



## Feasibility of sewage sludge derived hydrochars for agricultural application: Nutrients (N, P, K) and potentially toxic elements (Zn, Cu, Pb, Ni, Cd)

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### H I G H L I G H T S

- Soil amendment may be more suitable for hydrochar utilization than as char or fuel.
- Hydrochars had lower pH and higher CEC than pyrochars.
- Hydrochars had sufficient nutrients and better nutritional balance than pyrochars.
- Leaching risk of potentially toxic elements pollution was efficiently reduced.
- Partial nutrients of sludge dissolved in the process water may also be re-cycled.

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### A B S T R A C T

Hydrochars derived from municipal sewage sludge was analyzed for its feasibility for value-added recycling. Results of carbon content and elemental composition suggested that the hydrochars might not be comparable with pyrochars regarding to the carbon sequestration, long-term stability and fuel quality. Application as soil amendment would be a better approach for hydrochar utilization. To examine the potential benefits and risks of that, the total and available content of nutrients (i.e. N, P, and K) were measured, and the potentially toxic elements (PTEs, i.e. Zn, Cu, Pb, Ni and Cd) were analyzed for the total content, speciation, and leaching potential. Compared with pyrochars derived from the same feedstock, hydrochars had lower pH and higher cation exchange capacity. The available content of N (1.58–6.87 g/kg), P (0.270–0.901 g/kg), and K (0–0.873 g/kg) in the chars was less than the feedstock sludge (3.33 g/kg N, 3.02 g/kg P, 2.07 g/kg K), but still far higher than that of the agricultural soil (i.e. 0.014–0.488 g/kg N, 0.02 g/kg P, <0.1–0.272 g/kg). Remarkably, hydrochars showed better nutritional balance than pyrochars for its higher available K content. Risk of potentially toxic elements contamination by the sludge was efficiently reduced in either hydrochars or pyrochars, except the high leaching potential of Zn in pyrochars. Overall, in addition to the advantages of the hydrothermal carbonization process as energy saving

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and value-added liquid by-products, the hydrochars derived from sludge, with sufficient and balanced nutrients and limited PTEs pollution risk, can be a feasible and value-added material as soil amendment. © 2019 Elsevier Ltd. All rights reserved.

## 1. Introduction

The sewage sludge is a by-product generated during the municipal wastewater treatment process, with large volume and mass requiring proper reduction and disposal (Zhuang et al., 2017). On the other hand, the sludge contains rich organic materials and nutrient elements, and has attracted much attention for its conversion to value-added products such as biochars, which can not only reduce the large volume and mass, but also benefit to resource utilization (Lu et al., 2016).

Biochar, the carbonaceous solid residual from the thermal treatment of organic biomass under limited or no oxygen, has gained increasing attention in recent years for its role in carbon sequestration and the potential for applications as solid fuel, adsorbent, and soil amendment (Conte et al., 2015). The sludge-derived biochar usually has high ash content due to the mineral contents in the feedstock (Zhao et al., 2013), resulting in the relatively lower carbon content and lower heat value than the biochars derived from other feedstocks, i.e. phytomass. Considering the enriched nutrient elements from municipal wastewater in the sludge, agricultural application would be a better option for the sludge derived-biochars (Yuan et al., 2016; Fei et al., 2019). For this purpose, the actual values of the nutrients should be evaluated before application. Moreover, the risks for secondary contaminations from toxic substances including potentially toxic elements (PTEs), which might also be enriched during the conversion, should also be carefully examined.

Biochars can be produced using a traditional pyrolysis method, therefore called as pyrochars. However, for feedstocks with high moisture content, such as sludge, pre-drying of the raw materials is required, which is much energy-consuming. To save energy, hydrothermal carbonization (HTC), which does not ask for the drying pretreatment, would be a better approach for the conversion of sludge to biochars (hydrochars) (Wang et al., 2016; Zhuang et al., 2017).

Although reports could be found in literature on the hydrochars produced from various feedstocks such as poultry litter (Ghanim et al., 2016), food waste (Ul Saqib et al., 2018), corn stalk (Guo et al., 2015) and model woody materials (Kruse and Zevaco, 2018), hydrochars derived from sewage sludge has been less concerned. Among the reported studies, major concerns are focused on the hydrothermal reactions, physicochemical and structural properties, combustion characteristics, and stability of the hydrochars (Schulze et al., 2016; Nizamuddin et al., 2018; Ul Saqib et al., 2018). Only a few studies have paid attention to the soil related properties of the obtained hydrochars, including water holding capacity and cation exchange capacity (CEC) (Rohrdanz et al., 2016). Very few study mentioned the total content of nutrients (Zhuang et al., 2017; Dieguez-Alonso et al., 2018) or PTEs (Wang et al., 2016) in the hydrochars. Careful examination on the availability of the nutrients and the speciation as well as leaching risk of the PTEs of sludge derived-hydrochars are still missing and requiring future research efforts.

Therefore, the present study evaluated the feasibility of sludge-derived hydrochars for agricultural application from two aspects: nutritional values and PTEs contamination risks. Pyrochars were also obtained from the same municipal sludge as control samples.

The elemental composition and basic physicochemical properties was analyzed. Additionally, the values of inorganic nutrient elements, i.e. nitrogen (N), phosphorus (P) and potassium (K), and the speciation and leaching risks of PTEs, i.e. zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), and cadmium (Cd), which have not been thoroughly evaluated in previous studies yet, were emphatically investigated. The results would be helpful in comprehensively evaluate the potential of hydrothermally carbonizing sewage sludge for agronomic soil amendments.

## 2. Materials and methods

### 2.1. Sludge and carbonization

Dewatered sludge was collected from a municipal wastewater treatment plant in October, 2015. The sludge was collected during both the primary and the secondary treatments and was then dewatered by pressure filtration. The moisture of the dewatered sludge was around 80%.

The wet sludge was hydrothermally carbonized in a stainless steel reactor under N<sub>2</sub> atmosphere. The reactor was heated by 5 °C/min to peak temperature of 150, 180, 200, 220, 250, and 300 °C, respectively, and hold for 2 h under the spontaneous pressure (3–10 atm depending on the working temperature). After cooled to the room temperature and pressure, the mixed liquid was centrifugated at 5000 rpm for 10 min. The weight and volume of the supernatant liquid was recorded, while the precipitates, regarded as hydrochars, were collected, washed with de-ionized water (DI water), and dried in 40 °C oven before further analyses.

For comparison, another portion of sludge was pre-dried under 40 °C and then pyrolyzed in a tube furnace under N<sub>2</sub> atmosphere with ambient pressure. The furnace was heated by 5 °C/min to peak temperature of 350 and 550 °C, respectively, and hold for 2 h. After cooled to room temperature, the solid residual, regarded as pyrochars, were stored for following analysis.

### 2.2. Hydrochar and pyrochar characterization

Ash content of dry sludge (denoted as S in following text) and char samples was determined according to standard ASTM methods (Zhao et al., 2013). Total contents of carbon (C), hydrogen (H), N were measured by an element analyzer (Vario EL cube, Elementar, German) on a moisture-free basis. Content of oxygen (O) was then calculated by the equation as follow (Guo et al., 2015):

$$O\% = 100\% - C\% - H\% - N\% - A_{ad}\% \quad (1)$$

where, O%, C%, H%, N% and A<sub>ad</sub>% refer to the content in percentage of O, C, H, N and ash, respectively.

