Nutrient Behavior in Hydrothermal Carbonization Aqueous Phase following Recirculation and Reuse

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ABSTRACT: Hydrothermal carbonization (HTC) has received much attention in recent years as a process to convert wet organic waste into carbon-rich hydrochar. The process also generates an aqueous phase that is still largely considered a burden. The success of HTC is dependent on finding solutions for the aqueous phase. In the present study, we provide the first investigation of recirculation of the aqueous phase from HTC of poultry litter as a means to concentrate nutrients, and its subsequent application to agriculture as a fertilizer. Aqueous-phase recirculation generally resulted in an increase in nitrogen, phosphorus and potassium concentrations up to cycle 3 with maximum concentrations reaching up to 5400, 397, and 23300 mg L⁻¹ for N, P and K, respectively. Recirculation did not adversely affect hydrochar composition or calorific value. The recirculated and non-recirculated aqueous phases were able to support lettuce growth similar to a commercial fertilizer. Results from this study indicate that the combination of aqueous-phase recirculation and use as a fertilizer can be a suitable method to reutilize the aqueous phase and recycle nutrients back into agriculture, thus increasing HTC efficiency and economic feasibility.

INTRODUCTION

Over the last decade, hydrothermal carbonization (HTC) has become a focus of research for the treatment of wet organic waste. Special consideration has been given to HTC as a technology to treat animal manure, which is naturally high in moisture and nutrients.^{1,2} The success of this process depends on factors such as its process efficiency, economic feasibility, and uses for its products. HTC consists of heating wet organic matter to 180–250 °C in a closed reactor such that there is pressure buildup.³ These conditions maintain water in the liquid state, avoiding the energy-intensive process of drying the organic waste.⁴ The process lasts minutes to hours, generating three main products: hydrochar, which is a carbon (C)-rich solid, and aqueous and gaseous phases.³ The hydrochar is considered the main product, which can be used as an energy source,^{5,6} soil amendment,^{7,8} and adsorbent material.^{9–11} The aqueous phase is still considered a burden.

Studies have investigated possible ways of utilizing the aqueous phase, e.g., as a substrate for biogas production^{11–14} and as a nutrient source for algal biomass production.¹⁵ Aqueous-phase recirculation has been considered as a method to reduce the generated aqueous phase volume, with the added potential benefit of reusing heating energy. HTC aqueous-phase recirculation studies have been carried out with a range of substrates and HTC process parameters.^{16–20} Most of these experiments have been carried out with plant-based substrates, with only one investigating animal manure, specifically poultry litter.¹⁶ Recirculation of the aqueous phase as a means to concentrate nutrients has not been considered, and knowledge on nutrient behavior during recirculation is still lacking.

Another possible use of the aqueous phase is as a liquid fertilizer, taking advantage of its high nutrient content.²¹ While a few studies have considered the impact of the aqueous phase on germination,^{22–24} to our knowledge, only one study has considered its effect on plant growth.²⁵ Moreover, the combination of aqueous-phase recirculation and use as a liquid fertilizer has never been investigated. The present study aimed to fill this gap, focusing on HTC of poultry litter. Specifically, the objectives of this study were to (i) characterize the aqueous phase generated under multiple aqueous-phase recirculation cycles, particularly in terms of its nutrients; (ii) determine the effect of aqueous-phase recirculation on hydrochar properties; (iii) compare the capacity of recirculated and non-recirculated aqueous phases to support plant growth.

MATERIALS AND METHODS

A large batch of poultry litter was obtained from a broiler farm in Israel (Table S1). The poultry litter consisted of chicken droppings, wood chips, and feathers. It was dried at 65 °C and then mechanically ground to break large lumps and homogenize the material. The poultry litter was stored in a desiccator prior to the experiments.

Recirculation Experiments. HTC was performed in triplicate laboratory-scale reactors, at a 1:3 solid-to-liquid ratio and at two different temperature treatments—200 °C and 250°C. The stainless-steel tubular cylinder reactors (27 mm diameter, 50-mL volume) have been proven to withstand the expected temperatures and pressures in previous experiments.^{21,26} One of the reactors was equipped with a temperature probe to monitor internal temperature during the entire process. To ensure even and rapid heating, the reactors were submersed in a preheated oil bath containing Paratherm HR (Conshohocken, PA) heat-transfer fluid. The reaction lasted 1 h, starting from when

the reactors reached the desired temperature. The reaction was quenched by placing the reactors in an ice bath. The aqueous phase and hydrochar were collected and separated by centrifugation and vacuum filtration using 0.70- μm glass-fiber filters. The hydrochar was then oven-dried at 105 °C for 24 h and kept in sealed containers for analysis. The aqueous phase was stored at -18 °C.

