

Speciation Dynamics of Phosphorus during (Hydro)Thermal Treatments of Sewage Sludge

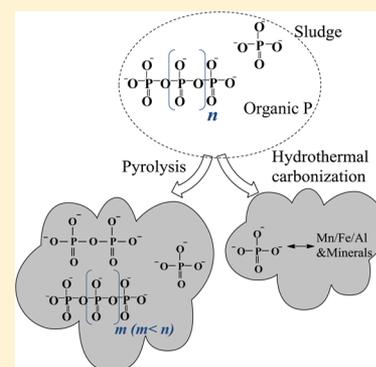
Rixiang Huang and Yuanzhi Tang*

School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr, Atlanta, Georgia 30324-0340, United States

S Supporting Information

ABSTRACT: (Hydro)thermal treatments of sewage sludge from wastewater treatment process can significantly reduce waste volume and transform sludge into valuable products such as pyrochar and hydrochar. Given the global concern with phosphorus (P) resource depletion, P recycling/reclamation from or direct soil application of the derived chars can be potential P recycling practices. In order to evaluate P recyclability as well as the selection and optimization of treatment techniques, it is critical to understand the effects of different treatment techniques and conditions on P speciation and distribution. In the present study, we systematically characterized P speciation in chars derived from thermal (i.e., pyrolysis) and hydrothermal treatments of municipal sewage sludge using complementary chemical extraction and nuclear magnetic resonance (NMR) spectroscopy methods. P species in the raw activated sludge was dominated by orthophosphate and long-chain polyphosphates, whereas increased amounts of pyrophosphate and short-chain polyphosphates formed after pyrolysis at 250–600 °C. In contrast, hydrothermal treatments resulted in the production of only inorganic orthophosphate in the hydrochar.

In addition to the change of molecular speciation, thermal treatments also altered the physical state and extractability of different P species in the pyrochars from pyrolysis, with both total P and polyphosphate being less extractable with increasing pyrolysis temperature. Results from this study suggest that P speciation and availability in sludge-derived chars are tunable by varying treatment techniques and conditions, and provide fundamental knowledge basis for the design and selection of waste management strategies for better nutrient (re)cycling and reclamation.



INTRODUCTION

Tremendous amounts of sewage sludges are being produced as the byproducts of wastewater treatment processes, bringing a daunting task for the solid waste management industry. In addition to the intrinsic high water content and large volume, sludges often contain a wide range of organic and inorganic contaminants, such as heavy metals, pesticides, herbicides, microorganisms, and pharmaceuticals and personal care products (PPCPs).^{1,2} On the other hand, sludges also consist of various nutrients and valuable metals at relatively high concentrations, and are increasingly recognized and treated as a resource for the recycling of critical nutrients such as phosphorus (P).³ In fact, a significant portion of P consumed by human activities is ultimately converged into wastewater treatment plants (WWTPs), making the sludges from WWTPs a great resource for P recycling and reclamation.^{4,5} For example, enhanced biological phosphorus removal (EBPR) technique with the precipitation of inorganic P fertilizers (e.g., struvite) is a common P recycling practice by WWTPs.

In recent years, thermal (e.g., pyrolysis) and hydrothermal treatments (e.g., hydrothermal carbonization; HTC) of sewage sludge have emerged as sustainable treatment techniques, because they can significantly decompose organic pollutants, reduce waste volume, and generate valuable byproducts (e.g., pyrochar from thermal treatments or hydrochar from hydro-

thermal treatments).^{6–9} During the production of chars, nutrients (e.g., P) mostly remain in the solid phase,^{6,10} making it a char-P composite with many potential applications, such as P reclamation from HTC produced hydrochars with acid extraction.¹¹ (Bio)chars produced from thermal treatments have also been recognized as good soil amendments to adjust soil physical and chemical properties and improve soil qualities.¹² With the significant decomposition of organic contaminants during thermal treatment processes, direct soil application of such char-P composite can also be an excellent alternative P recycling and fertilization practice with all the added benefits from chars.

One critical knowledge gap for the above-mentioned and any other P recycling/reclamation approaches is the evolution of P speciation during the thermal treatments, as it is well-known that the speciation of an element determines its mobility, transport, fate, and bioavailability. Speciation is defined as the chemical (e.g., oxidation state, molecular configuration, chemical phase) and physical states (e.g., distribution, association with other phases) of an element. In the case of

Received: August 26, 2015

Revised: November 12, 2015

Accepted: November 13, 2015

Published: November 13, 2015

phosphorus, it can exist in different molecular configurations (e.g., orthophosphate, phosphonate, organic phosphates, and polyphosphate) and these different entities can be present in different chemical states (e.g., cation complexes, surface adsorbed species on other minerals, incorporation into other mineral phases, or precipitation as P-containing minerals). Physically, these different P forms are likely to distribute heterogeneously within the solid feedstock and immigrate between solid and liquid phase during specific preconditioning or treatment processes. Thus, understanding the dynamic evolution of P speciation in the feedstock and the chars produced from (hydro)thermal treatments will provide fundamental knowledge basis for the evaluation, design, and development of suitable recycling and reclamation strategies. A variety of techniques can be used to characterize P speciation in environmental matrix such as soil, sediments, and wastes, such as sequential extraction, ^{31}P solid state NMR, chemical extraction coupled with liquid ^{31}P NMR, P K-edge X-ray adsorption spectroscopy, each with its own advantages and intrinsic limitations.^{13–15}

Although a few studies have tested pyrolysis¹⁶ and hydrothermal treatments⁶ for the transformation of sludge into char, little information exist on a systematic description of the change of P speciation during these treatments. For the few existing studies that characterized the P behavior during different treatment processes, P speciation was achieved indirectly through operationally defined fractionation and characterization methods.^{10,17} However, some of these fractionation methods could potentially alter the speciation of P during the extraction process.^{18–20} Also, operationally defined P fractions are not equivalent to specific chemical species or molecular structures.

In this study, we systematically characterized P speciation in raw sludges (activated and anaerobically digested sludge) as well as the pyro- and hydrochars derived from pyrolysis and hydrothermal carbonization (HTC) treatments of the sludges under varied conditions. Solid state ^{31}P nuclear magnetic resonance (NMR) spectroscopy was used to directly characterized P speciation in the feedstock and the derived chars. Liquid ^{31}P NMR was used to characterize the extractable P fraction from the solids to help validate the P speciation change in the solid and provide insights for the relatively labile P fractions for potential recycling and fertilization applications. The primary goal of this study is to understand the effect of treatment techniques and conditions on the transformation of different P entities, in order to provide critical knowledge basis for the potential application of (hydro)thermal treatments for sludge management and nutrient recycling/reclamation.

■ EXPERIMENTAL SECTION

Sludge Collection and Pretreatment. Sewage sludges were collected from F. Wayne Hill Water Resources Center (Gwinnett County, Atlanta, GA). The treatment plant has primary (physical), secondary (biological), and tertiary (membrane filtration) treatment units for treating municipal sewage from the County. Activated sludge was the waste sludge from the secondary treatment prior to dewatering treatment for anaerobic digestion, and anaerobically digested sludge was collected from the anaerobic digester receiving the activated sludge and primary sludge. The activated sludge collected still contains high amount of water, thus was centrifuged to further concentrate the sludge to ~26% dry mass content before storage at $-20\text{ }^{\circ}\text{C}$. The anaerobic digested sludge (dry mass

content ~21%) was stored at $-20\text{ }^{\circ}\text{C}$ without any pretreatment. For hydrothermal carbonization, a portion of both frozen samples was thawed at room temperature prior to treatments. For pyrolysis, a portion of both samples was freeze-dried before treatments. The activated sludge sample represents sludge in its most unprocessed form, while the anaerobic sludge represents sludge experienced common processing (mixing with sludges from other units, dewatering, and anaerobic digestion). Details of the sampling and the chemical characteristics of these sludges are presented in Table S1.