Surface functional groups were analyzed using fourier transform infrared spectroscopy (FTIR, Tensor II, Bruker, German) by recording the 4000–400 cm<sup>-1</sup> region using KBr pellet technique (Li et al., 2014).

PH was measured in a suspension of sludge or char samples in DI water (1:20, w/v) after hydration of 24 h (Zhao et al., 2013). CEC was determined through a modified barium chloride compulsive exchange method (Zhao et al., 2013).

### 2.3. Determination of total and available nutrients

Total content of N of the sludge and chars was analyzed by an element analyzer (Vario EL cube, Elementar, German). Alkali-hydrolyzable N determined by the Illinois Soil N Test was adopted as the indicator of N availability (Williams et al., 2007; Roberts et al., 2011).

Sludge and chars were digested by alkali (NaOH) fusion method for the total P content, which is commonly adopted for soil (Gao et al., 2017; Fei et al., 2019). Available P was extracted following the method established by Olsen (1954) by 0.5 M NaHCO<sub>3</sub> solution (Purakayastha et al., 2015). The digestion solution or extract was then measured by means of molybdenum antimony blue colorimetric method (Fei et al., 2019).

Alkali fusion method was also employed for total K digestion (Gao et al., 2017). Available K was extracted by 1 M NH<sub>4</sub>OAc (pH = 7) solution (Purakayastha et al., 2015). The digestion solution and extractants were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer, USA) for K concentration.

### 2.4. Determination of PTEs speciation and leaching potential

The sludge and chars were extracted to determine the PTEs speciation (Devi and Saroha, 2014). Four fractions, i.e. soluble, exchangeable, reducible, and oxidizable fractions was sequentially extracted by DI water (pH = 4.0), 0.1 M CH<sub>3</sub>COOH (pH = 4.0), 0.1 M NH<sub>2</sub>OH-HCl (pH = 2.0), and 30% H<sub>2</sub>O<sub>2</sub> followed by 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH = 2.0) for 16 h in a rotary shaker at 150 rpm at room temperature (25 °C), respectively. The residual fraction was finally digested by HNO<sub>3</sub>+HClO<sub>4</sub> (3:1, v/v).

The toxicity characteristic leaching procedure (TCLP) was also conducted to evaluate the leaching potential of the PTEs (EPAUS, 1990; Tsang et al., 2013). Sludge or chars was extracted by 0.1 M CH<sub>3</sub>COOH with a ratio of 10:1 (v/w) for 18 h in a shaker at 150 rpm at room temperature (25 °C).

After each extraction, the supernatant was collected by centrifugation at 5000 rpm for 10 min and filtered through a 0.45-μm nylon filter. All the extractants were analyzed using ICP-OES (Optima 5300DV, PerkinElmer, USA) for the five PTEs (including Ni, Zn, Cu, Cd, Pb).

### 2.5. Data processing and statistical analysis

Unless stated otherwise, all tests and analyses were conducted in triplicate. The experimental data were analyzed using Microsoft Office Excel (2013), and statistical analyses were carried out by SPSS (20.0) when necessary.

## 3. Results and discussion

### 3.1. Charring process and carbon sequestration

The proximate and ultimate analysis results are summarized in Table 1 and Table S1. As a result of organic matter decomposition, most labile and volatile matter as well as their further transformations were released to gaseous and liquid by-products (Ghanim et al., 2016). Thus, it was not surprisingly noted in this study that the char yield decreased along HTC or pyrolysis temperature (Table 1), while the aqueous and gaseous by-product yields increased in HTC procedures (Table S2). The content of volatile matter was largely reduced (Table S1), the bulk C content decreased while the ash content was enriched in chars (Table 1).

$$\text{carbon sequestration}(\%) = \frac{\text{C\% of char} \times \text{char yield\%}}{\text{C\% of dS}}$$

Sequestration of carbon is usually believed as one of the most important functions of biochars (Conte et al., 2015). According to the ash-free basis of bulk elemental composition (Table 1), C content was enriched in chars, and O content was reduced, suggesting a carbonization-like process. Evolutions of surface functional groups were observed by FTIR analysis (Fig. 1). The O-H stretch by hydroxyl or carboxyl groups was reduced, indicated by the broad absorbance in the range of 3200–3700 cm<sup>-1</sup>, which could be easily noted, especially for hydrochars. This was a strong evidence of dehydration reactions which could occur during both pyrolysis and hydrothermal processes (Zhao et al., 2013; Li et al., 2014; Guo et al., 2015; Ghanim et al., 2016). The diminished carboxyl C=O stretch, indicated by the peaks at 1658 cm<sup>-1</sup> and 1545 cm<sup>-1</sup>, owing to the decarboxylation reactions (Ghanim et al., 2016), was also observed. The peaks in the range of 2850–2950 cm<sup>-1</sup>, which was indicative of aliphatic C-H stretch (Ghanim et al., 2016), increased in hydrochars, but decreased in pyrochars. This can be attributed to the dehydrogenation of methylene groups in hydrochars and the formation of more condensed structures in pyrochars, respectively (Zhao et al., 2013; Li et al., 2014). The peaks in 1465–1340 cm<sup>-1</sup>, indicative of saturated C-H, diminished to disappear (Zhao et al., 2013; Ghanim et al., 2016) in all chars. Whilst, aromatic skeletal (C=C stretch, 1605 cm<sup>-1</sup>) was significantly enriched. Despite of the similarity with the feedstock, peaks became less and the spectra tended to be more smooth for chars. Owing to the carbonization processes, most groups were expected to be diminished when the feedstocks were pyrolyzed at higher than 400 °C (Chen et al., 2011).

Though increasingly condensed carbon structure was formed during the reactions, the sequestration of total C in chars were decreased (Table 1). This may result from multiple effects, including the decomposition of labile organic matters, the dissolution of low molecular components in the hydrothermal liquids, and the release of transformed organic vapors in the form of gaseous by-products (Table S3), (Ghanim et al., 2016). Compared with pyrochars, hydrochars had much higher char yields but similar C sequestration (Table 1).

Van-Krevelen plot is often employed to illustrate the elemental composition and fuel quality of char-like materials, as well as to elucidate the possible pathway of charring reactions (Guo et al., 2015; Ghanim et al., 2016). As presented in Fig. 2, hydrochars possessed both higher O/C and H/C ratio than pyrochars. Feedstocks like fresh biomass usually have high H/C and O/C values, which will decline owing to the decomposition of components when converted to chars (Guo et al., 2015). Dehydration and decarboxylation are the most important reactions. For hydrochars, it could be noted that the H/C ratio fell by 35.4%, at a less extent compared with the O/C by 61.2%. This may suggest that decarboxylation reaction was more dominant than dehydration reactions (Ghanim et al., 2016). In hydrochars, the high inorganic content, as in the present study, was reported to favor decarboxylation over dehydration (Dieguez-Alonso et al., 2018). Pyrochars stepped in more carbon-rich region in the Van-Krevelen plot (Fig. 2), which was the result of a series of destructive chemical reactions (Ghanim et al., 2016).