Recirculation experiments were performed by running five consecutive cycles of HTC treatment, reusing the obtained aqueous phase of a cycle as the liquid for the following cycle.¹⁸ For cycle 1, dry poultry litter was mixed with double-distilled water (DDW) to the desired 1:3 solid-to-liquid ratio. Aqueous-phase retrieval differed substantially between the two temperature treatments: for the 200 °C treatment, the average retrieval was 15.9 mL after the first cycle, and for the 250° C, it was 25.5 mL. These averages were rounded out and set as the amount of aqueous phase to recirculate in each cycle. In addition, sufficient DDW was added to the recirculated aqueous phase to maintain the 1:3 solid-to-liquid ratio across all cycles (Tables S2 and S3).

The initial composition of the aqueous phase before HTC treatment is referred to in the text and graphs as ‘initial’ and was determined by mixing poultry litter and DDW at a 1:3 ratio, and separating the aqueous phase by vacuum filtration after 1 h at ambient temperature (21 °C). The initial composition of the solid phase was given by the raw poultry litter.

Production of High-Volume Aqueous Phase. Large volumes of aqueous phase were generated to perform fertigation experiments, using a 30-L HTC pilot-scale reactor (Figure S1) that was custom made of stainless steel with an inner coating of enamel and a stainless-steel cap closed by screws (Düker GmbH, Germany). The reactor was heated by heat exchange with Paratherm HR heat-transfer fluid, which was heated in an electrical oil bath attached to a pump. Dried poultry litter (6 kg) was mixed with water inside the reactor at a solid-to-water ratio of 1:3. The sludge was

heated to 200 °C for 1 h. Due to the reactor's size, reactor heating and cooling times were longer than in the recirculation experiments. In total, the reactor remained above 180 °C for 3 h.

Based on the results from the recirculation experiments, the pilot-scale reactor was operated for three recirculation cycles. In the first cycle, 18 L of fresh water was mixed with the poultry litter. In the subsequent cycles, the water phase consisted of 9 L of aqueous phase from the previous cycle and 9 L of fresh water. At the end of each cycle, the sludge was removed from the reactor and centrifuged to separate the hydrochar and the aqueous phase. The recirculated aqueous phase obtained at the end of the third cycle was used for the fertigation experiment. The reactor was operated one additional time with fresh water to generate non-recirculated aqueous phase for the fertigation experiment. Samples from the aqueous phase generated in all cycles were collected for analysis.

Fertigation Experiments. The agronomic efficiency of the aqueous phase in supporting plant nutrition demand in nutrient-poor sandy soils was investigated by planter experiments with lettuce (*Lactuca sativa*) as a model plant. Lettuce was chosen because the effect of nitrogen (N) stress in this plant is commonly studied,²⁷ and it has a relatively short growth period of approximately 40 days.^{28,29} In total, 48 lettuce seedlings were transplanted in horticulture pots containing 3.6 kg of clean quartz sand screened with a 2-mm sieve to remove stones and large aggregates. Sand was used to simulate plant growth in nutrient-poor soil. The pots were placed in a greenhouse and were arranged in 16 blocks, each containing one pot randomly assigned to a fertigation treatment (randomized block design). Four different fertigation treatments were tested: (i) non-recirculated aqueous phase (F-AP); (ii) recirculated aqueous phase (F-RAP); (iii) a positive control composed of standard balanced commercial fertilizer; (iv) a negative control that consisted of tap water. Ecogan PERFECT (Elgo Irrigation Ltd., Caesarea, Israel) was used as the commercial

fertilizer in the positive control. The fertigation treatments were diluted to 80 mg L⁻¹ dissolved N. An additional 20 mg L⁻¹ dissolved N obtained by diluting the commercial fertilizer was added to each treatment, including the negative control, to ensure that all treatments had the minimum amount of micronutrients necessary for plant growth. A total fertigation rate of 100 mg L⁻¹ dissolved N was chosen since it is the typical application rate for lettuce.^{27,30} The fertigation treatments were prepared twice a week and stored in irrigation barrels. Samples were collected from each treatment at the time of preparation and disposal, and then characterized. Computerized irrigation was used to deliver between 213 and 568 mL (according to plant growth) of the fertigation treatments to each plant daily at 08:00 am.

During the growing season, every 10 days, four random blocks were sacrificed for analysis. The lettuce plant was removed from the pot and washed, and the roots and leaves were separated. A soil sample from each pot was collected as well. Before the experiment started, 10 lettuce seedlings were collected for analysis. All samples were weighed upon collection and after drying at 65 °C for at least 3 days. After drying, the samples were crushed and stored for further analysis. Leachate samples were collected from all pots four times during the growing season. The leachate volume was recorded, and a subsample was collected for analysis. The experiment lasted a total of 40 days. The effect of the aqueous phase as fertilizer was determined by analyzing lettuce yield and growth performance throughout the growing season.

Analytical Analyses.

