temperature of 105 °C for at  
190 least 24 hours.

191

## 192 **Scanning electron microscopy**

193 Images of raw samples and hydrochars of wild seaweed and solid digestate were  
194 obtained by scanning electron microscopy (SEM). A field emission scanning electron  
195 microscope (FE-SEM, Zeiss Ultra 55) was used to analyze apparent microstructure and  
196 morphology of the studied raw and hydrochar samples. One portion of each sample  
197 investigated (including powders and grains) were spread on carbon tape that was

198 attached to a sample rod. The samples on the carbon tape were inserted into the  
199 microscope for taking the SEM images.

200

## 201 **Chemical analyses**

202 We analysed concentrations of essential plant nutrients (N, P, K, Ca, Mg, S, B, Cl, Cu,  
203 Fe, Mn, Mo, Ni, Zn), and additionally some important potentially toxic elements, PTEs  
204 (As, Cd, Cr, Hg, Pb, Sr, Se). We also analysed the concentration of Si because it may be  
205 a structural element in plant tissue.

206

207 The concentrations of P, K Ca, Al, Mg, Fe, S, As, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sr  
208 and Zn were analyzed after a total digestion procedure using four acids (HF, HClO<sub>4</sub>,  
209 HNO<sub>3</sub> and HCl) and heating to 260 °C. Measuring of elemental concentrations was  
210 done by ICP-OES and ICP-MS. The concentration of Si, Se and B was analysed after  
211 sodium peroxide fusion as the digestion step, and concentrations measured by ICP and  
212 ICP-MS. For Cl, an ion-selective electrode was applied. Further details on analytical  
213 methods, equipment and standards are given at the laboratory website (Actlabs 2016).

214

## 215 **Sequential extraction of phosphorus**

216 The procedure for sequential extraction was based on Hedley et al. (1982), adapted for  
217 sewage sludge by Frossard et al. (1994). 150 mg of sample was crushed in a mortar, and  
218 30 ml of extractant was added (i.e., at 1:200 sample-to-solution ratio), with four  
219 analytical replicates per sample. The extraction sequence started with two anion

220 exchange resin strips (BDH 55164 2S, 12cm<sup>2</sup>), thereafter organic and inorganic P were  
221 extracted by 0.5 M NaHCO<sub>3</sub>. The sum of these pools is referred to as readily available  
222 P, assumed to be adsorbed to soil surfaces and easily available for plant uptake. The  
223 next step was extraction of organic and inorganic P by 0.1 M NaOH, to measure P  
224 chemisorbed to Al and Fe (hydr)oxides or -phosphates (Al/Fe-P), assumed to be  
225 available to plant uptake in a long-term perspective. Finally, 1 M HCl was used to  
226 extract P bound as calcium phosphate (Ca-associated P), assumed to be hardly available  
227 for plant uptake especially with high soil pH. During each extraction step, samples were  
228 shaken horizontally at 160 rpm during 16h, followed by centrifugation at 6870 x g and  
229 filtration (0.22 µm pore size). The concentration of inorganic P in the extracts was  
230 determined by spectrophotometer (Ohno & Zibilske 1991). For NaHCO<sub>3</sub> and NaOH  
231 extracts, organic matter was first precipitated, using 0.9 M H<sub>2</sub>SO<sub>4</sub> (Tiessen & Moir  
232 2008). For Resin-P and Ca-P, inorganic P was not measured. To measure total P, the  
233 resins and the extracts were digested by persulfate (Tiessen & Moir 2008); thereafter P  
234 was determined by spectrophotometer. Organic P in the extracts was determined as the  
235 difference between total P and inorganic P. When differences between total and  
236 inorganic P were statistically not significantly different, organic P values were set to  
237 zero. The sum of all fractions was compared with total P of the sample determined by  
238 total digestion (see below) to derive the total P recovery.

239

240

241 **Results and discussion**

242 Morphology of raw and processed samples

243 SEM images of the raw biomass samples as well as for the hydrochars obtained at 150  
244 and 200 °C are shown in Figure 1 for solid digestate and Figure 2 for seaweed.

245 The solid digestate was composed of particles with offshoots (Figure 1a). After  
246 conversion to hydrochars, the particles are still present (Figure 1b, c). They appear to be  
247 denser than the raw particles, but the processed particles show only minor degradation.