The lower O/C and H/C ratios indicated the higher degree of aromaticity and condensation of biochars, thus with higher combustion energy and carbon stability (Aller, 2016). Biochars with O/C in the range of 0.2–0.6 was predicted to have a long half-life of 100–1000 years (Spokas, 2010), which fit the situation of H250, H300 and P350, while for P550 whose O/C ratio was less than 0.2 might have a half-life even longer than 1000 years. Pyrolysis production of biochar was often with higher fuel quality (Ghanim et al.,

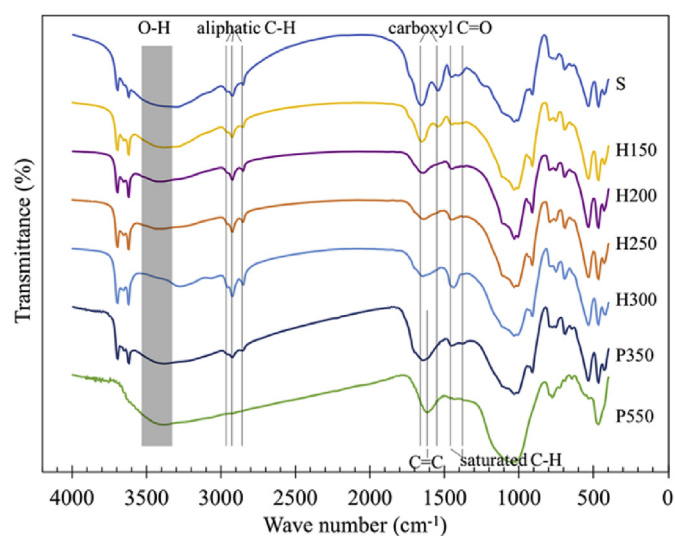
**Table 1**  
Bulk composition and carbon sequestration in sludge and derived chars.

Samples <sup>a</sup>	Ash (%)	Elemental composition (moisture-free, %)				Elemental composition (ash-free, %)				Char yield <sup>b</sup> (%)	Carbon sequestration <sup>c</sup> (%)
		C	H	N	O	C	H	N	O		
S <sup>a</sup>	51.9	18.6	3.37	3.04	23.1	38.6	7.02	6.32	48.0		
H150	71.1	12.6	2.41	1.39	12.6	43.4	8.32	4.81	43.5	92.8	62.9
H180	74.7	12.0	2.23	0.99	10.1	47.2	8.82	3.90	40.0	85.7	55.2
H200	75.9	11.7	2.08	0.82	9.56	48.3	8.60	3.40	39.6	84.2	53.0
H220	76.3	11.6	2.02	0.74	9.36	48.8	8.52	3.12	39.5	83.5	52.1
H250	77.8	11.0	1.86	0.65	8.65	49.7	8.37	2.92	39.0	82.6	48.9
H300	80.4	11.4	1.88	0.78	5.59	57.9	9.58	3.97	28.5	79.7	48.9
P350	67.0	18.7	2.20	3.05	9.02	56.7	6.66	9.23	27.3	68.7	69.2
P550	78.8	15.4	0.96	2.18	2.63	72.8	4.52	10.3	12.4	59.8	49.7

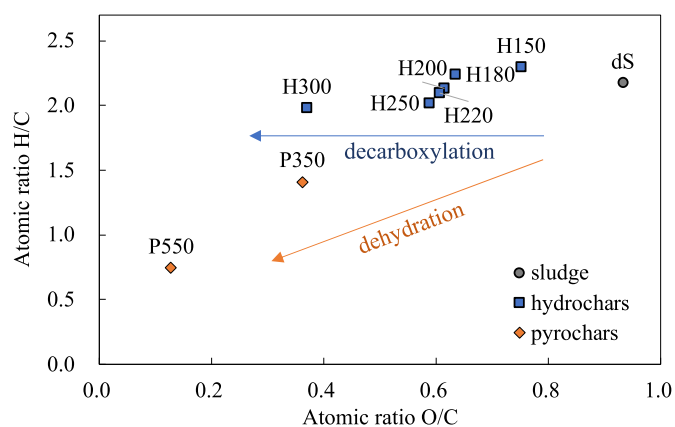
<sup>a</sup> The sample names of S, H and P refer to dry sludge, hydrochar and pyrochar, respectively, and the numbers following H or P refer to the carbonization temperatures of the chars.

<sup>b</sup> Char yields was calculated based on the dry weight of feedstock.

<sup>c</sup> Carbon sequestration ratio are estimated by the equation.



**Fig. 1.** FTIR spectra of sludge and derived chars.



**Fig. 2.** Atomic H/C and O/C ratios in sludge and derived chars.

### 3.2. Physicochemical properties: pH and CEC

When applying biochars as soil additives, pH and CEC are the two important agronomic properties due to their influence on the sorption and transport of nutrients and PTEs (Aller, 2016). Lower pH usually suggests easier leaching of PTEs, whilst higher pH can bring liming effects in the soils to reduce the mobility of cations. As displayed in Fig. 3A, pH values of the sludge derived-chars increased with the treating temperature. Loss of acidic functional groups like carboxyl and hydroxyl groups during the charring process might be one of the main causes (Aller, 2016; Kavitha et al., 2018). All the hydrochars in the present study were acidic (pH = 5.3–6.3), whilst all the pyrochars were slightly alkaline (pH = 7.2–7.9), which was consistent with others' report that hydrochars were usually more acidic than the pyrochars derived from the same feedstock (Fuertes et al., 2010). Compared with most biochars derived from phytomass, the chars in the present study were all more acidic (Purakayastha et al., 2019), which might be resulted from the initial composition including the acidic functional groups and the alkaline minerals of the feedstock. When applying as soil amendment, it should be noted that the sludge derived chars might not be as effective in liming acidified soil as those alkaline biochars.

CEC is another important physicochemical property of biochars since it is usually considered as an index for the capacity of soils to retain water and nutrients (Laird et al., 2010). As data shown in Fig. 3A, the CEC values of the studied chars decreased significantly as the treating temperature was elevated. This is caused by the release of various functional groups in the high temperature charring process, especially carboxyl and hydroxyl groups, which were crucial to attract positive charges and thus correlated closely with CEC (Kavitha et al., 2018). For soils, the CEC value of less than 8 cmol/kg is usually regarded as low, and larger than 20 cmol/kg as very high (Deumlich et al., 2015). The CEC values of the biochars obtained from various feedstocks in others' reports may vary from 6.0 cmol/kg to 66 cmol/kg (Ulyett et al., 2014; Munera-Echeverri et al., 2018). Hydrochars in this work were with much higher CEC values (11.8–25.3 cmol/kg) and should be beneficial to improve soil CEC while the pyrochars showed lower CEC values (1.22–5.10 cmol/kg). It has been reported that sludge derived-hydrochar enhanced soil CEC (Melo et al., 2018), but the practical effects might change depending on the type of chars, properties of the applied soils, as well as the interaction between chars and soils. As a result of CEC changes, nutrients like ammonium could be adsorbed through cation exchange as a preferential process in soils (Ding et al., 2010). On the other hand, CEC is also considered to be relevant with the

2016). From the view of carbon-rich material and solid fuel, the hydrochars obtained in this study, except H300, might be regarded as low quality char, as for only the chars with O/C ratio below 0.4 could be accepted as qualified chars by the European Biochar Certificate (Conte et al., 2015).