Liquid Samples. All liquid samples (HTC aqueous phase, fertigation treatments, and leachate) were filtered through a 0.45- μ m fiberglass filter before analysis. The pH and electrical conductivity (EC) were measured with a Cyberscan pH 11 meter and a Cyberscan Con 11 conductivity meter, respectively (Eutech Instruments Ptv. Ltd., Singapore). Dissolved organic carbon (DOC) and dissolved N were measured with the multi N/C 2100S analyzer (Analytik Jena, Germany), following Environmental Protection Agency (EPA) method 415.3. Dissolved N and phosphorus (P) species were measured by absorbance in the microtiter plate reader TECAN SparkTM 10M (TECAN, Switzerland). Standard procedures for the quantification of each species were as follows:³¹ total ammonium nitrogen (TAN) analysis by the Nesslerization method, nitrite nitrogen (NO_2^- -N) by colorimetric method, nitrate nitrogen (NO_3^- -N) by the UV method, and phosphorus (PO_4^{3-} -P) by the ascorbic acid method. Macro- and micronutrients were quantified with a Varian 720-ES ICP Optical Emission Spectrometer (Varian Australia PTY Ltd., Australia). For sample preparation and analysis, the EPA protocol method 6010C for inductively coupled plasma-atomic emission spectrometry (ICP-AES) was followed.³² The probable speciation and precipitation of the macro- and micronutrients were evaluated with PHREEQC software (USGS, Reston, VA) based on the geochemistry of the aqueous phase.³³ The simulations were run with the two models and databases Pitzer.dat and SIT.dat applicable for high-ionic-strength solutions of 0.1–4 M.³⁴

Solid Samples. The mass yields of hydrochar, and lettuce leaves and roots were given as dry weight after oven-drying for 24 h at 105 °C. The ash contents of the solid samples (poultry litter, hydrochar, lettuce leaves and roots, soil) were analyzed using the standard method for dry ashing of plant samples.³⁵ The concentrations of the major elements C, hydrogen (H), N, sulfur (S) and oxygen (O) were measured with a FlashSmart™ Elemental Analyzer (ThermoFisher Scientific Inc., Germany). The macro- and micronutrients were extracted using the double-acid extraction procedure,³⁵ and then analyzed by ICP-AES as described for the aqueous phase. The higher heating value (HHV) on dry basis, also referred to as calorific value, was calculated following Channiwala and Parikh³⁶ for the poultry litter and hydrochar.

Calculations. Due to the need for dilution to maintain a constant solid-to-liquid ratio in all recirculation cycles, the extracted DOC concentration from the poultry litter to the aqueous phase after n recirculation cycles ($c_{e,n}$) was calculated according to the following equation:

$$c_{e,n} = c_n - c_{n-1} * f \quad (1)$$

where c is the measured DOC concentration for cycles n and $n-1$, and f is the fraction of recirculated water,¹⁸ which in this study was 0.44 and 0.69 at 200 and 250 °C, respectively.

Mass balances for N, P, and potassium (K) in the fertigation experiment were calculated for the entire growing period. Nutrient inputs consisted of the nutrients present in the fertigation treatments, and in the sand and seedlings at the beginning of the experiment. The nutrient distribution in each experimental component (leaves, roots, leachate, soil) was calculated according to the following equation:

$$F_i = \frac{m_i C_i}{m_f C_f + m_s C_s + m_0 C_0} * 100\% \quad (2)$$

where F_i represents the nutrient fraction, m the component mass, and C the nutrient concentration. The subscript i denotes each experimental component, f the fertigation treatment, and s and 0 the

soil and seedlings at the beginning of the experiment, respectively. The overall mass balance can be obtained by the summation of F_i for each experimental component.

Statistics. The data were statistically analyzed to determine significant differences between treatments using STATISTICA v.10.0 software (StatSoft, USA). In the recirculation experiments, differences in aqueous phase and hydrochar characteristics between recirculation cycles and the two temperature treatments were analyzed by means of two-way, fixed-factor ANOVA. Differences between the initial substrate and hydrochar generated in cycle 1 under the two temperature treatments were analyzed by one-way ANOVA. Results from the fertigation experiments were analyzed by two-way ANOVA, with the blocks treated as a random factor. If significant differences ($p < 0.05$) were found, Tukey's test was performed post-hoc.

RESULTS AND DISCUSSION

Aqueous-Phase Recirculation. The aqueous phases generated in the various recirculation cycles were characterized in terms of pH and EC (Table 1). With the first cycle of HTC treatment, the pH decreased for both tested temperatures ($p < 0.05$), due to accumulation of organic acids.^{18,20} At 200 °C, pH values were significantly lower than at 250 °C for all cycles ($p < 0.05$), and were relatively stable. HTC treatment increased the aqueous phase salinity, measured by a higher EC than the initial substrate ($p < 0.05$). This increase continued for both temperatures up to cycle 3 ($p < 0.05$), and then approached a steady state, as no differences were seen between subsequent cycles ($p > 0.05$).