248 The raw seaweed was composed of flat particles, like small flakes (Figure 2a). During  
249 HTL, these particles were subject to much more degradation than was found for solid  
250 digestate. The flakes seem to have stuck together into aggregates in the chars (Figure  
251 2b, c). Since the substrates for anaerobic digestion were already treated by steam  
252 explosion as a pre-step, a smaller degradation effect of the HTL process was to be  
253 expected for the solid digestate. There seems to be no significant effect of rising the  
254 temperature from 150 to 200 °C on the morphology of the these hydrochars.

255 *Figure 1+2 in this section*

256

257 Mass balances during HTL

258 The amounts of solids + liquids used for HTL were 42 g + 108 g for solid digestate, and  
259 30 g + 120 g for seaweed. For both substrates, HTL produced more liquids than chars,  
260 and only a minor fraction as gas (Table 1). The mass losses were acceptable; only 4-6%  
261 of the initial 150 g of slurry could not be accounted for. These losses did not vary  
262 systematically with feedstock or temperature. This was to be expected, since most of the

263 losses occur during separation and material recovery after the HTL process is  
264 completed.

265 *Table 1 about here*

266 During HTL, 13-25 % of the solids were dissolved for solid digestate, and 55-59 % for  
267 seaweed. For both substrates, the proportion of dissolved solids increased with  
268 temperature. For seaweed, the difference between the amounts of dissolved solids at 150  
269 and 200°C was < 10 %, while for digestate the amount of dissolved solids doubled  
270 when the temperature was increased by 50 °C. This large effect of temperature on the  
271 proportions of dissolved solids is important. E.g. if the purpose of HTL is to maximize  
272 the output of hydrochar, the temperature should be kept as low as possible. The amount  
273 of gas evolved increased with increasing temperature, reaching about 4% at 200 °C. For  
274 the gases, there were no significant differences between the two substrates.

275

276 Element concentrations

277 When volatile elements transform to gas and dissolvable elements transform into the  
278 liquid phase during HTL, the composition of the solid material changes (Table 2).  
279 Carbon (C) is the main constituent of substrates and hydrochars, and the proportion of C  
280 in DM increased by HTL, especially for seaweed. Many elements have a parallel  
281 increase, but some decreased, e.g. N. When a significant part of the solids, in the case of  
282 seaweed above 50%, dissolve or evaporate during HTL, the changes in proportions of  
283 DM have to be interpreted with care. For P, the proportion of P in DM was quite stable  
284 in raw material and char of solid digestate, whereas in seaweed the proportion increased  
285 during HTL. The recovery of P in hydrochars was high, especially for seaweed at the

286 lowest temperature where 97% of the total P was recovered in solids. By 200 °C, the  
287 recovery rate was 84%. For solid digestate the recovery was less dependent on  
288 temperature, being 86 % at 150 °C and 85 % at 200 °C. Potassium (K) dissolves readily  
289 in water, as shown by the low concentration in raw solid digestate. A decreased  
290 proportion in the hydrochars could be expected. However, the decrease for seaweed was  
291 quite small, from about 3% of DM in raw seaweed to about 2.5% of the char DM.  
292 Calcium (Ca) constituted a significant proportion of both raw substrates and chars, and  
293 the proportion increased slightly in seaweed whereas it was stable in solid digestate.  
294 The proportion of magnesium (Mg) was quite stable in both substrates. It could have  
295 been expected that sulphur (S) would get lost as gas, but the proportion kept quite  
296 stable. Siloxanes form during anaerobic digestion, as indicated by a significant  
297 proportion of silicon (Si) in solid digestate. Chlorine (Cl) is a common element in  
298 marine environment, as shown by the large proportion in seaweed, where it increased  
299 with increasing temperature. High proportions of Al and Fe in chars of solid digestate is  
300 explained by the addition of iron and aluminum salts for precipitation of P during  
301 treatment of sewage. Arsenic (As) and strontium (Sr) are common elements in marine  
302 environment, as shown by a high proportion in seaweed char. The increase in proportion  
303 of metals such as copper (Cu), manganese (Mn), nickel (Ni), chrome (Cr) and zinc (Zn)  
304 can be a result of relative increase due to volatilization or dissolution of other elements,  
305 but we cannot exclude that the HTL treatment has caused some oxidation of metal ions  
306 from the reactor which may have become trapped in the hydrochars.