Pyrolysis and Hydrothermal Carbonization. Pyrolysis is a dry thermochemical process typically conducted on dry feedstock in the absence of oxygen and at elevated temperatures, whereas HTC is a wet thermochemical process that operates at relatively low temperature in combination with the autogenic pressure, and does not require specific atmosphere. Both of which can transform biomass into carbonaceous materials, while HTC has the advantage of accommodating wet feedstock. Pyrolysis of the activated sludge was conducted in a tube furnace (Thermo Scientific) under N_2 flow (~1 mL/sec) at 250, 350, 450, and 600 $^{\circ}\text{C}$, with a heating and cooling rate of 200 $^{\circ}\text{C}/\text{h}$ and a soaking duration of 4 h. The anaerobic sludge was treated at only at 450 $^{\circ}\text{C}$. For each treatment condition, 1.0 g of dried activated sludge was added into a crucible and inserted into the glass tube. All samples were processed in duplicates.

Hydrothermal carbonation (HTC) treatments used a solid:liquid ratio of 1:9 (w/w). To achieve this, 4 g centrifuged wet paste of activated sludge or anaerobic sludge (equivalent to ~1 g dried mass) and 6 g solution (DI water or 5% HNO_3) were mixed in a 20 mL Teflon lined stainless steel hydrothermal reactor (Parr instrument). The reactor was sealed and heated in an oven at 225 $^{\circ}\text{C}$ for 24 h, then allowed to naturally cool down to 50 $^{\circ}\text{C}$ in an oven for overnight. Solid hydrochar produced from HTC was collected by centrifugation, and was dried at 70 $^{\circ}\text{C}$ for at least 24 h until no further weight loss. All samples were processed in duplicates.

Both raw and treated sludges were characterized for the content and speciation of total P, as well as P in the liquid extracts and solid residuals of sludges and chars after P extraction (see section below).

P Extraction. P extraction was conducted on the raw sludges and chars to assess the speciation of the extractable P portion from these solids. A portion of the freeze-dried sludges and their (hydro)thermal-derived chars were extracted using a solution containing 0.25 M NaOH and 0.05 M EDTA at a solid:liquid ratio of 0.2:4 g/mL and was shaken at 150 rpm for 16 h at room temperature. At the end of extraction, liquid extracts and solid residuals were separated by centrifugation. All extractions were conducted in duplicates. The liquid extract and residual solids were analyzed for P content using combustion and for P speciation using liquid and solid state ^{31}P nuclear magnetic resonance (NMR) spectroscopy. This NaOH/EDTA extraction method has been widely used for P extraction from various environmental matrix²¹ including sludge^{22,23} and has been demonstrated to be a relatively effective P extraction method with high P extraction efficiency and with the most diverse P peaks by liquid NMR analysis, suggesting more representativeness and less destruction than other extraction methods.^{24,25}

P Content Quantification. Concentrations of P in all liquid or solid samples were measured using a combustion method. Solid samples were combusted at 600 $^{\circ}\text{C}$ for 2 h in a

furnace, followed by an HCl extraction (1 M) for 16 h. The total P in the extract was analyzed as orthophosphate using the ascorbic acid assay²⁶ on an UV–vis spectrophotometer (Carey 60, Agilent). To quantify P in the liquid NaOH/EDTA extracts, due to the presence of organics, the solution was dried first, followed by the above-mentioned combustion and acid extraction steps before quantification.

³¹P Solid State NMR Analysis. Solid-state ³¹P NMR spectra were acquired on the raw sludges and their derived chars with magic angle spinning (MAS) and proton decoupling on a Bruker Avance 400 spectrometer operated at a ³¹P frequency of 161.9 MHz. Solid samples (~20 mg) were packed into the insets for a 4 mm diameter zirconia rotor with Kel-F Caps (Wilmad, NJ) and spun at 12 kHz. Direct polarization (DP) data collection parameters were 2048 data points (TD) over an acquisition time (AQ) of 12.6 ms, a recycle delay (RD) of 180 s, and 128 scans. Variable RD experiments were conducted and 180 s were verified to be sufficient to prevent signal saturation during data acquisition (see [Supporting Information, Figure S3](#)). The DP-MAS ³¹P NMR spectra were acquired with a ³¹P 90° pulse of 5.0 μs and an attenuation level (PL1) of 12.1 dB. Chemical shifts were externally referenced to NH₄H₂PO₄ at 0.72 ppm. ³¹P spin counting experiments were based on Dougherty et al.,²⁷ where NH₄H₂PO₄ was used as an external intensity standard, and its ³¹P DP NMR spectrum was acquired in one scan after equilibration for 1000 s (16.7 min). ³¹P{¹H} cross-polarization (CP)/MAS spectra were also collected on activated sludge and its hydrochar, as well as anaerobic sludge. The CP contact time was set at 1 ms, and 960 scans were collected for all samples.

³¹P Liquid NMR Analysis. Because the P concentration in the extracted solution is high enough, the supernatant (600 μL) was directly mixed with D₂O (100 μL) for liquid ³¹P NMR measurements without further drying and resuspension. NMR spectra of the liquid samples were obtained using a Bruker AMX 400 MHz spectrometer operated at 162 MHz at 297 K. Parameters of 90° pulse width, 6.5k data points (TD) over an acquisition time of 0.51 s, and relaxation delay of 15 s were applied. T1 value of all phosphorus signals in the activated sludge extracts (which has the most peaks) was determined in preliminary inversion–recovery experiments, which showed that all the signals have a T1 less than 3 s, thus a relaxation time of 15 s was used. Between 256 and 512 scans were acquired for each sample. An 85% H₃PO₄ was used as the external standard for chemical shift calibration.