DOC. Organic carbon is one of the key compounds found in poultry litter, which partly dissolves in the aqueous phase during HTC treatment. For both temperature treatments, DOC

204 concentrations were significantly higher than in the initial substrate ($p < 0.05$), ranging from 24 to
205 49 g L⁻¹ (Figure 1a). The DOC values were similar to previously reported values for aqueous-phase
206 recirculation using poultry litter as feedstock.¹⁶ Similar to the EC, the concentration of DOC
207 increased significantly ($p < 0.05$) for both temperatures until HTC cycle 3. No significant
208 differences were found from cycles 3 to 5 within each temperature treatment, showing that a steady
209 state of DOC was approached at cycle 3. In general, the DOC concentrations at 200 and 250 °C
210 were very similar, except in cycles 4 and 5, where DOC was significantly higher at 250 °C ($p <$
211 0.05).

The $c_{e,n}$ was calculated for each cycle, and it was relatively constant (Table S4) for all cycles except for cycle 1, where the aqueous phase consisted of DDW only. This indicated that despite the plateau generally observed in DOC concentration,^{16–19,37} the actual amount of DOC transferred from the feedstock to the aqueous phase remains constant throughout all recirculation cycles. The observed plateau is, therefore, a consequence of the need to dilute the aqueous phase between each recirculation cycle. The $c_{e,n}$ was lower than the DOC extracted when only DDW was used. It is assumed that part of the DOC that was recirculated took part in further reactions, leading to precipitation, as previously suggested.¹⁸ Therefore, $c_{e,n}$ is the net DOC extracted, mainly that extracted from the feedstock minus that precipitating during recirculation. The $c_{e,n}$ was also calculated using data from previous recirculation studies, and was found to be constant and lower than the concentration obtained after the first HTC treatment.^{18,19,37} This confirms that the process explained in this study also applies to previous findings.

Dissolved N and TAN. N is a key nutrient dissolved in the aqueous phase, which is also essential for plant growth. Total dissolved N and TAN were measured (Figure 1b). The aqueous phase generated at 200 and 250 °C contained dissolved N at higher concentrations than the initial substrate ($p < 0.05$). The dissolved N followed a trend similar to that of the DOC, with a general increase from cycle 1 to 3 and a steady state from cycle 3 to 5. There was no significant difference in dissolved N concentration between the temperature treatments ($p > 0.05$). TAN concentration increased with HTC treatment compared to the initial substrate ($p < 0.05$), but no other significant differences were found between treatment temperatures or cycles ($p = 0.54$).

Of the total dissolved N, about 20–25% was present as TAN (Figure 1b), less than ca. 0.02% as $\text{NO}_2\text{-N}$, and <1% as $\text{NO}_3\text{-N}$. These low concentrations of oxidized N species are to be expected, as the reaction occurs in a limited O_2 environment. Abiotic thermochemical TAN to

NO₃⁻ reactions on mixed ferric–manganese (Fe–Mn) oxides have been reported,³⁸ and such minerals could have precipitated under HTC treatment conditions,³⁹ as for example, saturation was reached for various Fe oxides (Table S5). However, the absence of NO₃⁻ and substantial TAN concentrations have been previously observed in the aqueous phase of poultry litter (without recirculation).^{21,25} Therefore, the N in the aqueous phase seemed to consist mainly of organic N which, together with DOC, accumulated with recirculation to a certain degree, while TAN was unaffected by recirculation. Similar trends and ranges have been reported for HTC recirculation studies of poultry litter.¹⁶

Total Dissolved P and PO₄³⁻-P. P is another important nutrient for plant growth and dissolved P was measured in the aqueous phase, along with one of its bioavailable species, PO₄³⁻. For both dissolved P and PO₄³⁻-P, the temperature treatments led to lower concentrations than measured in the initial substrate ($p < 0.05$). In contrast to the DOC and N results, at 200 °C, dissolved P and PO₄³⁻-P contents were significantly higher than at 250 °C ($p < 0.05$), except for dissolved P levels in cycles 1 and 5 which were statistically similar ($p > 0.05$). Concerning recirculation however, temperature affected the rise in concentration: for 200 °C, both species increased significantly in the initial cycles (dissolved P: cycle 1 to 2, $p < 0.05$; PO₄³⁻-P: cycle 1 to 3, $p < 0.05$), but then stayed constant for the remaining cycles, similar to EC, DOC and N. For 250 °C, however, no significant differences were found for either species, except that in cycle 5, where dissolved P was higher than in the prior cycles ($p < 0.05$) (Figure 1c).

The measurements showed that PO₄³⁻-P and dissolved P follow similar trends. Looking at absolute values, PO₄³⁻-P contributed approximately 90% to dissolved P for the 200 °C treatment, and 50% for 250 °C, indicating that dissolved P consisted in large part of inorganic P. To the best of our knowledge, no other study has reported PO₄³⁻ concentrations in HTC aqueous-phase

recirculation experiments. Notably with dissolved P and $\text{PO}_4^{3-}\text{-P}$, temperature had the opposite effect, as seen with DOC and N. In other words, higher temperatures decreased P concentrations in the HTC recirculated aqueous phase. This phenomenon was likely due to P precipitation, as discussed further on.