307 *Table 2 about here*

308  
309

310 PTEs may accumulate in soil, with negative effects on soil organisms, other animals and  
311 humans. No universally accepted threshold for PTE concentrations in organic fertilizers  
312 and soil amendments have yet been defined, but comprehensive compost standards were  
313 recently published for 11 elements in Ontario, Canada (Ontario Ministry of the  
314 Environment 2016). For application on agricultural land, compost should be of quality  
315 AA or A, where A has somewhat higher thresholds for Cu and Zn. Compost quality B  
316 may be used as a soil conditioner for reclamation purpose, e.g. reforestation, and with  
317 certain restrictions on agricultural land, but not on areas with close contact to humans  
318 such as recreational areas. The maximum concentrations in DM (ppm) for composts  
319 AA/A/B are as follows: As 13/13/75; Cd 3/3/20; Cr 210/210/1060; Cu 100/400/760; Hg  
320 0.8/0.8/5; Mo 5/5/20; Ni 62/62/180; Pb 150/150/500; Se 2/2/14; Zn 500/700/1850. For  
321 As, the hydrochars from wild seaweed are above or close to the limit for compost  
322 quality B. For Cd, Cr, Hg, Mo, Ni, Pb and Se, both types of chars are well below the  
323 limits for compost quality AA. For Cu and Zn, chars from digestate would come in class  
324 A. Hence, for most elements assessed by the Canadian standard, both hydrochars fulfill  
325 the requirements for high quality composts as soil amendments. However, attention  
326 should be paid to strontium (Sr), where no threshold level was proposed in the Canadian  
327 standard but values are very high especially for wild seaweed. Since radioactive Sr is  
328 leached to the sea from nuclear power plants, it is a risk that such isotopes are enriched  
329 in marine biomass. This deserves further study. The high content of arsenic may pose a  
330 problem for recycling of marine biomass to terrestrial environments.

331

332 Since the study was conducted in Norway, Norwegian standards may also be assessed.

333 These comprise somewhat less elements, and are significantly stricter than the Canadian

334 standard for most elements, but surprisingly less strict for mercury (Lovdata 2017). For  
335 use on agricultural land, the maximum concentrations of the elements Cd, Cr, Cu, Hg,  
336 Ni, Pb and Zn may be 2, 100, 650, 3, 50, 80 and 800 ppm in DM. The regulations are  
337 under revision.

338

### 339 Element balances

340 To better understand the transformation of elements from solid phase to gas and/or  
341 liquid, the recovered yields of each element in hydrochars are compared with the initial  
342 amounts of elements applied by solid digestate and wild seaweed in the reactors (42 and  
343 30 g, respectively). Elements with concentrations below a detection limit in at least one  
344 sample (Table 2), and Cd which was present in very low concentrations, were not  
345 included in these calculations. The decrease in C (Figure 3) compares well with the  
346 dissolution of solid material, which was 13-25 % for digestate and 55-59 % for  
347 seaweed. Significant proportions of N, K and S (about 50 %) were lost from the  
348 hydrochars (Figure 3), especially for seaweed, and are likely present in the liquid phase  
349 since gas losses were very low (maximum 4 % of initial dry mass). For P, close to 100  
350 % of this element was still present in the chars, especially in hydrochars of seaweed at  
351 the lowest temperature. For the divalent cations Ca and Mg, the recovery in chars were  
352 higher than for K in solid digestate, but low in seaweed.

353 When recovery has a value above 100 %, two explanations are possible. Either, the  
354 recovery value is an artefact, caused by incomplete dissolution of the actual amount  
355 present in the raw material or inaccuracy in analytical procedures. Alternatively, the

356 recovery value is caused by dissolution of elements from materials in the reactor. The  
357 latter explanation may be valid for metals, such as Cu, Ni and Cr.