RESULTS AND DISCUSSION

Overall Characteristics of the Raw Sludges and Their Derived Chars. The sources and general chemical characteristics of the untreated activated and anaerobically digested sludges were present in [Table S1](#). The ash and metal content in the anaerobic sludge agree with previously reported range,^{16,28} and are higher than that of activated sludge due to the mixing of other sludges in anaerobic digester. We quantified the mass recovery of chars under different treatment conditions, total P content, and P recovery rates in the sludge-derived pyro- and hydro-chars ([Figure S1](#)). Information regarding sample nature, thermal treatment conditions, sample labeling, and sample characterizations can be found in [Table S2](#). For pyrolysis, P content increased with increasing temperature due to the loss of solid mass and the remaining of P in solid phase. For HTC treatment, mass recovery with DI and 0.5% HNO₃ treatments was 37% and 32%, respectively, and P content was 7.9% and

7.2%, respectively. The lower P recovery in HTC compared to pyrolysis is due to the dissolution of phosphate into the processed water ([Figure 2B](#)). FT-IR spectra confirmed the transformation of the carbohydrate (biomass) dominated feedstock to aromatics-intense chars after thermal treatment ([Figure S2](#)).²⁹

Both solid and liquid state ³¹P NMR were used to characterize the speciation of P in raw and treated sludges. Since the quantitative analysis of P by solid state NMR relies on the maximum observation of P in the sample,^{27,30} variable recycle delays were tested to determine the minimal recycle delay. Spin counting experiments were also conducted to quantify the percentage of P being observed. As shown in the series of spectra collected for activated sludge, maximum intensity was achieved at 180 s recycle delays ([Figure S3](#)). Spin counting experiments showed that more than 85% of the P were observed for activated sludge and its chars pyrolyzed at 250 and 450 °C, with only 49%, 40%, and 30.9% for anaerobic sludge, 600 °C char and HTC hydrochars, respectively. The low P observation in anaerobic sludge and HTC hydrochars is most likely due to the homogenization of P species and their subsequent direct interactions with paramagnetic metals such as Fe and Mn. Indeed, sewage sludges commonly consist of abundant Fe (3 and 9% in this study) and studies have shown increasing association between heavy metals and phosphate upon aging.^{2,28}

Microorganisms in WWTPs remove phosphorus from wastewater and store it in a wide range of organic and inorganic forms at different cellular locations.^{31–34} As is shown in the NMR spectrum of activated sludge ([Figure 1](#)), there are broad signals ranging from 10 to –40 ppm and with two distinctive peaks. Signal from the low field (more positive

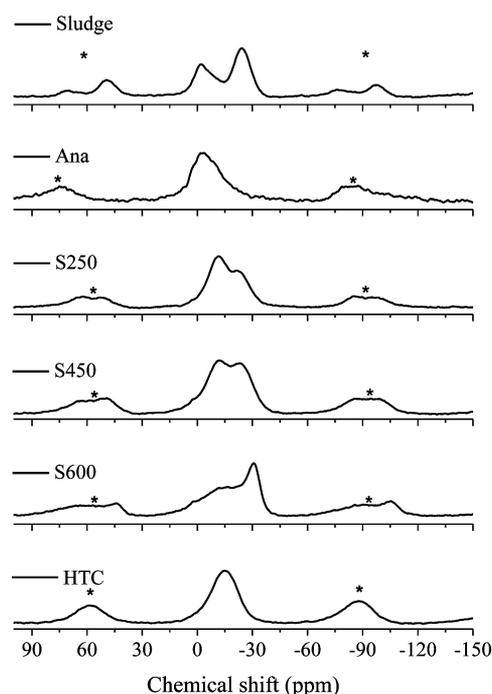


Figure 1. ³¹P solid-state NMR spectra of raw activated sludge (Sludge), raw anaerobically digested sludge (Ana), and the chars produced from HTC and pyrolysis (250, 450 and 600 °C) treatments of the activated sludge (HTC, S250, S450, and S600, respectively). Asterisks denote spinning side bands.

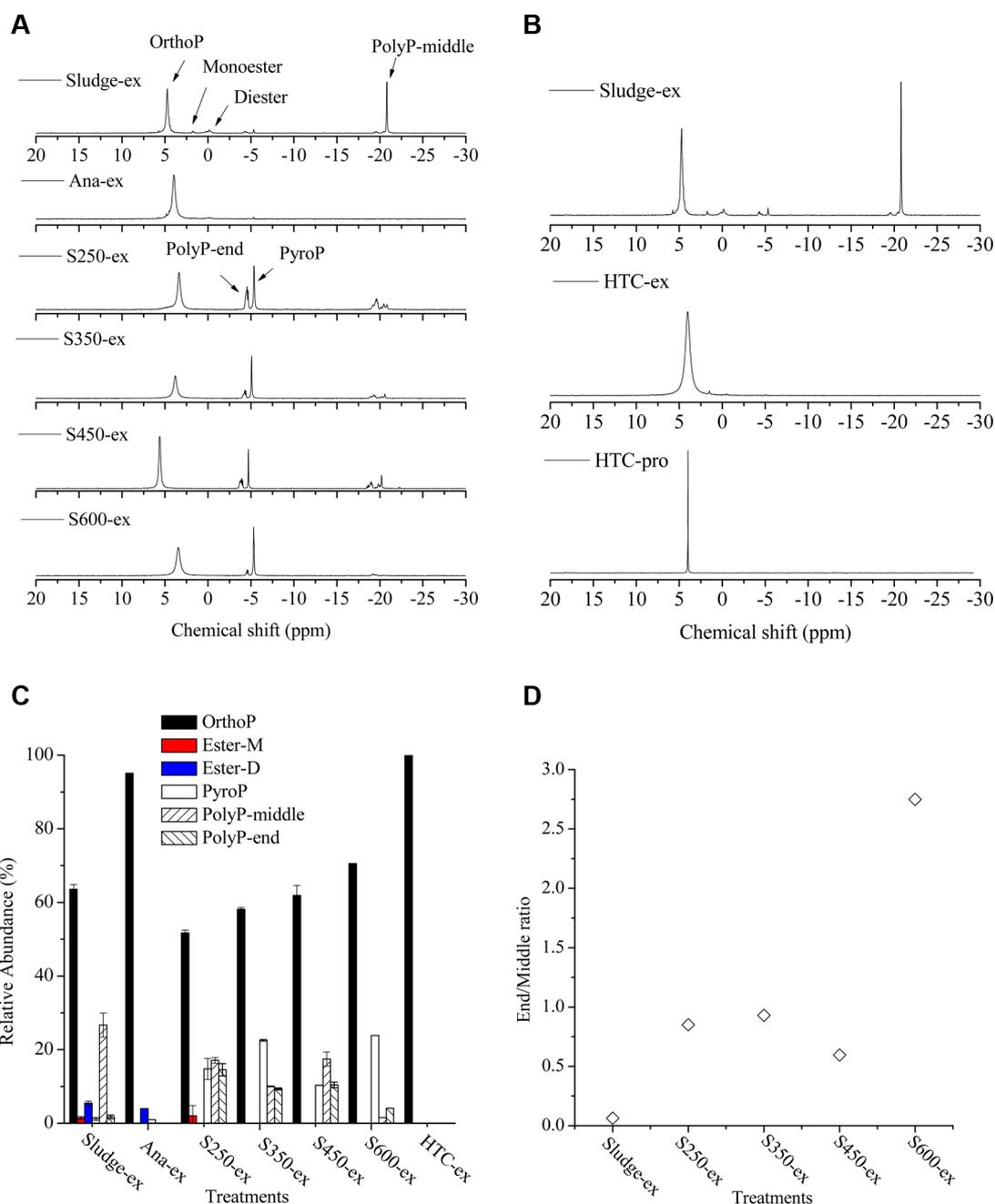


Figure 2. (A) ^{31}P liquid NMR spectra of the extracts from activated sludge (Sludge-ex), anaerobically digested sludge (Ana-ex) and pyrochars produced at 250–600 °C (S250-ex to S600-ex). (B) Spectra of the extracts from activated sludge, its hydrochar extract (HTC-ex), and the processed water from the HTC treatment (HTC-pro). Chemical shifts for main P species are labeled, including orthophosphate (OrthoP), monoester P species (Monoester), diester P species (Diester), polyphosphate middle P groups (PolyP-middle), polyphosphate end P groups (PolyP-end), and pyrophosphate (PyroP). (C) Relative abundance of different P species in the liquid extracts of raw sludges (Sludge-ex, Ana-ex) and activated sludge-derived chars produced by pyrolysis at 250–600 °C (S250-ex to S600-ex) and by HTC (HTC-ex). Data were calculated from the area integration of their ^{31}P liquid NMR spectra. (D) ratio of polyphosphate end group to middle group abundance in activated sludge and its pyrochars.