Macro- and Micronutrients. Calcium (Ca), K, magnesium (Mg) and S were also measured, and their concentrations are listed in Table 1 alongside the micronutrient concentrations (Fe, Mn, sodium [Na], and zinc [Zn]). In all cases except for Fe and Zn, HTC treatment and aqueous-phase recirculation led to higher inorganic concentrations in the aqueous phase compared to the initial substrate. In terms of cycling, for 200 °C, concentrations of all elements increased significantly except for Ca and S from cycle 1 to 2 ($p < 0.05$), remaining constant thereafter—similar to the DOC and N trends. Ca and S concentrations were unaffected by aqueous-phase recirculation at 200 °C. In comparison, during the 250 °C treatment, the concentrations of Ca, K, Mg, Mn, Na and Zn increased continuously with recirculation ($p < 0.05$). Fe only increased from cycle 1 to 2 at 250 °C ($p < 0.05$), whereas S was unaffected by recirculation irrespective of temperature ($p > 0.05$). These results are in general agreement with a previous study on poultry litter, which also measured Ca, K, Mg and Na concentrations across recirculation cycles.¹⁶ In addition, the concentration ranges of both studies were congruent, when the slight concentration differences in the respective poultry litters were taken into account.

The concentration of most elements rose with higher temperature, probably due to their increased solubility with increasing temperature. However, the concentrations of P, Mg, Fe, and Zn decreased with temperature. These elements form compounds such as MgSiO_4 , which have exothermic dissolution reactions, and therefore show retrograde solubility.⁴⁰ The dissolution or precipitation of compounds depends on other factors, such as pH, ionic strength, and solution

complexes, whereas pressure is mostly negligible in this context.⁴¹ These factors were considered in a PHREEQC simulation, which determined the probable speciation and precipitation of compounds in the solution (Table S5).³³ The saturation indices obtained in the simulation for the two temperature treatments and at cycles 1 and 5 indicated that supersaturation had probably been reached, leading to the precipitation of minerals, and thus lowering the nutrient concentrations of Mg, Fe, and Zn in the recirculated aqueous phase. Importantly, Mg and Fe can form insoluble phosphate salts with dissolved P,¹ leading to co-precipitation of P and explaining the similar temperature trends of P, Mg and Fe concentrations in the aqueous phase. Previous studies have also indicated the association of P with metal cations such as Fe in the hydrochar.^{42,43}

Recirculation Effect on Hydrochar. The calorific value of the hydrochar, represented by the HHV on dry basis, increased from 14.2 MJ kg⁻¹ in the poultry litter to 19.3 MJ kg⁻¹ in the hydrochar generated in cycle 5 at 250 °C (Figure S2). This is comparable to previously obtained values for HTC of poultry litter with aqueous-phase recirculation.¹⁶ The HHV of the hydrochar generated at 250 °C was significantly higher than that generated at 200 °C ($p < 0.05$), except for cycle 1. Within temperatures, no significant differences were observed among the cycles of 200 °C ($p > 0.05$). For 250 °C, the HHV was also constant among cycles, except that cycle 5 was significantly higher than cycle 1 ($p < 0.05$). Both temperatures had a higher HHV for the hydrochar vs. initial substrate ($p < 0.05$), showing that the calorific value of the poultry litter was improved by the HTC process.

A common rationale for aqueous-phase recirculation is that the accumulation of organic acids and salts in the aqueous phase catalyzes dehydration and decarboxylation, thus lowering O:C and H:C ratios and raising HHV, as shown in a few previous studies.^{44,45} There is no

consensus on HHV trends among the different recirculation studies. A slight increase in HHV due to aqueous-phase recirculation has been reported^{18,46} in accordance with our results at 250 °C. Most studies, however, did not detect an effect, with HHV remaining stable,^{16,19,20} or with small fluctuations,^{17,37} across all cycles despite significant increases in aqueous phase acid and salt concentrations.^{19,44} Importantly, recirculation of the aqueous phase did not negatively affect HHV, and even showed a slight increase, at least for 250 °C, from cycle 1 to 5. In addition, HTC recirculation experiments working with sweet potato waste as feedstock reported improved combustion properties of hydrochar due to recirculation.⁴⁶ Generally, however, as previously observed,¹⁹ temperature clearly had a stronger effect on HHV than aqueous-phase recirculation, resulting in a 30% increase in HHV from 200 °C to 250 °C.

The Van Krevelen diagram is a good way to visualize the change in C, H and O elemental composition (Figure 2), and is commonly used to group fuel types according to their elemental composition. According to the reaction vectors displayed in the diagram, decarboxylation is the main process affecting the hydrochar during recirculation, as found in a previous study.⁴⁶ A significant decrease ($p < 0.05$) in O:C ratio was found from cycle 1 to subsequent cycles at 250 °C, and a marginally significant decrease was found at 200 °C ($p = 0.11$). This decrease in O:C ratio after cycle 1 could be from the polymerization and precipitation of recirculated DOC from the aqueous phase onto the hydrochar surface. In general, the Van Krevelen diagram of this study shows that the elemental composition is primarily influenced by temperature treatment, whereas during recirculation, the hydrochar stays within the same fuel-type range.