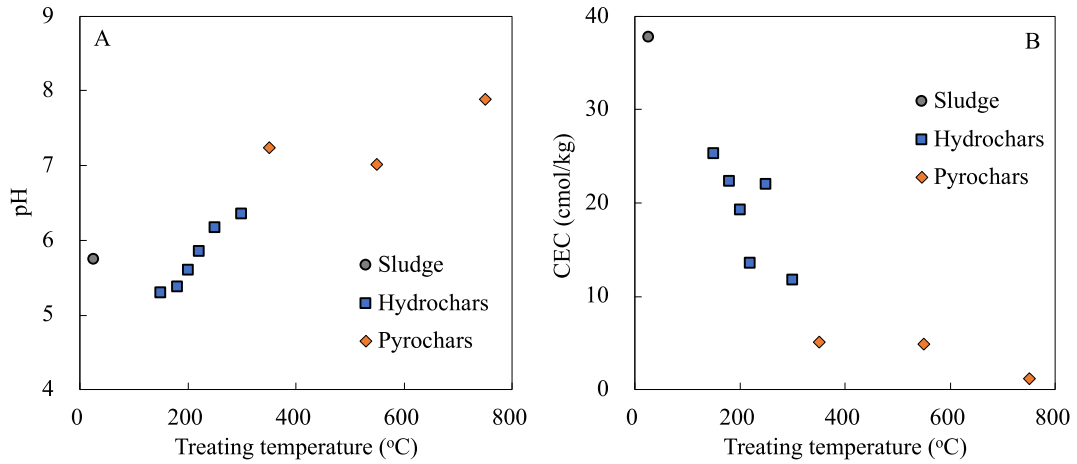


Fig. 3. pH (A) and CEC (B) of sludge and derived chars.

capacity for trace element attraction (Kavitha et al., 2018). With the significant differences in pH and CEC, hydrochars and pyrochars may also vary in the nutrients and PTEs retention and will be evaluated and discussed in the following.

3.3. Content and availability of nutrients: N, P, and K

The total and available content of nutrients are summarized in Fig. 4. As results suggested, the total N decreased by 54.2%–74.4% in HTC process, while it can be largely retained during the pyrolysis even at higher treating temperature (i.e. 0.00% and 60.5% loss at

350 °C and 750 °C, respectively). By calculating the N balance among chars and by-products (Table S4), it could be noticed that most of the N components (54.0%–77.8%) were transformed to liquid and gaseous products in HTC process. The highest liquid N concentration could be found at 200 °C and then more N-containing products turned in gas, indicating a hydrolysis-dissolution-evaporation pathway. It was reported by Liu et al. (2017) that inorganic-N and labile-N could be efficiently converted to more stable forms during HTC. Amino-N could be enriched in the liquid phase first and further decomposed to NH<sub>4</sub><sup>+</sup>-N or NH<sub>3</sub> (Zhuang et al., 2017). By contrast, the loss of N in pyrochars were much less.

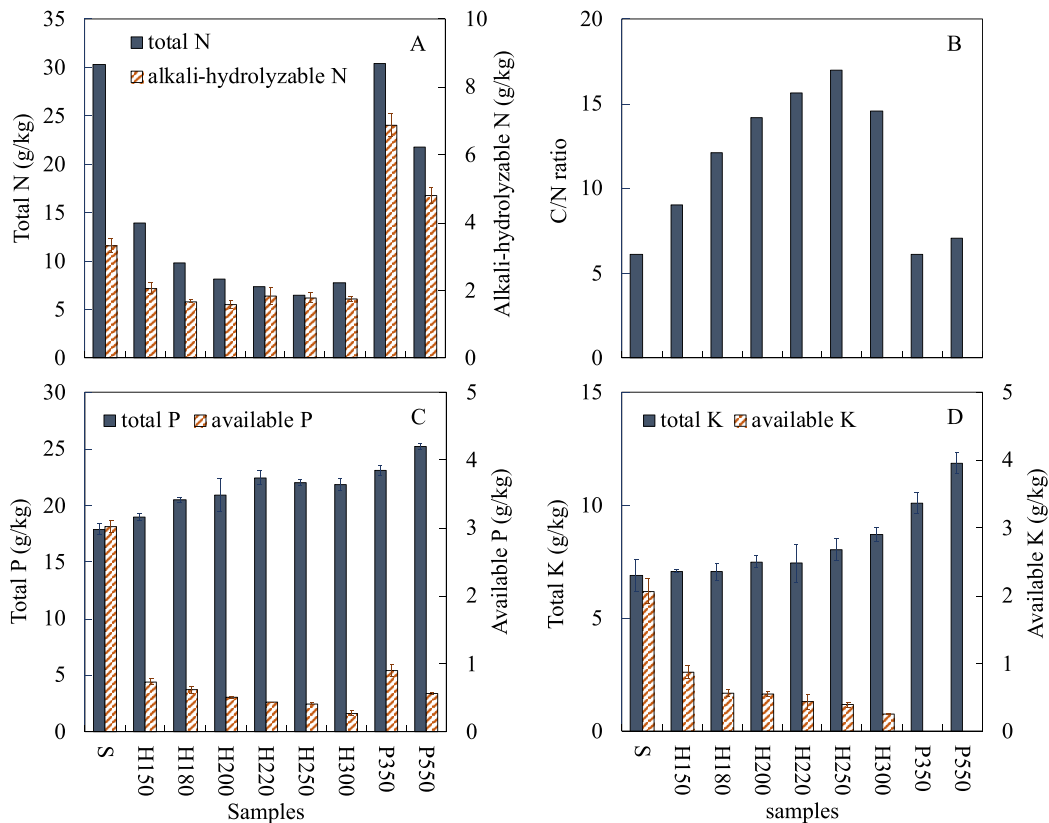


Fig. 4. Total and available contents of N (A), P (C), K (D) and the C/N ratio (B) in sludge and derived chars.

Cracking of N-containing molecules directly produce gaseous products during pyrolysis, counting 25%–53% of total N contents of the feedstock.

HTC transformed certain portion of N into the liquid products, leaving less retained in chars or emitted to gas (Table S4), which was similar to the C sequestration. Emission of gaseous contaminants, including C-containing compounds like polycyclic aromatic hydrocarbons, and N-containing compounds like  $\text{NH}_3$  and HCN, etc., was often an unfavorable issue about pyrolysis (Liu et al., 2017; Ko et al., 2018). From this aspect, HTC demonstrated its environmental benefits of reducing gaseous pollution (Liu et al., 2017; Zhuang et al., 2017). Besides, the HTC process water containing considerable quantity of organic C and amino-N may also provide value-added by-products (Kambo et al., 2018).