chemical shift) is generally attributed to orthophosphate, whereas that from high field (more negative chemical shift) is from pyrophosphate and polyphosphate.¹³ However, the chemical shift of orthophosphate in solid state NMR can be shifted and even broader, a known phenomenon that is caused by a wide range of factors such as hydration, cation complexation, adsorption onto minerals, and different P salt types.^{30,35,36} For example, the chemical shift of different phosphates can range from 9 to -30 ppm in solid state NMR.¹³ This phenomenon makes it difficult for the direct

assignment of chemical shift regions to specific P species in these highly complex and heterogeneous matrix. Based on ^{31}P liquid NMR spectra of the NaOH/EDTA extracts (Figure 2A and 2C, see discussion later), the dominant P species in the extracts from activated sludge are orthophosphates and polyphosphate, qualitatively consistent with the solid state NMR results. Phosphate esters and pyrophosphate were also identified, but in a relatively small amount.

Compared to that of activated sludge, solid state NMR spectrum of anaerobically digested sludge showed a predom-

inant broad peak at the 10 to -30 ppm region (centering at ~ -5 ppm) (Figure 1). In agreement with that of solid state NMR, ^{31}P liquid NMR spectrum of the aqueous NaOH/EDTA extract from anaerobic sludge is dominated by orthophosphate, with small fractions of organic P and pyrophosphate (Figure 2A, see discussion later), suggesting that polyphosphate was possibly released from bacterial cells and hydrolyzed into orthophosphate during anaerobic digestion. This is also consistent with the low observation of P in these samples by solid state NMR, as orthophosphate is known to interact strongly with paramagnetic metals such as Fe and Mn as previously discussed.

Many studies have been devoted to reveal P speciation in sewage sludge using solid state and liquid ^{31}P NMR. Diverse P entities (mostly orthophosphate, polyphosphate, and organic P) were found to be the dominant species in most activated sludges, with their relative abundance depending on WWTP techniques and operational conditions.^{23,37,38} Sludges that are ready for disposal usually have experienced mechanical and thermal dewatering as well as anaerobic digestion processes. In those sludges, orthophosphate was the primary P entity and can present in various metal complexed forms.³⁹ These results were in agreement with our study. However, none of the previous studies systematically traced the P speciation dynamics during sludge treatment processes, and the percent of P observed by solid state NMR and the percent of P being extracted and characterized by liquid NMR were rarely constrained in these studies.

P Speciation in Pyrochars Derived from Pyrolysis. We used complementary solid state NMR, chemical extraction, and liquid NMR techniques to systematically and quantitatively characterize the change of P speciation during pyrolysis. As shown in Figure 1, the spectra of chars were significantly different from that of pristine activated sludge, with the signal became more homogenized and without clear peak separation.

In order to ensure the representativeness of ^{31}P liquid NMR results for speciation comparison, we quantified the P extraction efficiency of the NaOH/EDTA method for different treatment conditions and also characterized their residual solids using solid state ^{31}P NMR (Figure 3). Results showed that the extraction efficiency ranges from 40% to 70%, indicating that P in the extracts can account for a significant portion of the total P. As previously discussed, this extraction method imposed little alteration to the P species, thus the speciation information from liquid NMR of the extracted solution can provide rich information on the speciation of extractable and more labile P species. Although the nonextractable P species were not directly characterized by liquid NMR, they can be identified and inferred by combining solid state NMR results of the solids before and after extraction, as well as liquid NMR of the extracts. As can be seen from Figure 3A, P extraction efficiency for the pyrochars decreases with increasing pyrolysis temperature, which can be caused by physical constraints as a result of carbon condensation during pyrolysis. We also note that the signals in the extracted residues shifted toward low field (more positive chemical shifts) (Figure 3B), which is likely due to the intrinsic heterogeneity of sludge and its derived chars. As previously discussed, the chemical shift of orthophosphate in solid state NMR can be broad and shifted as affected by a wide range of factors such as hydration, cations, adsorbed minerals, and salt types.^{30,35,36} Different P species can present in very diverse physical and chemical forms, and it is possible that different P salts and/or cation-P complexes with NMR

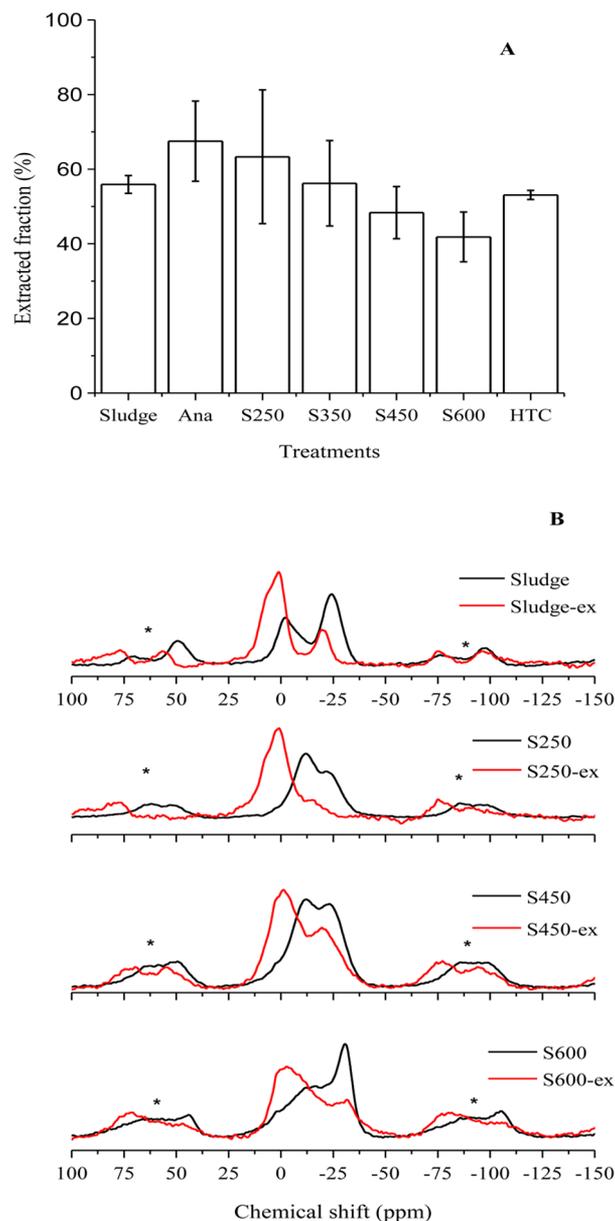


Figure 3. (A) Extraction efficiency of the NaOH/EDTA method for raw sludges (Sludge, Ana) and their derived chars, as calculated by P content in extracted solution divided by total P in the pristine samples; (B) ^{31}P solid-state NMR spectra of activated sludge and its pyrolyzed biochars produced at 250–600 °C (S250 to S600) (black lines), as well as their corresponding solid residuals after extraction (red lines). Asterisks denote spinning side bands.

shielding effects were extracted from the solid, thus causing the observed spectra shifting.