358 *Figure 3 in this section*

359

360 P solubility assessed by sequential extraction

361 The total P levels of raw substrates and hydrochars as measured by sequential extraction  
362 (Table 3), were very comparable to total P values derived by elemental analysis, in spite  
363 of differences in digestion procedures. The differences between the two methods seem  
364 not to be systematical. Solid digestate contained a much larger amount of P than wild  
365 seaweed. The HTL treatment affected the amounts of P which could be extracted per g  
366 DM from the substrates, as well as the proportions of P pools determined by sequential  
367 extractions (Figure 4). Especially for seaweed, much more P was extracted per mass  
368 unit from the chars than from the raw substrate. This implies that most of the P was still  
369 present in the chars, while other solids transformed to liquids or gas during HTL. The  
370 dominating fraction of extractable P in seaweed hydrochars was NaHCO<sub>3</sub>-extractable  
371 inorganic P and Ca-associated P (Figure 4). Concurrently, resin-P and organic P  
372 extracted by NaHCO<sub>3</sub> and NaOH decreased by HTL and almost disappeared at the  
373 highest temperature. This confirms the expected pattern that thermal treatment implies a  
374 sort of mineralization, increasing the proportions of inorganic P while organic P  
375 migrates to inorganic forms. The low proportion of NaOH-extractable P corresponds  
376 well with the low concentrations of Al and Fe in wild seaweed (Table 2). About 80 % of  
377 the P was readily available (resin-P + NaHCO<sub>3</sub>-P) in raw seaweed. In the hydrochars,

378 the proportion of readily available P decreased with increasing temperature, but was still  
379 about 60 % after HTL at 200 °C.

380 *Figure 4 about here*

381 The amount of P that could be extracted per g DM of substrate increased by HTL also  
382 for solid digestate (Figure 4). In this type of biomass, only 6.5% of the P was  
383 characterized as readily available in the raw substrate, and very little organic P was  
384 found. This can be explained by the intensive processing this substrate has already been  
385 subject to during sewage treatment, sanitation and anaerobic digestion. The readily  
386 available fraction decreased significantly during HTL, while the increase in extractable  
387 P occurred both for Al/Fe-P and for Ca-associated P. By the highest temperature,  
388 relatively more P was assigned to Ca-associated P. The large proportion of P assigned to  
389 Al/Fe-P is explained by the addition of iron and aluminum salts to the sewage being one  
390 of the substrates for the anaerobic digestion. The proportion of Ca-associated P  
391 increased with HTL and with increasing temperature during HTL, for both substrates.  
392 Hence, the availability to plants of P found in the solid phase of organic materials seems  
393 to become reduced by HTL, even if the treatment temperatures are low as compared  
394 with incineration or pyrolysis. Since most of the P is maintained in the chars during  
395 HTL (Figure 4), the fate of the P solubility in the chars should be relevant to  
396 characterize the effect of HTL on the plant availability of the studied substrates in  
397 general.

398

399 The reduced P availability with HTL and with increasing temperature will be affected  
400 by the characteristics of the input substrate, such as the concentrations of Al, Fe and Ca.

401 This confirms earlier studies of migrations between P pools of different solubility in  
402 sewage sludge treated by HTC (Huang & Tan, 2015; 2016). Based on findings of Brod  
403 et al. (2016) and Nanzer et al. (2014), the effect of HTL on the fertilizer value of  
404 hydrochars made from wild seaweed and solid digestate can be estimated. At 150 °C,  
405 the readily available P fraction accounts for more than 70% in seaweed, which is  
406 comparable to a sample of animal manure studied by Brod et al. (2016). This manure  
407 showed a relative fertilizer use efficiency of about 60%. Already by a temperature of  
408 200 °C, the plant availability of P may decrease by about 10%. The effect of higher  
409 temperatures commonly used for HTL on P availability should be further studied.

410

411 The plant availability of raw solid digestate can be considered as rather low, since the  
412 readily available P accounts for less than 10% of the total extractable P. This substrate  
413 is comparable with a sample of calcium treated sewage sludge ash, where only 4% of  
414 the total P was found to be readily plant available (Nanzer et al. 2014). By HTL, the  
415 plant availability of P is further decreased. Hence, HTL treatment of solid digestate  
416 might provide an inefficient P fertilizer, especially on neutral to alkaline soils. On the  
417 other side, if the purpose of HTL (or HTC) is to produce hydrochars for soil storage of  
418 C, low availability of P may be seen as a beneficial characteristic.