Aqueous phase as a fertilizer. The aqueous phase and hydrochar produced in the pilot-scale reactor demonstrated compositions similar to those obtained in the laboratory (Table S6). The composition of the fertigation treatments F-AP, F-RAP, and controls are presented in Table S7. The fertigation treatments contained about 103 mg L⁻¹ dissolved N, and the negative control contained 21 mg L⁻¹ dissolved N. The N in the positive control consisted of 50% TAN and 50% NO₃⁻-N, whereas in the F-AP and F-RAP, about 20% was TAN, 15% was NO₃⁻-N, and the remaining fraction was likely organic N since no NO₂⁻-N was detected. The F-AP and F-RAP had a slightly lower pH than the controls, and a slightly higher EC ($p < 0.05$). The F-AP and F-RAP contained about three times more K and twice the P compared to the positive control, over 98% of which was in the form of PO₄³⁻-P for all treatments. The liquids also contained significantly more DOC, Mg, S, Fe, and Na than the positive control treatment. The sodium adsorption ratio (SAR), a measure of the suitability of water for use in agricultural irrigation, was calculated with the concentration of Na relative to those of Ca and Mg. The SAR of all treatments was around 2, which in combination with the measured EC, is unlikely to affect water infiltration in soils, and can be considered suitable for crop irrigation.⁴⁷

Analysis of the F-AP and F-RAP during disposal indicated that DOC and dissolved N decreased by 30% during the 3 to 4 days following preparation (Table S8). Based on turbidity and problematic filtration, microbiological growth is likely responsible for this decrease. These results are especially interesting since the undiluted aqueous phase and recirculated aqueous phase are both toxic (Table S9), and do not demonstrate significant degradation of DOC, dissolved N (Table S10), inorganic N, or P.²⁵ This toxicity is beneficial since the pure aqueous phase can be stored without microbial degradation, and when diluted for field application, the toxicity will no longer be apparent.

Plant growth was assessed throughout the growing season by root and leaf dry weight (Figure 3). There were no significant differences between F-AP and F-RAP treatments. In the first 20 days the F-AP and F-RAP did not affect lettuce growth, performing similarly to the negative control. After that, the treatments began to stimulate growth, such that by day 40, the plants' dry weight was similar to the positive control ($p > 0.05$), except for the leaf weight of F-RAP which was similar to F-AP, but slightly lower than the control ($p < 0.05$). This difference in growth rate could be due to the higher presence of organic N in the F-AP and F-RAP treatments in comparison to the positive control. Organic N is less readily available to plants than TAN and NO_3^- -N. F-AP and F-RAP treatments demonstrated significantly higher lettuce growth than the negative control ($p < 0.05$). Poultry litter HTC aqueous phase used as a one-time application to corn seedlings also demonstrated satisfactory plant productivity, though slightly lower than obtained with commercial fertilizer.²⁵ A previous study determined that the HTC aqueous phase is toxic to lettuce seed germination and early growth.²² However, the current study demonstrated the HTC aqueous phase can successfully support plant growth when applied as a fertigation treatment at later stages of crop growth.

Despite no significant differences in lettuce biomass at the end of the growing period, the treatments resulted in different macronutrient concentrations in the leaves. The plants that received F-AP and F-RAP contained 1% less N than the positive control, and 5% more K. The P concentration in the leaves was similar in the three treatments. More research is needed to determine the reaction of other plants to HTC aqueous phase, and its effect on nutrition content.

The leachate from the plants that received F-AP and F-RAP contained no NO_3^- -N, and only a little TAN, whereas the leachate from the positive control plants contained 160 mg L^{-1} NO_3^- -N along with little TAN. This indicates that TAN was completely nitrified, and that in the

positive control, N was supplied in excess of the plants' requirements. The soils from F-AP and F-RAP contained more N than the control at the end of the growing season, indicating that N, likely as organic N, was stored there. Long-term experiments are needed to determine if this organic N eventually becomes available to plants. The presence of higher N in the positive control leachate, and in the soil for F-AP and F-RAP treatments, was also clear in the N mass balance (Figure 4a). The total N recovery ranged from 90 to 127%. The leaves and roots in the positive control contained a higher N concentration than in the F-AP and F-RAP treatments, resulting in more input N being stored in the plants.

The P mass balance indicated that almost all of the P supplied during the growing season is stored in the soil (Figure 4b). The P recovery for F-AP was low for unknown reasons, although the general trend was still clear. As already discussed, F-AP and F-RAP contained significantly more K than the controls, and were able to supply all of the plant's K demand. A small fraction of the total K was present in the positive control leachate due to K deficit, whereas about 19% of the total K in F-AP and F-RAP was present in the leachate (Figure 4c). Since the lettuce in the negative control did not grow significantly, a large fraction of N, P and K was stored in the soil. The K recovery was also high, ranging from 76 to 92%.