We now turned to discuss P speciation by liquid NMR observations before further comparison and interpretation of the solid state NMR spectra of the pristine and extracted samples. Although solid state NMR can directly observe the P species in solid samples, ^{31}P liquid NMR spectra of the liquid extracts possess better resolution and provide straightforward information for the identification and quantification of different P species. ^{31}P liquid NMR spectra of the extracts and their quantification were present in Figure 2 and Figure S4. After pyrolysis, the most distinct change is the appearance of pyrophosphate (chemical shift at ~ -5 ppm) in the pyrochars

of activated sludge, with relative abundance ranging from 10% to 24%, as compared to ~1% pyrophosphates in the raw activated sludge (Figure 2A and C). No significant alteration was found after the pyrolysis of anaerobic sludge, with orthophosphate still being the dominant P entity (with ~3% of pyrophosphate) in the extract of A450, except for the complete disappearance of the trace amount of mono- and diesters (Figure S4).

Another noticeable change is that polyphosphate signals are affected by pyrolysis temperature. Polyphosphate is a polymer of phosphate ions joined by phosphoanhydride (P–O–P) bonds, with variable chain lengths ranging from a few to thousands of P atoms.^{40,41} Polyphosphate can occur in ring and branched structures (meta- and ultraphosphates, respectively), although the linear structures are the most common form in nature. Polyphosphates can be organic (e.g., ATP and other nucleotide triphosphates), or inorganic. The NMR signal of linear inorganic polyphosphate typically consists of two regions: those from the end group P atoms (chemical shift ~ -4.5 ppm) and those from the middle group P atoms (chemical shift ~ -20 ppm).⁴² The sum of these two peak areas represents the overall polyphosphate abundance, whereas the relative ratio of these two peak areas can be used to estimate the average chain length of polyphosphate (e.g., longer chained polyphosphate will result in higher middle group P signal than end group P signal). For the thermal treated solids, in general, polyphosphate abundance in their extracts decreases with increasing pyrolysis temperature. The relative abundance of polyphosphates was 31.5, 19.3, 27.8, and 5.6% for S250, S350, S450, and S600 pyrochar, respectively (Figure 2A and C). Liquid NMR spectra also showed that the relative abundance of polyphosphate end groups increased after pyrolysis and was equal to or more than that of the middle groups, as compared to the predominance of middle group P signal in the raw sludge sample (Figure 2D).

The presence of significant amounts of pyrophosphate and polyphosphate end groups suggests that a portion of the longer-chained polyphosphates were broken down into shorter-chained polyphosphates or pyrophosphate (Figure 2A). Although the contribution from organic phosphates such as adenosine triphosphate (ATP) and DNA can not be excluded, their contribution should be small since their abundance in the raw sludge is less than 6%, as calculated by the sum of integrated peak areas for monoester (chemical shift of ~2.5 ppm) and diester (chemical shift of ~0 ppm) P species (Figure 2C). The formation of pyrophosphates and increased abundance of polyphosphate end groups in liquid NMR results are also consistent with the increased intensity at the middle range chemical shift (5–15 ppm) in solid state NMR data (Figure 1). Previous studies on the pyrolysis of plants and manure also showed the formation of pyrophosphate after pyrolysis at a wide range of temperatures, although their starting P source mostly consisted of phytate.⁴³ During pyrolysis, reactions such as dehydration, fragmentation, rearrangement, polymerization, and condensation are involved.⁴⁴ These reactions possibly striped off functional groups associated with P species and fragmented the long chain polyphosphates into shorter chain polyphosphates.

Comparison between the solid state NMR spectra of samples before and after extraction showed that P species at high field (-15 to -40 ppm) were preferentially extracted, especially for activated sludge and S250 char (Figure 3B). This is in agreement with liquid NMR observations of more polyphos-

phate and pyrophosphate in extracts from raw sludge and S250 than those from higher temperature chars (e.g., S450 and S600) (Figure 2A). The causes of such nonequivalent extraction efficiency are most likely due to the heterogeneous cellular distribution of different P species in microbial cells (e.g., dissolved vs granular, intracellular vs extracellular) and the different degrees of alterations resulted from different treatment conditions. Although there are some polyphosphates in extracellular polymeric substances,³⁸ most polyphosphates exist as solid granules within the cells.^{32,34} It is possible that the charring and stabilization of carbon during pyrolysis physically constrained the intracellular polyphosphate granules and prevented them from being extracted by the NaOH/EDTA method.

We note that a close comparison between the solid state NMR spectra of samples before and after extractions (Figure 3B) and of the relative abundance of different P species from liquid NMR (Figure 2C) showed a discrepancy. If the signals in the high field (-15 to -40 ppm) of solid state NMR were exclusively contributed from pyrophosphate and polyphosphate, preferential extraction of them would result in more pyrophosphate and polyphosphate than orthophosphate in the extracts. In contrast, the orthophosphate contents in the extracts were >50% and increased with increasing pyrolysis temperatures. Since polyphosphate is relatively stable in the NaOH/EDTA solution (as shown by Figure S5), the degradation of polyphosphate into orthophosphate during extraction is unlikely the cause of this discrepancy. Instead, this again may be caused by intrinsic heterogeneity of P speciation in the sludge and its derived chars, as well as the nature of ³¹P solid state NMR being easily affected by many factors as previously discussed. Signal in the high field (-15 to -40 ppm) may have partial contribution from orthophosphates in different physical and chemical forms.

P Speciation in Hydrochars Derived from Hydrothermal Treatment. Solid state ³¹P NMR spectrum of the HTC hydrochar from activated sludge is similar to that of anaerobically digested sludge, with the presence of only one predominant peak centered at -15 ppm chemical shift (Figure 1), which can be assigned to orthophosphate based on their high P extraction efficiency (~53%, Figure 3A) and the simplicity of both the liquid and solid NMR spectra (Figure 2). The percentage of observable P by solid state NMR is very low for the hydrochar (30.9%; see Supporting Information Table S1), and this peak shifted toward high field (more negative chemical shift) (Figure 1). We characterized both the process water from HTC treatment and liquid extract by NaOH/EDTA, both showed only one peak at ~4 ppm chemical shift (Figure 2B), and no pyrophosphates or polyphosphates were detected. Similarly, the extract from hydrochar of anaerobic sludge consists of only orthophosphate, with the trace amount of organic P and pyrophosphate disappearing after HTC treatment (Figure S4). Therefore, all P species were hydrolyzed into orthophosphate during HTC treatment, which can form various types of phosphate salts or be associated with other mineral phases. This can also explain the low P observation of HTC hydrochar by solid state NMR (30.9%). CP/NMR spectra showed that a portion of P in the activated sludge was observable by CP, which suggests that they remain protonated. However, there was no observable P for the activated sludge hydrochar and much less observable P for anaerobic sludge, which suggests the formation of more metal complexes (Figure S6). This result at least substantiates that the P complexation