419

420 **Conclusion**

421 By hydrothermal liquefaction of wild seaweed and solid digestate, most of the P was  
422 recovered in the hydrochars (solid phase). The P solubility was reduced with increasing  
423 temperature during HTL. In spite of reduced solubility, hydrochars from wild seaweed  
424 still had high P availability, but also high levels of arsenic and strontium. Hydrochars  
425 from solid digestate where sewage sludge was used as substrate had low P availability  
426 due to addition of iron and aluminium salts in sewage processing. Contents of PTEs  
427 were low in hydrochars from digestate, except for copper and zinc. Low availability of  
428 P may facilitate the use of hydrochars from solid digestate for carbon storage in soil,  
429 due to reduced eutrophication risk.

430

431

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531

532 Table 1. Mass balances (dry weights) and proportions (%) of dry weights, of solids,  
 533 liquids and gases from hydrothermal liquefaction of solid digestate (Dig) and wild  
 534 seaweed (Seaw) at 150 and 200 °C. Values are averages of two parallel experiments.

535  
 536

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537	<b>Treatment</b>	<b>Solids</b>		<b>Liquids</b>		<b>Gases</b>		<b>Losses</b>		<b>Total</b>	
538		g	%	g	%	g	%	g	%	g	%
539	<b>Dig 150</b>	37	24	104	69	1	1	8	6	150	100
540	<b>Dig 200</b>	31	21	108	71	6	4	5	4	150	100
541	<b>Seaw150</b>	14	9	127	85	3	2	6	4	150	100
542	<b>Seaw200</b>	12	8	124	83	6	4	8	5	150	100

543

544 Table 2. Dry matter content (% of air-dried weight), ash content (% of dry matter, DM)  
 545 and element concentrations (% of air-dried weight) in raw samples and hydrochars of  
 546 solid digestate (SD) and wild seaweed (WW) treated by hydrothermal liquefaction at  
 547 150 or 200 °C. Number of decimals vary as they were received from the laboratory.

548	<hr/>						
549							
550	<b>Characteristic</b>	<b>SD raw</b>	<b>SD150</b>	<b>SD200</b>	<b>WW raw</b>	<b>WW150</b>	<b>WW200</b>
551	<hr/>						
552	<b>DM, %</b>	93.9	98.3	98.8	95.8	98.4	97.1
553	<b>Ash, % DM</b>	35.3	38.2	44.0	23.2	25.0	25.3
554	<b>Element</b>						
555	<b>C, %</b>	33.1	35.5	35.4	35.2	43.7	42.9
556	<b>N, %</b>	4.7	3.9	3.0	3.4	2.9	2.9
557	<b>P, %</b>	2.45	2.42	2.78	0.17	0.36	0.34
558	<b>K, %</b>	0.63	0.48	0.45	3.04	2.32	2.52
559	<b>Ca, %</b>	4.76	4.52	5.09	3.98	5.38	4.91
560	<b>Mg, %</b>	0.49	0.48	0.56	0.72	0.62	0.63
561	<b>S, %</b>	1.22	0.94	0.99	1.23	1.46	1.41
562	<b>Si, %</b>	2.44	2.88	3.78	0.42	1.03	0.68
563	<b>Cl, %</b>	0.23	0.52	0.21	6.41	7.03	8.25
564	<b>Fe, %</b>	2.69	2.65	2.99	0.10	0.23	0.19
565	<b>Al, %</b>	4.62	4.63	5.33	0.14	0.30	0.25
566	<b>Sum, %</b>	57.33	58.92	60.58	54.81	65.33	64.98
567							
568	<b>As, ppm</b>	3	4	9	67	82	83
569	<b>B, ppm</b>	<10	<10	<10	70	110	110
570	<b>Cd, ppm</b>	0.6	0.7	0.7	0.7	1.7	1.5
571	<b>Cr, ppm</b>	29	36	40	5	18	15
572	<b>Cu, ppm</b>	138	151	179	4	56	69
573	<b>Hg, ppm</b>	<1	<1	<1	<1	<1	<1
574	<b>Mn, ppm</b>	278	299	345	42	91	50
575	<b>Mo, ppm</b>	3	4	5	<1	2	2

576	<b>Ni, ppm</b>	17	19	24	3	21	24
577	<b>Pb, ppm</b>	11	12	12	5	3	<3
578	<b>Se, ppm</b>	<0.8	<0.8	<0.8	2.1	1.1	<0.8
579	<b>Sr, ppm</b>	149	151	174	1080	1470	1400
580	<b>Zn, ppm</b>	452	467	540	48	74	71

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588 Table 3. Total P concentrations, % of DM, in raw substrates and hydrochars of solid  
 589 digestate and wild seaweed treated by hydrothermal liquefaction at 150 or 200 °C, as  
 590 measured by sequential extraction (seq.) compared with elemental analysis (elem.).