This study showed that aqueous-phase recirculation can increase the nutrient concentration in the aqueous phase without leading to significant changes to the hydrochar. Moreover, the recirculated phase performed similarly to the aqueous phase and a commercial fertilizer in supporting lettuce growth and providing nutrients. More research is needed to determine the effect on other plants, and the effect on soil over prolonged fertigation periods. The combination of aqueous-phase recirculation and use as a fertilizer can be an appropriate method

to reutilize the aqueous phase and return nutrients to support plant growth, thus increasing HTC efficiency and economic feasibility.

SUPPORTING INFORMATION

Poultry litter characterization, recirculation schemes, fraction of recirculated water, calculation of DOC extracted from poultry litter, saturation index for various minerals, composition of aqueous phase and hydrochar generated in the pilot-scale reactor, composition of fertigation treatments fresh and during disposal, aqueous phase microbial growth inhibition, DOC and dissolved N concentrations in aqueous phase stored under different conditions, HTC pilot plant, HHV of poultry litter and hydrochar.

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Figure 1. Concentration of (a) DOC, (b) dissolved N, and (c) dissolved P. Dotted diamonds and dashed lines represent total ammonia N (b), and $\text{PO}_4^{3-}\text{-P}$ (c). Values represent averages of triplicate analyses. Error bars represent standard error.

Figure 2. (a) Atomic H:C and O:C ratios of initial poultry litter and derived hydrochar from 200 °C and 250 °C treatments. Insets (b) and (c) are closeups of the graph. Symbols represent cycles 1 to 5: circle (1), line (2), triangle (3), diamond (4), square (5).

Figure 3. Dry weight of lettuce (a) leaves and (b) roots throughout the growing season. Values represent averages of four replicate analyses. Error bars represent standard error.

Figure 4. Distribution of (a) N %, (b) P %, and (c) K % in the system components (soil, leachate, lettuce roots and leaves) on day 40 of the fertigation experiments. Values represent averages of four replicate analyses. Error bars represent standard error.

Table 1. Aqueous-Phase Characterization for the Recirculation Experiment^a

Parameters	Initial	200 °C				
		1	2	3	4	5
pH	6.9 ± 0.01 ^a	5.7 ± 0.00 ^b	5.7 ± 0.03 ^{bc}	5.8 ± 0.02 ^c	5.7 ± 0.02 ^{bc}	5.7 ± 0.01 ^{bc}
EC (mS cm ⁻¹)	22.1 ± 0.39 ^a	38.4 ± 0.62 ^b	42.1 ± 0.53 ^c	54.2 ± 0.79 ^d	49.7 ± 0.09 ^e	52.8 ± 0.69 ^{de}
DOC (g L ⁻¹)	13.8 ± 0.42 ^a	24.1 ± 0.96 ^b	32.8 ± 0.78 ^c	40.5 ± 1.58 ^{def}	38.5 ± 0.65 ^{cde}	39.3 ± 1.08 ^{de}
<i>Macronutrients</i>						
TN (mg L ⁻¹)	2200 ± 68 ^a	3540 ± 79 ^{bc}	4190 ± 88 ^{cde}	4970 ± 175 ^f	4750 ± 73 ^{def}	4840 ± 64 ^{ef}
N-NH ₄ (mg L ⁻¹)	83.2 ± 4 ^a	644 ± 105 ^{bc}	727 ± 70 ^{bc}	861 ± 34 ^b	776 ± 22 ^{bc}	866 ± 73 ^b
TP (mg L ⁻¹)	1030 ± 19 ^a	178 ± 28 ^{be}	323 ± 29 ^{cd}	390 ± 28 ^{cd}	397 ± 7 ^d	356 ± 2 ^{cd}
P-PO ₄ (mg L ⁻¹)	742 ± 20.6 ^a	132 ± 9.7 ^b	280 ± 21.2 ^c	390 ± 18.0 ^d	379 ± 7.9 ^d	341 ± 9.8 ^{cd}
K (mg L ⁻¹)	7070 ± 134 ^a	7800 ± 747 ^a	10300 ± 115 ^b	11100 ± 329 ^b	10900 ± 139 ^b	11100 ± 122 ^b
<i>Secondary nutrients</i>						
Ca (mg L ⁻¹)	200 ± 8 ^a	668 ± 44 ^{bc}	660 ± 5 ^{bc}	794 ± 61 ^{bcd}	749 ± 21 ^{bc}	618 ± 11 ^b
Mg (mg L ⁻¹)	573 ± 3 ^a	1020 ± 106 ^{bde}	1350 ± 51 ^{cf}	1470 ± 104 ^c	1510 ± 18 ^c	1470 ± 33 ^c
S (mg L ⁻¹)	1540 ± 40 ^a	1300 ± 149 ^a	1750 ± 107 ^{abc}	1880 ± 117 ^{bc}	1760 ± 65 ^{abc}	1770 ± 76 ^{abc}
<i>Micronutrients</i>						
Fe (mg L ⁻¹)	18.7 ± 0.28 ^a	12.8 ± 1.56 ^{bc}	18.9 ± 1.34 ^{de}	22.6 ± 1.79 ^d	24.2 ± 0.76 ^d	21.8 ± 0.35 ^d
Mn (mg L ⁻¹)	2.53 ± 0.02 ^a	5.73 ± 0.58 ^b	8.14 ± 0.30 ^{cd}	8.80 ± 0.70 ^c	9.54 ± 0.05 ^c	8.18 ± 0.19 ^{cd}
Na (mg L ⁻¹)	1390 ± 21 ^a	1300 ± 140 ^a	1890 ± 60 ^b	2000 ± 128 ^b	2090 ± 15 ^b	2100 ± 38 ^b
Zn (mg L ⁻¹)	5.52 ± 0.09 ^a	10.7 ± 1.08 ^b	15.5 ± 0.54 ^c	16.6 ± 1.30 ^c	17.0 ± 0.27 ^c	16.7 ± 0.72 ^c