Hydrochars in this work showed considerable total N contents (6.48–13.9 g/kg, Fig. 4A) when compared with biochars in literature reports (i.e. 0.4–49 g/kg) (Purakayastha et al., 2019), while the pyrochars (21.8–30.5 g/kg) and the feedstock of dry sludge (30.4 g/kg) were in the high range (Purakayastha et al., 2019). The alkali-hydrolyzable N may be more closely related with the potential benefits in agricultural application (Roberts et al., 2011). The alkali-hydrolyzable N was much higher in pyrochars (4.81–6.87 g/kg) than that in the feedstock of sludge (3.33 g/kg). Though relatively lower than sludge and pyrochars, the alkali-hydrolyzable N in hydrochars (1.58–2.07 g/kg) were still significantly higher than that of the reported soils (i.e. 0.014–0.488 g/kg) (Williams et al., 2007; Roberts et al., 2011), suggesting considerable potential in soil amendment as N fertilizer.

The C/N ratio is considered to be related with the organic matter decomposition and N immobilization in soils. High C/N ratio would lead to reduced soil availability N, and may further reduce the composition of plant litter (Chao et al., 2018) and microbial P demand (Gao et al., 2019). As a result of C sequestration and N decomposition during the charring processes, the C/N ratio in the chars increased along with the HTC or pyrolysis temperature, but hydrochars generally obtained higher C/N ratio than pyrochars (Fig. 4B). However, the chars in the present study had very low C/N ratio (<20) according to Geo et al. (2019)'s category, which could be mainly attributed to the feedstock (Mukome et al., 2013; Geo et al., 2019). This result may suggest that the application of such sludge-derived chars would not cause significant change to soil organic matter decomposition or nutrients immobilization behaviors (Bargmann et al., 2014). But remarkably, the predictability of biochar C/N ratio might be different with that of soil C/N ratio (Chao et al., 2018; Gao et al., 2019). The actual effects of the chars to the nutrients immobilization behavior in the applied soil would be more complex and need to be further examined.

With regard to P, it was enriched in the solid products through either HTC or pyrolysis (Fig. 4C). The highest total P contents (22.5 g/kg) was obtained at 220 °C for HTC, while for pyrolysis higher temperature yielded higher total P contents (23.1–25.2 g/kg). During the charring process, labile fractions from the original sludge was lost due to the reactions like vaporization, degradation, dissolution and other possible mechanisms, while conservative elements such as P were retained in the produced chars (Wang et al., 2016). Benefited from the high initial content of P in the feedstock, sludge-derived chars usually had higher total P contents than chars derived from phytomass (Zhang et al., 2016; Purakayastha et al., 2019).

However, the available P contents (i.e. Olsen-P) in hydrochars (0.270–0.735 g/kg) and pyrochars (0.566–0.901 g/kg) was largely limited compared to the feedstock (3.02 g/kg) (Fig. 4C). In our another study focusing on P transformation and availability (Fei et al., 2019), it was found that soluble and exchangeable P were converted to minerals-bound P. As Fe-containing or/and Al-

containing reagents were often applied in wastewater treatment and then remained in the residual sludge, these minerals provided with chemisorption sites for P retention (Ottosen et al., 2013; Zhang et al., 2016). Nevertheless, the available P contents of the chars were still far higher than those of typical arable soils (<0.02 g/kg) (Zhang et al., 2016) and the recommended P concentration in soils for crop yield (0.045–0.050 g/kg) (Yao et al., 2013). It was proven by our another study that the sludge-derived chars, especially the hydrochars, could be developed as soil P mediator owing to the high P content as well as good ability in soil P retention (Fei et al., 2019).

Similarly, K was also enriched in the chars along with the processing temperature (Fig. 4D), which was consistent with others' report (Tan et al., 2017). According to Purakayastha's summary (2019), K content of biochars derived from various feedstock may vary in a wide range from below 0.0001 g/kg to 264 g/kg. The total K content in the chars obtained in this study (7.06–11.9 g/kg) was comparable with typical sludge-derived pyrochars obtained at the temperature of 300–500 °C (7.47–10.1 g/kg) (Yuan et al., 2016). Though some organic K might be lost due to low thermal-stability, most of the K was remained and converted to stable mineral fractions in the solid products (Yuan et al., 2016; Tan et al., 2017). Thus, it was not surprising to note that the available K was reduced after carbonization (Fig. 4D). However, the available K amount in hydrochars (0.256–0.873 g/kg) was still higher than typical agricultural soils (e.g. <0.1–0.272 g/kg) (Gao et al., 2017; Xiu et al., 2019). Remarkably, the available K was below detection limits in pyrochars, indicating a more severe stabilization of K by pyrolysis, and suggesting its weakness in K fertility when compared with hydrochars. Insufficient K supply was often reported in sludge derived-biochars, and thus it was suggested to add K-rich raw material to co-pyrolyze with sludge in order to make the derived-biochar a more complete source of plant nutrients (Faria et al., 2017). From this point, hydrochars in this study showed a better nutritional balance than pyrochars.

Overall, although available inorganic nutrients (i.e. N, P and K) were reduced after charring treatment, compared with the feedstock sludge, the exact contents of the available nutrients were still far higher than the soil demands. The nutritional values of N, P and K in hydrochars had better balance than pyrochars, and were generally comparable with traditional organic fertilizers (i.e. composts) (Warman and Termeer, 2005; Schulze and Glaser, 2012; Jakubus, 2016). Pot experiment by Melo et al. (2018) indicated significant improvement of soil available and plant uptake of N and P by sludge derived hydrochars. Furthermore, the application of hydrochars to soil showed promising residual effects that could last for a longer time, which was probably benefited from the slow release of nutrients (Melo et al., 2018). However, the elements availability and nutrition uptake efficiency would vary depending on the exact applied soil and the plants. More careful examinations including not only pot experiments but also field trials are required.

### 3.4. PTEs contents and mobility

The total contents of PTEs, i.e. Zn, Cu, Pb, Ni and Cd, were enriched as well (Fig. 5), which was consistent with others' reports (Devi and Saroha, 2014; Lu et al., 2016; Wang et al., 2016). Zn (457–728 mg/kg) and Cu (131–210 mg/kg) were the major PTEs in the sludge and derived chars, followed by Pb (77.2–109 mg/kg), Ni (28.8–40.8 mg/kg) and Cd (1.80–2.44 mg/kg). All the heavy metal contents were below the Chinese control standards of pollutants in sludge for agricultural use (GB 4284-2018), i.e. Zn < 1200 mg/kg, Cu < 500 mg/kg, Pb < 300 mg/kg, Ni < 100 mg/kg and Cd < 3 mg/kg. The enrichment of PTEs was more significant in pyrochars than in hydrochars, probably as the result of more mass loss during pyrolysis than HTC process. Although PTEs might be evaporated under