591

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<b>Analysis</b>	<b>Solid digestate</b>			<b>Wild seaweed</b>		
	<b>Raw</b>	<b>150</b>	<b>200</b>	<b>Raw</b>	<b>150</b>	<b>200</b>
<b>Tot-P seq. % DM</b>	2.24	2.59	3.08	0.14	0.34	0.35
<b>Tot-P elem. % DM</b>	2.62	2.46	2.81	0.18	0.37	0.35

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598

599 **Figure captions**

600

601 Figure 1. SEM image of (a) raw digestate, (b) hydrochar obtained at 150 °C and (c)  
602 hydrochar obtained at 200 °C.

603

604 Figure 2. SEM image of (a) raw seaweed, (b) hydrochar obtained at 150 °C and (c)  
605 hydrochar obtained at 200 °C.

606

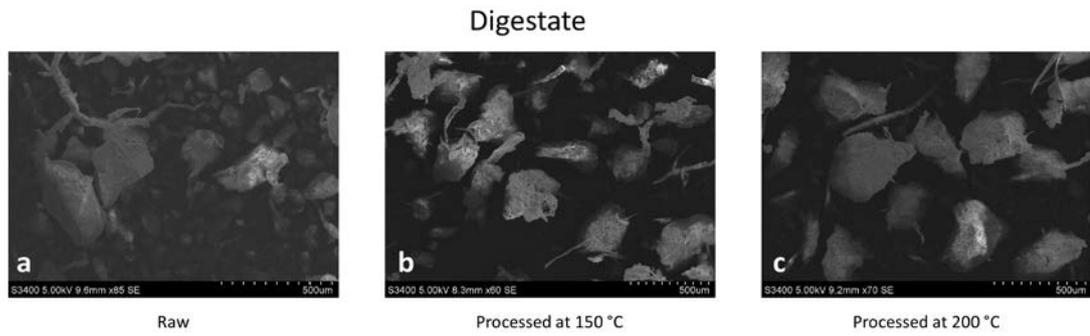
607 Figure 3. Recovered yields in % of the initial amount of each element C, N, Zn in  
608 hydrochars from wild seaweed and solid digestate, produced by hydrothermal  
609 liquefaction at 150 or 200 °C.

610

611 Figure 4. Fractions of resin-, NaHCO<sub>3</sub>-, NaOH- and HCl extractable inorganic P (Pi)  
612 and organic P (Porg) in sequentially extracted raw substrates and hydrochars from  
613 hydrothermal liquefaction at 150 or 200 °C. Absolute (g P kg<sup>-1</sup> dry matter) (left) and  
614 relative (% of total recovered P) (right) fractions of wild seaweed (SW, SW150 and  
615 SW200) (top) and solid digestate (Dig, Dig150 and Dig200) (bottom). Error bars  
616 indicating standard deviation of four replicates.

617 Figure 1. *Files for each picture are uploaded separately.*

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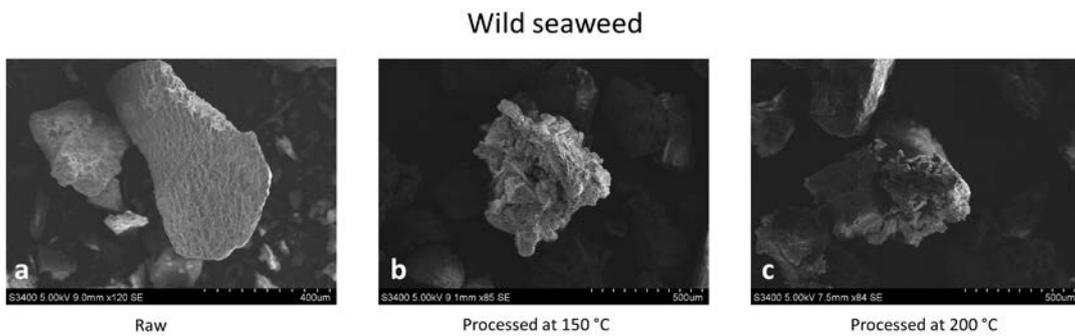
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623 Figure 2. *Files for each picture are uploaded separately.*