Parameters	250 °C				
	1	2	3	4	5
pH	6.7 ± 0.04 ^d	6.7 ± 0.01 ^d	6.6 ± 0.03 ^{de}	6.2 ± 0.02 ^f	6.5 ± 0.04 ^e
EC (mS cm ⁻¹)	33.0 ± 0.21 ^f	55.0 ± 0.25 ^d	69.4 ± 0.22 ^g	76.9 ± 1.28 ^h	77.5 ± 1.06 ^h
DOC (g L ⁻¹)	26.1 ± 0.98 ^b	36.1 ± 1.00 ^{cd}	43.9 ± 1.14 ^{efg}	46.2 ± 1.91 ^{fg}	48.6 ± 1.98 ^g
<i>Macronutrients</i>					
TN (mg L ⁻¹)	3060 ± 113 ^b	4170 ± 116 ^{cd}	5080 ± 98 ^f	5200 ± 227 ^f	5400 ± 186 ^f
N-NH ₄ (mg L ⁻¹)	538 ± 46 ^c	704 ± 22 ^{bc}	721 ± 22 ^{bc}	811 ± 60 ^{bc}	727 ± 93 ^{bc}
TP (mg L ⁻¹)	147 ± 42 ^b	157 ± 16 ^b	165 ± 26 ^{bc}	159 ± 13 ^b	277 ± 13 ^{ce}
P-PO ₄ (mg L ⁻¹)	63.8 ± 9.9 ^e	55.0 ± 7.4 ^e	97.2 ± 13.1 ^{eb}	93.4 ± 13.4 ^{eb}	117 ± 12.8 ^{ef}
K (mg L ⁻¹)	10100 ± 277 ^b	16200 ± 172 ^c	19000 ± 135 ^d	21600 ± 334 ^e	23300 ± 162 ^f
<i>Secondary nutrients</i>					
Ca (mg L ⁻¹)	614 ± 23 ^b	1020 ± 47 ^e	963 ± 49 ^{de}	822 ± 9 ^{cd}	1260 ± 55 ^f
Mg (mg L ⁻¹)	807 ± 44 ^{ab}	972 ± 27 ^{bd}	1080 ± 26 ^{bde}	1080 ± 5 ^{def}	1260 ± 17 ^{cef}
S (mg L ⁻¹)	1540 ± 139 ^{ab}	2270 ± 146 ^{cd}	2650 ± 118 ^d	2450 ± 36 ^d	2680 ± 56 ^d
<i>Micronutrients</i>					
Fe (mg L ⁻¹)	6.85 ± 0.10 ^f	12.3 ± 0.41 ^{bc}	14.2 ± 0.56 ^{bce}	11.3 ± 0.37 ^b	16.1 ± 0.26 ^{ce}
Mn (mg L ⁻¹)	4.48 ± 0.31 ^b	6.50 ± 0.72 ^{bd}	8.62 ± 0.33 ^c	9.31 ± 0.15 ^c	13.9 ± 0.26 ^e
Na (mg L ⁻¹)	1860 ± 78 ^b	2700 ± 56 ^c	3270 ± 32 ^d	3540 ± 24 ^{de}	3790 ± 63 ^e
Zn (mg L ⁻¹)	2.14 ± 0.06 ^d	2.20 ± 0.16 ^{de}	2.86 ± 0.07 ^{ef}	2.80 ± 0.09 ^{ef}	3.47 ± 0.02 ^f

^aInitial aqueous phase, and that of cycles 1 to 5 under temperature treatments 200 °C and 250 °C.

Values represent averages of triplicate analyses ± standard error. Different superscript letters in a row represent significant difference (at $p \leq 0.05$).

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