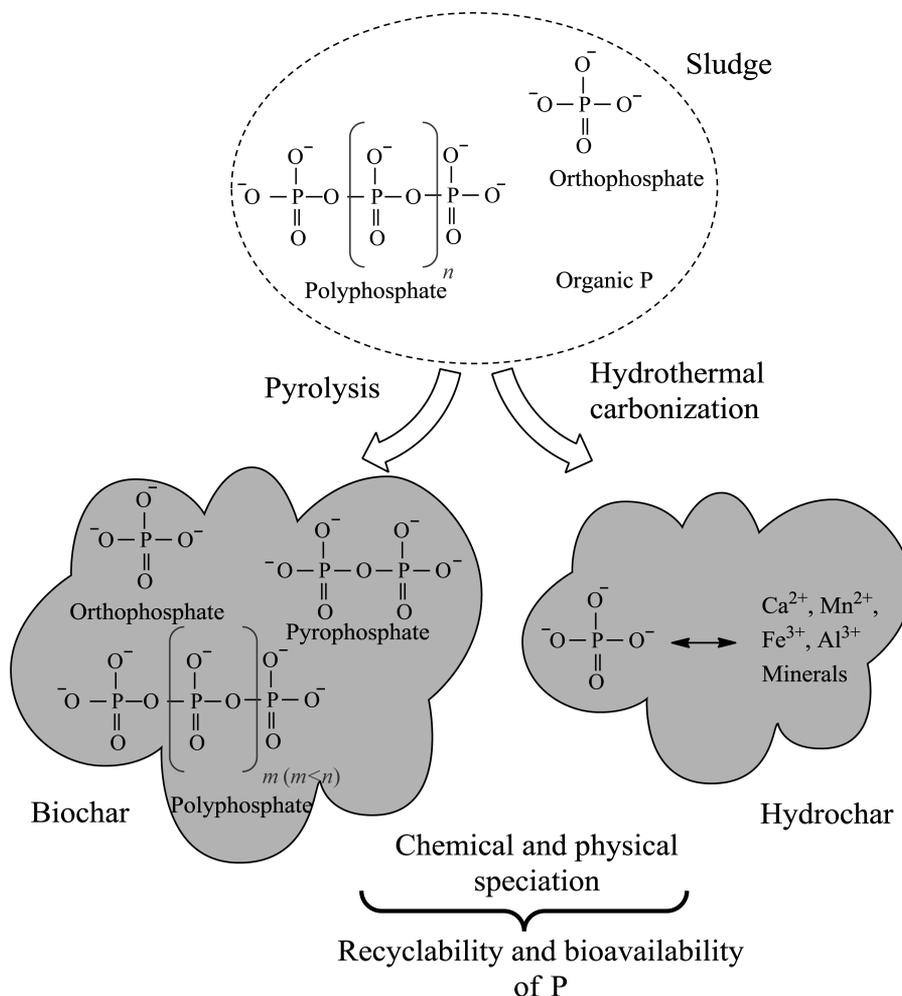


Figure 4. Schematic illustration of the proposed phosphorus transformation pathways during pyrolysis and hydrothermal treatments of activated sewage sludge.

environment was significantly altered after anaerobic digestion and HTC. A previous study quantified P transformation during supercritical water gasification of sewage sludge using chemical fractionation method and showed that most organic P was transformed into inorganic P (apatite-P and nonapatite inorganic P).¹⁷ Compared to pyrolysis, reactions in HTC mostly occur in the liquid phase and hydrolysis is considered to be the first step.^{45,46} Because sludge consists of mostly biomass (e.g., microbial cells), small nonbiological particles, and salts, they are likely to be thoroughly mixed and altered during HTC process. Intracellular polyphosphates can also be released, hydrolyzed, and subsequently interact with dissolved cations or other mineral phases.

ENVIRONMENTAL IMPLICATIONS

Growing global interests in sustainability has promoted the recycling and reclamation of critical nutrients from waste streams⁴⁷ and are pressing for the transition of wastewater management system and its integration with energy and agricultural management systems. Significant amounts of phosphorus from human activities ultimately converge into WWTPs and end up in sewage sludge, presenting an excellent opportunity for P recycling. P content in sewage sludges can range from thousands of ppm to several weight percent, especially for sludges from enhanced biological phosphorus

removal (EBPR) process.^{4,5,17} Furthermore, recently emerging (hydro)thermal treatment techniques can further enrich P in the produced chars, which makes the sludge-derived char-P composite an excellent candidate for P recycling and/or alternative fertilization.

At present, little is known about the nutrient cycling processes following the application of the residual P from various sources (e.g., sludge, manure, and crop residues) to soil, the effects of pretreatments on the cycling processes, and the determining factors.^{48,49} This information is important for developing guidelines to incentivize P recovery from waste streams such as from sewage sludge. A recent study showed that P in sludge and manure can be more recyclable than in inorganic P fertilizer, depending on the pretreatment methods (e.g., anaerobic digestion, composting, lime stabilization of biosolids, and P capture by metal precipitation),⁴⁹ yet direct P speciation information was missing.

Since speciation largely determines the mobility and availability of an element, P speciation information is critical for the design and selection of waste treatments and P recovery/recycling practices. First of all, depending on the feedstock and treatment conditions, P entities potentially available from sludge and its derived products are different (Figure 4). This can possibly affect the overall P recyclability by crops, since the mobility, transformation, and bioavailability of different P entities are species-dependent. Activated sludge and

its pyrochars possess more diverse P configurations than its hydrochars and anaerobic sludge and derived chars, and the pyrophosphate and polyphosphates that are not directly bioavailable may serve as P reservoirs for plants and/or organisms. Although the transport and transformation of polyphosphates in soil environment is unclear and warrants future study. Second, results from chemical extraction and NMR analysis indirectly suggest that treatment techniques and conditions may have significantly altered the chemical and physical states of these identified P entities. The chemical and physical states intrinsically determine whether particular P species can be dissolved into aqueous phase and the associated kinetics, which is closely relevant to fertilization strategy with optimal P release rate that enhances P recyclability while simultaneously mitigates P runoff. Due to the intrinsic complexity and heterogeneity of sludge and its chars, detailed information regarding the phases (e.g., cation complexes, surface adsorption, structural incorporation, or mineral precipitation) of the identified P entities is not addressed in the current study, but is under investigation and will be published elsewhere. Regarding the physical states, it has been well-established that biomass will be chemically stabilized after pyrolysis and HTC treatments, the chars are more stable with increasing pyrolysis temperatures (correspondingly increasing aromatic C condensation).^{50,51} Therefore, the pyrochars and hydrochars will be more stable than their raw feedstocks and can potentially serve as slow-releasing P reservoirs. Further speciation characterization, P leaching test and bioavailability assessments based on simulated chemical extraction or soil incubation test are needed to correlate intrinsic speciation and overall P recyclability.

Moreover, soil application of sludges and their derived chars can alter the biogeochemical processes in the soil environment to which they are applied, the alteration are greatly affected by their overall physicochemical properties (e.g., elemental composition, chemical structure, stability, and dissolvable components). For example, depending on pyrolysis or hydrothermal carbonization and their conditions, the leaching behaviors of dissolved organic matters and inorganics are different, subsequently affects the receiving environments.^{16,52}

In summary, this study aims to provide the first systematic and direct characterization of P entity dynamics during thermal treatments of sewage sludges. The combination of chemical extraction and NMR spectroscopy provides unique information on the molecular entities of P during the treatments. Information from this study lays the foundation for evaluating P recyclability from solid biowastes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04140.