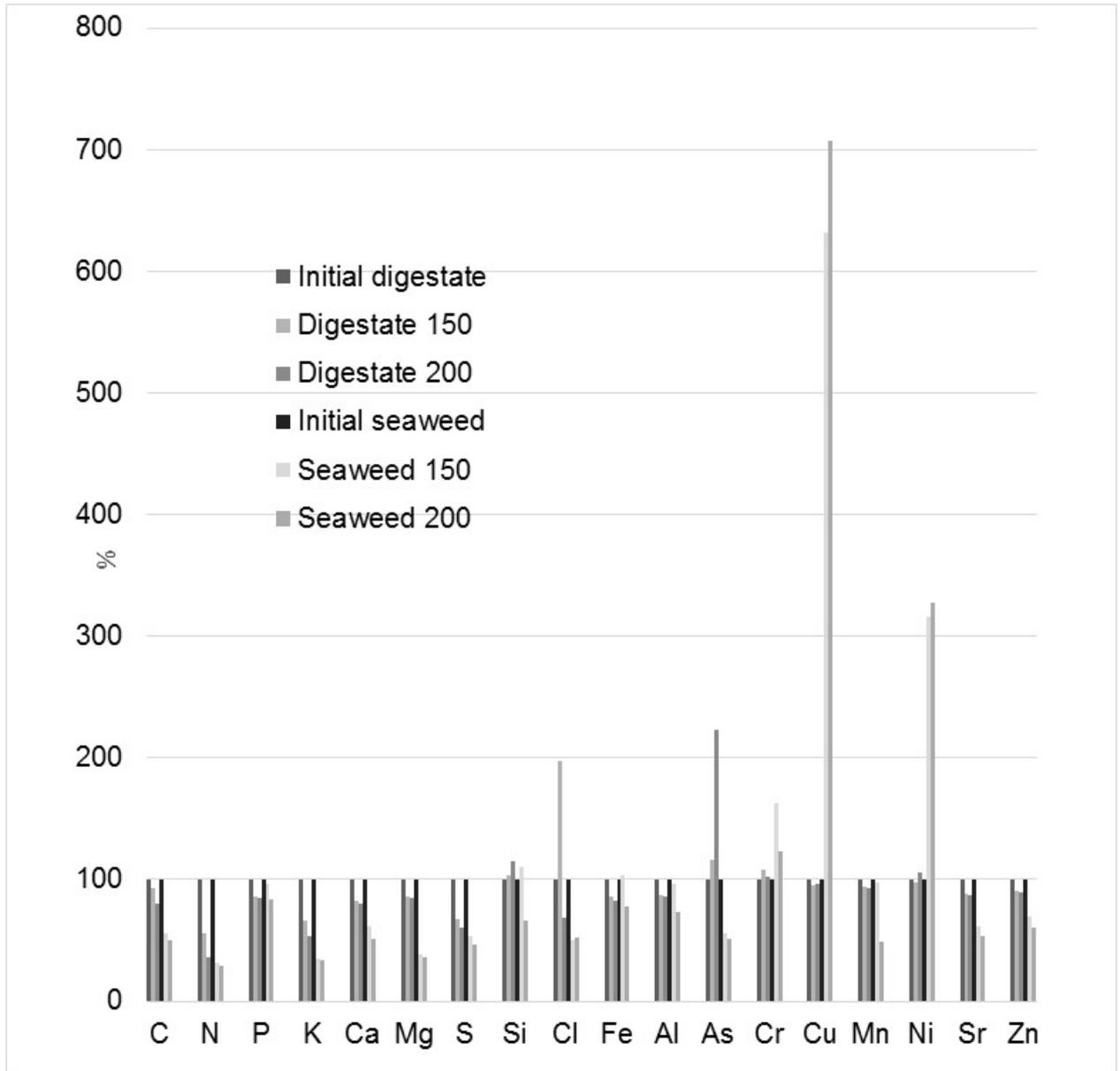
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627 Figure 3.