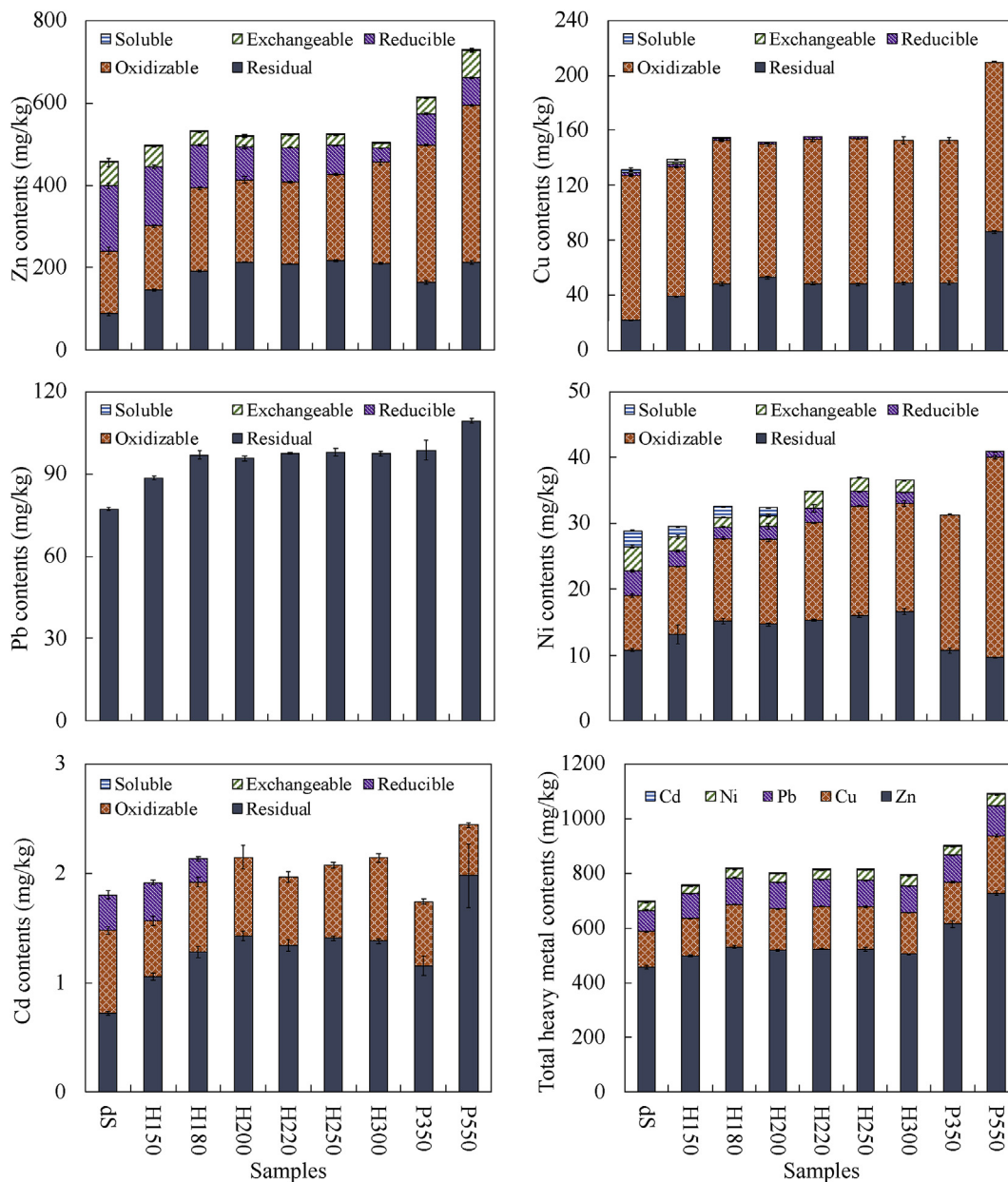


Fig. 5. Potentially toxic elements (Zn, Cu, Pb, Ni and Cd) speciation and total heavy metal contents in sludge and derived chars.

very high temperature, most were retained in the solid products (Devi and Saroha, 2014).

Speciation of PTEs was often closely related to the mobility and bioavailability of the PTEs. Water soluble and exchangeable fractions are easily prone to leaching, and thus are regarded as readily bioavailable. Reducible fractions refer to the fractions that could be released when reduced, e.g. the fractions bound to ferric (hydr) oxides and manganese oxide. Oxidizable fractions refer to the fractions that could be leached when oxidized, e.g. the fractions bound to sulfides and organic matter. The reducible and oxidizable fractions are considered as potentially bioavailable. The residual fraction which is resistant to leaching and degradation is considered as non-bioavailable category (Devi and Saroha, 2014). As results showed (Fig. 5), soluble and exchangeable fractions accounted for small proportions in the sludge, or was even undetectable for Pb and Cd. Most of the PTEs existed in the sludge in the forms of minerals salts, sulfides, hydroxides, oxides, as well as complexed

with organic fractions, i.e. the reducible, oxidizable and even refractory fractions. These results indicated relatively low bioavailability of PTEs in the feedstock sludge.

The soluble and exchangeable fractions could possibly be dissolved and leached during HTC process. However, the concentration of PTEs in the process water was below the detection limit (data not presented), probably due to the initial small proportion of the soluble and exchangeable fractions. The great proportion of the PTEs may be converted to oxide or sulfides with better stability during the thermal and reductive charring condition (Lu et al., 2016). Thus, consistent with previous reports (Devi and Saroha, 2014; Lu et al., 2016), soluble and exchangeable fractions were reduced or disappeared, whilst the oxidizable fraction was the most significantly increased in the derived chars. Two possible processes may contribute to the increase of oxidizable fraction. One was the conversion of heavy metal salts into sulfides. Another was the formation of organic carbon skeleton, which could provide

complexation sites for PTEs. The thermal treatment also gave rise to the incorporation of the PTEs into more stable forms. As a result, the residual fractions of PTEs in the chars were also increased. Results of the speciation distribution indicated that the initially limited bioavailable fractions in the sludge were transformed to potentially bioavailable and non-available fractions in the hydrochars and pyrochars.

Attributed to the fraction transformation, the leaching potential of PTEs was largely reduced. As TCLP results suggested (Table 2), the Pb and Cd concentrations were not detectable in all the leachates. The Zn, Cu and Ni concentration in the leachate of derived chars were all lower than that of the sludge, and the leaching concentration kept decreasing with elevated HTC temperature. Except Zn, none of the other studied PTEs was detectable in pyrochar leachates, suggesting a minimum risk of secondary PTEs pollution. However, the leached Zn from pyrochars were higher than that from hydrochars, and even higher than from the sludge. This was consistent with the results of Zn speciation distribution (Fig. 5A). The exchangeable fraction of Zn in pyrochars was larger than that in the sludge, whilst that was efficiently reduced in hydrochars. The concentration of all the PTEs in the leachate was below the threshold, suggesting the very limited risk of secondary PTEs pollution by the chars if applied to soil.

When the chars are applied to soil, the mobility, bioavailability and ecotoxicity of PTEs in the sludge derived-chars would vary a lot, depending on the soil properties such as soil pH, organic matter, minerals and redox condition, and also the plant behaviors, such as the uptake capacity and detoxication ability. In the pot experiment reported by Melo et al. (2018), PTEs like Zn and Cu were introduced by the sludge derived-hydrochars, nevertheless no phytotoxicity was observed. Even though, the long-term risk of pollution may still need to be carefully examined, especially for the case of accumulative application in practice.