Chemical characteristics of the feedstock sludges; Summary of sample and treatment conditions and NMR results; Comparison of the solid and P recovery, and P content after different (hydro)thermal treatment conditions; FT-IR spectra of the sludge and derived chars; solid-state ³¹P NMR spectra of sludge with variable recycle delays; ³¹P liquid NMR spectra of sludge extracts after 1 and 4 d and of the extracts of anaerobic sludge chars (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 404-894-3814; e-mail: yuanzhi.tang@eas.gatech.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by American Chemical Society Petroleum Research Fund # 54143-DNIS. We thank Brandon Brown (F. Wayne Hill Water Resources Center) for help with sewage sludge collection, Dr. Johannes E. Leisen and Dr. Leslie Gelbaum (Georgia Tech NMR Center) for assistance with NMR setup, and Dr. Hailong Chen (Georgia Tech) for help with the hydrothermal treatment setup.

■ REFERENCES

- (1) Rogers, H. R. Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Sci. Total Environ.* **1996**, *185* (1–3), 3–26.
- (2) Westerhoff, P.; Lee, S.; Yang, Y.; Gordon, G. W.; Hristovski, K.; Halden, R. U.; Herckes, P. Characterization, Recovery Opportunities, and Valuation of Metals in Municipal Sludges from U.S. Wastewater Treatment Plants Nationwide. *Environ. Sci. Technol.* **2015**, *49*, 9479.
- (3) Koppelaar, R. H. E. M.; Weikard, H. P. Assessing phosphate rock depletion and phosphorus recycling options. *Global Environmental Change* **2013**, *23* (6), 1454–1466.
- (4) Le Corre, K. S.; Valsami-Jones, E.; Hobbs, P.; Parsons, S. A. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39* (6), 433–477.
- (5) Kuroda, A.; Takiguchi, N.; Gotanda, T.; Nomura, K.; Kato, J.; Ikeda, T.; Ohtake, H. A simple method to release polyphosphate from activated sludge for phosphorus reuse and recycling. *Biotechnol. Bioeng.* **2002**, *78* (3), 333–338.
- (6) Escala, M.; Zumbühl, T.; Koller, C.; Junge, R.; Krebs, R. Hydrothermal Carbonization as an Energy-Efficient Alternative to Established Drying Technologies for Sewage Sludge: A Feasibility Study on a Laboratory Scale. *Energy Fuels* **2012**, *27* (1), 454–460.
- (7) vom Eyser, C.; Palmu, K.; Otterpohl, R.; Schmidt, T. C.; Tuerk, J. Determination of pharmaceuticals in sewage sludge and biochar from hydrothermal carbonization using different quantification approaches and matrix effect studies. *Anal. Bioanal. Chem.* **2015**, *407*, 1–10.
- (8) Kim, Y.; Parker, W. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. *Bioresour. Technol.* **2008**, *99* (5), 1409–1416.
- (9) Bridle, T.; Pritchard, D. Energy and nutrient recovery from sewage sludge via pyrolysis. *Water Science & Technology* **2004**, *50* (9), 169–175.
- (10) Qian, T.-T.; Jiang, H. Migration of Phosphorus in Sewage Sludge during Different Thermal Treatment Processes. *ACS Sustainable Chem. Eng.* **2014**, *2* (6), 1411–1419.
- (11) Heilmann, S. M.; Molde, J. S.; Timler, J. G.; Wood, B. M.; Mikula, A. L.; Vozhdayev, G. V.; Colosky, E. C.; Spokas, K. A.; Valentas, K. J. Phosphorus Reclamation through Hydrothermal Carbonization of Animal Manures. *Environ. Sci. Technol.* **2014**, *48* (17), 10323–10329.
- (12) Van Zwieten, L.; Kimber, S.; Morris, S.; Chan, K. Y.; Downie, A.; Rust, J.; Joseph, S.; Cowie, A. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* **2010**, *327* (1–2), 235–246.
- (13) Cade-Menun, B. J. Characterizing phosphorus in environmental and agricultural samples by ³¹P nuclear magnetic resonance spectroscopy. *Talanta* **2005**, *66* (2), 359–371.
- (14) Shober, A. L.; Hesterberg, D. L.; Sims, J. T.; Gardner, S. Characterization of phosphorus species in biosolids and manures using XANES spectroscopy. *J. Environ. Qual.* **2006**, *35* (6), 1983–1993.