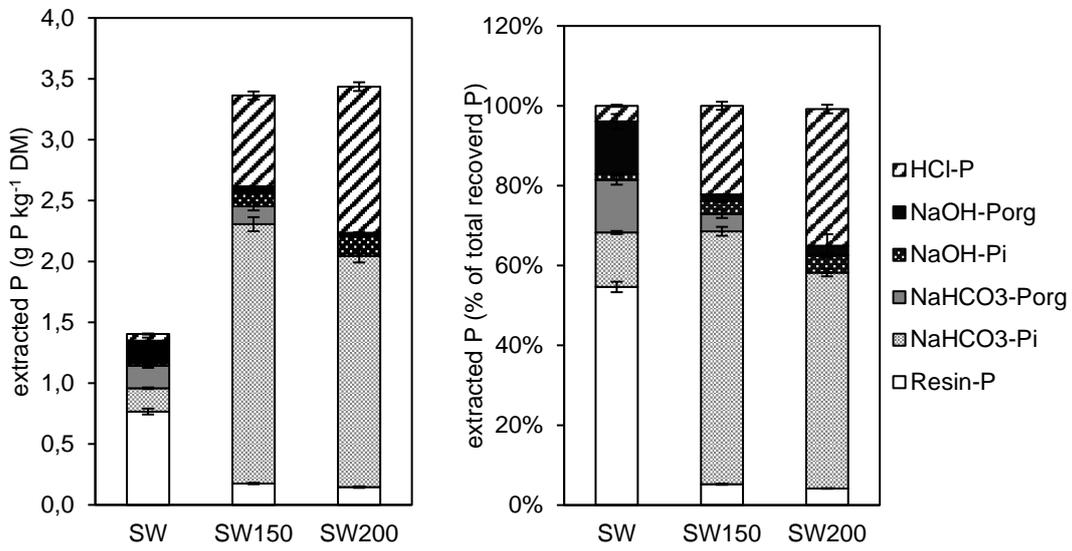


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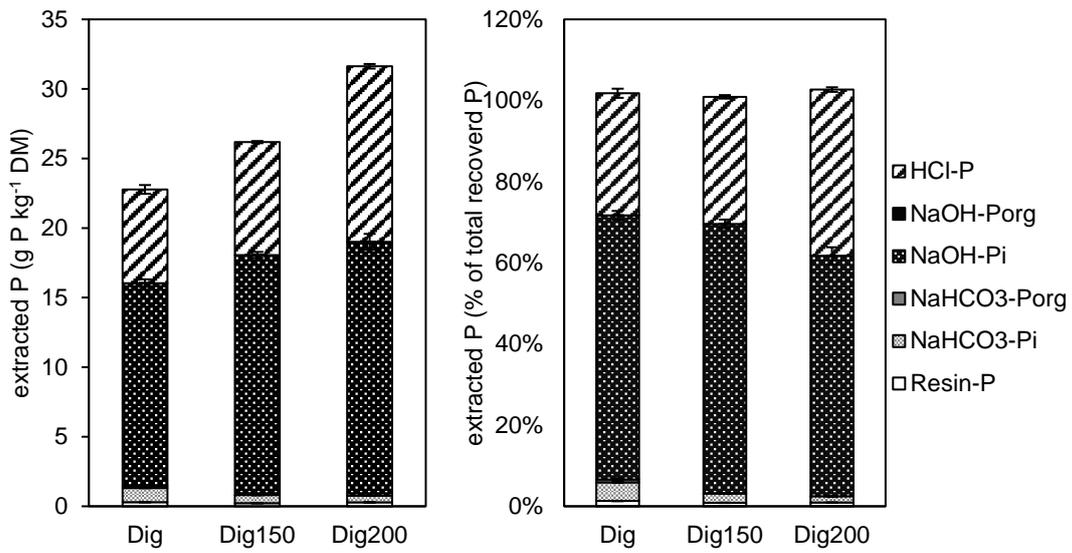
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630 Figure 4.

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