#### 4. Conclusions

Additionally to C content, elemental composition and basic physicochemical properties, value of nutrients and risk of PTEs in sludge derived hydrochars were examined and compared with pyrochar in the present study. Results could be summarized as follows:

- The carbon sequestration, long-term stability and potential fuel quality of hydrochars may not be comparable as the traditional biochar, i.e. pyrochars. Application for agricultural improvement might be a more suitable way for hydrochar utilization.
- The pH of hydrochars were more acidic than that of pyrochars, and the CEC were significantly higher.
- The available content of N (1.58–6.87 g/kg), P (0.270–0.901 g/kg), and K (0–0.873 g/kg) in the chars was reduced compared

**Table 2**  
TCLP of potentially toxic elements in sludge and derived chars.

	Zn mg/L	Cu	Pb	Ni	Cd
S	1.313	0.100	–	0.154	–
H150	1.085	0.108	–	0.103	–
H180	0.599	0.042	–	0.088	–
H200	0.425	0.026	–	0.064	–
H220	0.508	–	–	0.083	–
H250	0.462	–	–	0.081	–
H300	0.361	–	–	0.094	–
P350	1.237	–	–	–	–
P550	2.620	–	–	–	–
Limit <sup>a</sup>	5	–	5	5	1

<sup>a</sup> From (EPAUS, 1990).

with the feedstock sludge (3.33 g/kg N, 3.02 g/kg P, 2.07 g/kg K), but still far higher than that of the agricultural soil (i.e. 0.014–0.488 g/kg N, 0.02 g/kg P, <0.1–0.272 g/kg). Hydrochars showed better nutritional balance than pyrochars for its higher available K content.

- Risk of PTEs (i.e. Cu, Pb, Ni and Cd) contamination by the sludge was efficiently reduced through either HTC or pyrolysis. The leaching potential evaluated by TCLP was all under the threshold and decreased with the HTC or pyrolysis temperature. Except that the leaching potential of Zn was increased in pyrochars, that of PTEs was reduced efficiently in all the hydrochars.

Overall, hydrochars derived from sludge could be a feasible material as soil amendment for its values in CEC and nutrients. Further careful examination in practical application was kindly suggested, for the reason that the statement summarized above was based on simple mass analysis while more complex mediation processes would occur in actual soils.

Besides, compared with pyrolysis, HTC would also produce process water with considerable concentration of organic C, N and undetectable PTEs for safe value-added recycling, which was another characteristic advantage of HTC than pyrolysis besides the advantage of energy-saving in handling high-moisture feedstocks.

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#### Appendix A. Supplementary data

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#### References

- Aller, M.F., 2016. Biochar properties: transport, fate, and impact. *Crit. Rev. Environ. Sci. Technol.* 46, 1183–1296.
- Bargmann, I., Rillig, M.C., Kruse, A., Greef, J., Kucke, M., 2014. Effects of hydrochar application on the dynamics of soluble nitrogen in soils and on plant availability. *J. Plant Nutr. Soil Sci.* 177, 48–58.
- Chao, L., Zhang, W.D., Wang, S.L., 2018. Understanding the dominant controls on biochar decomposition using boosted regression trees. *Eur. J. Soil Sci.* 69, 512–520.
- Chen, B., Chen, Z., Lv, S., 2011. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour. Technol.* 102, 716–723.
- Conte, P., Schmidt, H.P., Cimo, G., 2015. Research and application of biochar in Europe. In: Guo, M.e.a. (Ed.), *Agricultural and Environmental Applications of Biochar: Advances and Barriers*. Soil Science Society of America, Madison, WI, pp. 409–422.
- Deumlich, D., Thiere, J., Altermann, M., 2015. Characterization of cation exchange capacity (CEC) for agricultural land-use areas. *Arch. Agron Soil Sci.* 61, 767–784.
- Devi, P., Saroha, A.K., 2014. Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. *Bioresour. Technol.* 162, 308–315.
- Dieguez-Alonso, A., Funke, A., Anca-Couce, A., Rombola, A.G., Ojeda, G., Bachmann, J., Behrendt, F., 2018. Towards biochar and hydrochar engineering-influence of process conditions on surface physical and chemical properties, thermal stability, nutrient availability, toxicity and wettability. *Energies* 11, 26.
- Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. *Water Air Soil Pollut.* 213, 47–55.