- (15) Kizewski, F.; Liu, Y. T.; Morris, A.; Hesterberg, D. Spectroscopic Approaches for Phosphorus Speciation in Soils and Other Environmental Systems. *J. Environ. Qual.* **2011**, *40* (3), 751–766.
- (16) Hossain, M. K.; Strezov, V.; Chan, K. Y.; Ziolkowski, A.; Nelson, P. F. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J. Environ. Manage.* **2011**, *92* (1), 223–228.
- (17) Zhu, W.; Xu, Z. R.; Li, L.; He, C. The behavior of phosphorus in sub- and super-critical water gasification of sewage sludge. *Chem. Eng. J.* **2011**, *171* (1), 190–196.
- (18) Turner, B. L.; Cade-Menun, B. J.; Condrón, L. M.; Newman, S. Extraction of soil organic phosphorus. *Talanta* **2005**, *66* (2), 294–306.
- (19) Condrón, L.; Newman, S. Revisiting the fundamentals of phosphorus fractionation of sediments and soils. *J. Soils Sediments* **2011**, *11* (5), 830–840.
- (20) Werner, F.; Prietzel, J. Standard protocol and quality assessment of soil phosphorus speciation by P K-edge XANES spectroscopy. *Environ. Sci. Technol.* **2015**, *49* (17), 10521–10528.
- (21) Ahlgren, J.; De Brabandere, H.; Reitzel, K.; Rydin, E.; Gogoll, A.; Waldeback, M. Sediment phosphorus extractants for phosphorus-31 nuclear magnetic resonance analysis: A quantitative evaluation. *J. Environ. Qual.* **2007**, *36* (3), 892–898.
- (22) Huang, W. L.; Cai, W.; Huang, H.; Lei, Z. F.; Zhang, Z. Y.; Tay, J. H.; Lee, D. J. Identification of inorganic and organic species of phosphorus and its bio-availability in nitrifying aerobic granular sludge. *Water Res.* **2015**, *68*, 423–431.
- (23) Li, R. D.; Yin, J.; Wang, W. Y.; Li, Y. L.; Zhang, Z. H. Transformation of phosphorus during drying and roasting of sewage sludge. *Waste Manage.* **2014**, *34* (7), 1211–1216.
- (24) Cade-Menun, B. J.; Preston, C. M. A comparison of soil extraction procedures for ³¹P NMR spectroscopy. *Soil Sci.* **1996**, *161* (11), 770–785.
- (25) Liu, J.; Hu, Y. F.; Yang, J. J.; Abdi, D.; Cade-Menun, B. J. Investigation of Soil Legacy Phosphorus Transformation in Long-Term Agricultural Fields Using Sequential Fractionation, P K-edge XANES and Solution P NMR Spectroscopy. *Environ. Sci. Technol.* **2015**, *49* (1), 168–176.
- (26) Murphy, J.; Riley, J. P. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1962**, *27* (0), 31–36.
- (27) Dougherty, W. J.; Smernik, R. J.; Chittleborough, D. J. Application of spin counting to the solid-state P-31 NMR analysis of pasture soils with varying phosphorus content. *Soil Sci. Soc. Am. J.* **2005**, *69* (6), 2058–2070.
- (28) Donner, E.; Howard, D. L.; Jonge, M. D. d.; Paterson, D.; Cheah, M. H.; Naidu, R.; Lombi, E. X-ray Absorption and Micro X-ray Fluorescence Spectroscopy Investigation of Copper and Zinc Speciation in Biosolids. *Environ. Sci. Technol.* **2011**, *45* (17), 7249–7257.
- (29) Keiluweit, M.; Nico, P. S.; Johnson, M. G.; Kleber, M. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). *Environ. Sci. Technol.* **2010**, *44* (4), 1247–1253.
- (30) Conte, P.; Smejkalova, D.; Piccolo, A.; Spaccini, R. Evaluation of the factors affecting direct polarization solid state (³¹P)-NMR spectroscopy of bulk soils. *Eur. J. Soil Sci.* **2008**, *59* (3), 584–591.
- (31) Hirota, R.; Kuroda, A.; Kato, J.; Ohtake, H. Bacterial phosphate metabolism and its application to phosphorus recovery and industrial bioprocesses. *J. Biosci. Bioeng.* **2010**, *109* (5), 423–432.
- (32) Kulakova, A. N.; Hobbs, D.; Smithen, M.; Pavlov, E.; Gilbert, J. A.; Quinn, J. P.; McGrath, J. W. Direct Quantification of Inorganic Polyphosphate in Microbial Cells Using 4'-6-Diamidino-2-Phenylindole (DAPI). *Environ. Sci. Technol.* **2011**, *45* (18), 7799–7803.
- (33) Zhang, H.-L.; Fang, W.; Wang, Y.-P.; Sheng, G.-P.; Xia, C.-W.; Zeng, R. J.; Yu, H.-Q. Species of phosphorus in the extracellular polymeric substances of EBPR sludge. *Bioresour. Technol.* **2013**, *142*, 714–718.
- (34) Majed, N.; Matthäus, C.; Diem, M.; Gu, A. Z. Evaluation of Intracellular Polyphosphate Dynamics in Enhanced Biological Phosphorus Removal Process using Raman Microscopy. *Environ. Sci. Technol.* **2009**, *43* (14), 5436–5442.
- (35) Li, W.; Pierre-Louis, A. M.; Kwon, K. D.; Kubicki, J. D.; Strongin, D. R.; Phillips, B. L. Molecular level investigations of phosphate sorption on corundum (alpha-Al₂O₃) by P-31 solid state NMR, ATR-FTIR and quantum chemical calculation. *Geochim. Cosmochim. Acta* **2013**, *107*, 252–266.
- (36) Li, W.; Feng, X.; Yan, Y.; Sparks, D. L.; Phillips, B. L. Solid-State NMR Spectroscopic Study of Phosphate Sorption Mechanisms on Aluminum (Hydr)oxides. *Environ. Sci. Technol.* **2013**, *47* (15), 8308–8315.
- (37) Huang, W. L.; Huang, W. W.; Li, H. F.; Lei, Z. F.; Zhang, Z. Y.; Tay, J. H.; Lee, D. J. Species and distribution of inorganic and organic phosphorus in enhanced phosphorus removal aerobic granular sludge. *Bioresour. Technol.* **2015**, *193*, 549–552.
- (38) Zhang, H. L.; Fang, W.; Wan, Y. P.; Sheng, G. P.; Zeng, R. J.; Li, W. W.; Yu, H. Q. Phosphorus Removal in an Enhanced Biological Phosphorus Removal Process: Roles of Extracellular Polymeric Substances. *Environ. Sci. Technol.* **2013**, *47* (20), 11482–11489.
- (39) Frossard, E.; Tekely, P.; Grimal, J. Y. Characterization of phosphate species in urban sewage sludges by high-resolution solid-state ³¹P NMR. *Eur. J. Soil Sci.* **1994**, *45* (4), 403–408.
- (40) Kornberg, A.; Rao, N. N.; Ault-Riche, D. Inorganic polyphosphate: A molecule of many functions. *Annu. Rev. Biochem.* **1999**, *68*, 89–125.
- (41) Omelton, S. J.; Grynopas, M. D. Relationships between Polyphosphate Chemistry, Biochemistry and Apatite Biomineralization. *Chem. Rev.* **2008**, *108* (11), 4694–4715.
- (42) Turner, B. L.; Mahieu, N.; Condrón, L. M. Phosphorus-31 nuclear magnetic resonance spectral assignments of phosphorus compounds in soil NaOH-EDTA extracts. *Soil Sci. Soc. Am. J.* **2003**, *67* (2), 497–510.
- (43) Uchimiya, M.; Hiradate, S. Pyrolysis Temperature-Dependent Changes in Dissolved Phosphorus Speciation of Plant and Manure Biochars. *J. Agric. Food Chem.* **2014**, *62* (8), 1802–1809.
- (44) Degenstein, J. C.; Murria, P.; Easton, M.; Sheng, H.; Hurt, M.; Dow, A. R.; Gao, J.; Nash, J. J.; Agrawal, R.; Delgass, W. N.; Ribeiro, F. H.; Kenttämaa, H. I. Fast Pyrolysis of ¹³C-Labeled Cellobioses: Gaining Insights into the Mechanisms of Fast Pyrolysis of Carbohydrates. *J. Org. Chem.* **2015**, *80* (3), 1909–1914.
- (45) Libra, J. A.; Ro, K. S.; Kammann, C.; Funke, A.; Berge, N. D.; Neubauer, Y.; Titirici, M.-M.; Fühner, C.; Bens, O.; Kern, J.; Emmerich, K.-H. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2* (1), 71–106.
- (46) Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, Bioprod. Biorefin.* **2010**, *4* (2), 160–177.
- (47) Wang, X.; McCarty, P. L.; Liu, J.; Ren, N.-Q.; Lee, D.-J.; Yu, H.-Q.; Qian, Y.; Qu, J. Probabilistic evaluation of integrating resource recovery into wastewater treatment to improve environmental sustainability. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (5), 1630–1635.
- (48) Misselbrook, T. H.; Menzi, H.; Cordovil, C. Preface – Recycling of organic residues to agriculture: Agronomic and environmental impacts. *Agric., Ecosyst. Environ.* **2012**, *160* (0), 1–2.
- (49) Kahiluoto, H.; Kuisma, M.; Ketoja, E.; Salo, T.; Heikkinen, J. Phosphorus in Manure and Sewage Sludge More Recyclable than in Soluble Inorganic Fertilizer. *Environ. Sci. Technol.* **2015**, *49* (4), 2115–2122.
- (50) Zimmerman, A. R. Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar). *Environ. Sci. Technol.* **2010**, *44* (4), 1295–1301.
- (51) Bruun, S.; Jensen, E. S.; Jensen, L. S. Microbial mineralization and assimilation of black carbon: Dependency on degree of thermal alteration. *Org. Geochem.* **2008**, *39* (7), 839–845.
- (52) Uchimiya, M.; Hiradate, S.; Antal, M. J. Influence of Carbonization Methods on the Aromaticity of Pyrogenic Dissolved Organic Carbon. *Energy Fuels* **2015**, *29* (4), 2503–2513.