- EPAUS, 1990. Method 1311, Toxicity Characteristic Leaching Procedure.
- Faria, W.M., de Figueiredo, C.C., Coser, T.R., Vale, A.T., Schneider, B.G., 2017. Is sewage sludge biochar capable of replacing inorganic fertilizers for corn production? Evidence from a two-year field experiment. *Arch. Agron Soil Sci.* 1–15.
- Fei, Y.H., Zhao, D., Cao, Y.D., Huot, H., Tang, Y.T., Zhang, H.G., Xiao, T.F., 2019. Phosphorus retention and release by sludge-derived hydrochar for potential use as a soil amendment. *J. Environ. Qual.* 48, 502–509.
- Fuertes, A.B., Arbestain, M.C., Sevilla, M., Macia-Agullo, J.A., Fiol, S., Lopez, R., Smernik, R.J., Aitkenhead, W.P., Arce, F., Macias, F., 2010. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. *Aust. J. Soil Res.* 48, 618–626.
- Gao, L., Wang, R., Shen, G.M., Zhang, J.X., Meng, G.X., Zhang, J.G., 2017. Effects of biochar on nutrients and the microbial community structure of tobacco-planting soils. *J. Soil Sci. Plant Nutr.* 17, 884–896.
- Gao, S., DeLuca, T.H., Cleveland, C.C., 2019. Biochar additions alter phosphorus and nitrogen availability in agricultural ecosystems: a meta-analysis. *Sci. Total Environ.* 654, 463–472.
- Ghanim, B.M., Pandey, D.S., Kwapinski, W., Leahy, J.J., 2016. Hydrothermal carbonisation of poultry litter: effects of treatment temperature and residence time on yields and chemical properties of hydrochars. *Bioresour. Technol.* 216, 373–380.
- Guo, S., Dong, X., Wu, T., Shi, F., Zhu, C., 2015. Characteristic evolution of hydrochar from hydrothermal carbonization of corn stalk. *J. Anal. Appl. Pyrolysis* 116, 1–9.
- Jakubus, M., 2016. Estimation of phosphorus bioavailability from composted organic wastes. *Chem. Speciat. Bioavailab.* 28, 189–198.
- Kambo, H.S., Minaret, J., Dutta, A., 2018. Process water from the hydrothermal carbonization of biomass: a Waste or a valuable product? *Waste and Biomass Valorization* 9, 1181–1189.
- Kavitha, B., Reddy, P.V.L., Kim, B., Lee, S.S., Pandey, S.K., Kim, K.H., 2018. Benefits and limitations of biochar amendment in agricultural soils: a review. *J. Environ. Manag.* 227, 146–154.
- Ko, J.H., Wang, J.C., Xu, Q.Y., 2018. Impact of pyrolysis conditions on polycyclic aromatic hydrocarbons (PAHs) formation in particulate matter (PM) during sewage sludge pyrolysis. *Chemosphere* 208, 108–116.
- Kruse, A., Zevaco, T.A., 2018. Properties of hydrochar as function of feedstock, reaction conditions and post-treatment. *Energies* 11, 12.
- Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B.Q., Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* 158, 443–449.
- Li, J., Li, Y., Wu, Y., Zheng, M., 2014. A comparison of biochars from lignin, cellulose and wood as the sorbent to an aromatic pollutant. *J. Hazard Mater.* 280, 450–457.
- Liu, T.T., Guo, Y.C., Peng, N.N., Lang, Q.Q., Xia, Y., Gai, C., Liu, Z.G., 2017. Nitrogen transformation among char, tar and gas during pyrolysis of sewage sludge and corresponding hydrochar. *J. Anal. Appl. Pyrolysis* 126, 298–306.
- Lu, T., Yuan, H., Wang, Y., Huang, H., Chen, Y., 2016. Characteristic of heavy metals in biochar derived from sewage sludge. *J. Mater. Cycles Waste Manag.* 18, 725–733.
- Melo, T.M., Bottlinger, M., Schulz, E., Leandro, W.M., de Aguiar Filho, A.M., Wang, H., Ok, Y.S., Rinklebe, J., 2018. Plant and soil responses to hydrothermally converted sewage sludge (sewchar). *Chemosphere* 206, 338–348.
- Mukome, F.N.D., Zhang, X., Silva, L.C.R., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J. Agric. Food Chem.* 61, 2196–2204.
- Munera-Echeverri, J.L., Martinsen, V., Strand, L.T., Zivanovic, V., Cornelissen, G., Mulder, J., 2018. Cation exchange capacity of biochar: an urgent method modification. *Sci. Total Environ.* 642, 190–197.
- Nizamuddin, S., Siddiqui, M.T.H., Baloch, H.A., Mubarak, N.M., Griffin, G., Madapusi, S., Tanksale, A., 2018. Upgradation of chemical, fuel, thermal, and structural properties of rice husk through microwave-assisted hydrothermal carbonization. *Environ. Sci. Pollut. Control Ser.* 25, 17529–17539.
- Olsen, S.R., 2019. Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate. United States Department of Agriculture, Washington.
- Ottosen, L.M., Kirkelund, G.M., Jensen, P.E., 2013. Extracting phosphorus from incinerated sewage sludge ash rich in iron or aluminum. *Chemosphere* 91, 963–969.
- Purakayastha, T.J., Bera, T., Bhaduri, D., Sarkar, B., Mandal, S., Wade, P., Kumari, S., Biswas, S., Menon, M., Pathak, H., Tsang, D.C.W., 2019. A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security. *Chemosphere* 227, 345–365.
- Purakayastha, T.J., Kumari, S., Pathak, H., 2015. Characterisation, stability, and microbial effects of four biochars produced from crop residues. *Geoderma* 239, 293–303.
- Roberts, T.L., Ross, W.J., Norman, R.J., Slaton, N.A., Wilson, C.E., 2011. Predicting nitrogen fertilizer needs for rice in Arkansas using alkaline hydrolyzable-nitrogen. *Soil Sci. Soc. Am. J.* 75, 1161–1171.
- Rohrdanz, M., Rebling, T., Ohlert, J., Jasper, J., Greve, T., Buchwald, R., von Frieling, P., Wark, M., 2016. Hydrothermal carbonization of biomass from landscape management - influence of process parameters on soil properties of hydrochars. *J. Environ. Manag.* 173, 72–78.
- Schulze, H., Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *J. Plant Nutr. Soil Sci.* 175, 410–422.
- Schulze, M., Mummie, J., Funke, A., Kern, J., 2016. Effects of selected process conditions on the stability of hydrochar in low-carbon sandy soil. *Geoderma* 267, 137–145.
- Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Manag.* 1, 289–303.
- Tan, Z.X., Liu, L.Y., Zhang, L.M., Huang, Q.Y., 2017. Mechanistic study of the influence of pyrolysis conditions on potassium speciation in biochar "preparation-application" process. *Sci. Total Environ.* 599, 207–216.
- Tsang, D.C.W., Olds, W.E., Weber, P.A., Yip, A.C.K., 2013. Soil stabilisation using AMD sludge, compost and lignite: TCLP leachability and continuous acid leaching. *Chemosphere* 93, 2839–2847.
- Ul Saqib, N., Baroutian, S., Sarmah, A.K., 2018. Physicochemical, structural and combustion characterization of food waste hydrochar obtained by hydrothermal carbonization. *Bioresour. Technol.* 266, 357–363.
- Ulyett, J., Sakrabani, R., Kibblewhite, M., Hann, M., 2014. Impact of biochar addition on water retention, nitrification and carbon dioxide evolution from two sandy loam soils. *Eur. J. Soil Sci.* 65, 96–104.
- Wang, L.P., Li, A.M., Chang, Y.Z., 2016. Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering: heavy metals, volatile organic compounds and combustion characteristics of hydrochar. *Chem. Eng. J.* 297, 1–10.
- Warman, P.R., Termeer, W.C., 2005. Evaluation of sewage sludge, septic waste and sludge compost application to corn and forage: yields and N, P and K content of crops and soils. *Bioresour. Technol.* 96, 955–961.
- Williams, J.D., Crozier, C.R., White, J.G., Heiniger, R.W., Sripada, R.P., Crouse, D.A., 2007. Illinois soil nitrogen test predicts southeastern US corn economic optimum nitrogen rates. *Soil Sci. Soc. Am. J.* 71, 735–744.
- Xiu, L.Q., Zhang, W.M., Sun, Y.Y., Wu, D., Meng, J., Chen, W.F., 2019. Effects of biochar and straw returning on the key cultivation limitations of Albic soil and soybean growth over 2 years. *Catena* 173, 481–493.
- Yao, Y., Gao, B., Chen, J.J., Yang, L.Y., 2013. Engineered biochar reclaiming phosphate from aqueous solutions: mechanisms and potential application as a slow-release fertilizer. *Environ. Sci. Technol.* 47, 8700–8708.
- Yuan, H.R., Lu, T., Wang, Y.Z., Chen, Y., Lei, T.Z., 2016. Sewage sludge biochar: nutrient composition and its effect on the leaching of soil nutrients. *Geoderma* 267, 17–23.
- Zhang, H.Z., Chen, C.R., Gray, E.M., Boyd, S.E., Yang, H., Zhang, D.K., 2016. Roles of biochar in improving phosphorus availability in soils: a phosphate adsorbent and a source of available phosphorus. *Geoderma* 276, 1–6.
- Zhao, L., Cao, X., Masek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. *J. Hazard Mater.* 256, 1–9.
- Zhuang, X.Z., Huang, Y.Q., Song, Y.P., Zhan, H., Yin, X.L., Wu, C.Z., 2017. The transformation pathways of nitrogen in sewage sludge during hydrothermal treatment. *Bioresour. Technol.* 245, 463–470.