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# Highly efficient phosphorus recovery from sludge and manure biochars using potassium acetate pre-treatment

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## Abstract

Pyrolysis converts nutrient-rich residues (e.g., sewage sludge and manures) into biochar with low levels of organic contaminants and high nutrient contents. However, the availability of phosphorus (P) as one of the key nutrients in such biochar tends to be low and new approaches are needed to enhance P-availability. In this work we tested and optimised one such method, doping biomass prior to pyrolysis with potassium (K) as potassium acetate. The treatment worked effectively in both pyrolysis units tested (microscale and lab-scale, continuous unit) and all three feedstocks (two types of sewage sludges and swine manure). The most dramatic effect was observed in the microscale pyrolysis unit at 400°C where 5% K doping increased the water-extractable P content 700-fold to 43% of total P. Of the added K, on average 90% was retained after pyrolysis of which ~50% was water-extractable. The proposed method enables conversion of low-value residues into valuable resources with agronomically relevant total and available P and K levels. This approach does not require specialised equipment or process modifications and is therefore easy to implement and relatively cheap (~US\$ 60-80 t<sup>-1</sup> treated feedstock). It can present an urgently required solution to fulfil regulatory requirements for P-recovery.

**Keywords:** fertilizer; potentially toxic elements; sewage sludge; pig slurry; biochar doping

# 1 Introduction

Phosphorus (P) recycling from residues, such as sewage sludge and animal manures, is an essential strategy to prolong limited P resources (Cordell et al., 2009). In some regions, P from sewage sludge could satisfy a significant amount of crop requirements, e.g., up to ~50% of the mineral P-fertiliser amounts used in agriculture in Germany (Krüger and Adam, 2017). Because of the high P recovery potential and frequent eutrophication issues in waterways, regulations for mandatory P recovery from wastewater will come into effect in 2026 and 2029 in Switzerland and Germany, respectively (AbfKlärV, 2017; Schweizer Bundesrat, 2015). A new Fertilising Product Regulation of the European Union (EU) also focuses on facilitating trade with alternative fertiliser materials and hence, encourage P recycling from residues (The European Parliament and the Council of the European Union, 2019).

Such P-rich residues are, however, often contaminated with compounds of concern, including pharmaceuticals and microplastics (Clarke and Smith, 2011; Goss et al., 2013; Hill et al., 2019; Wohde et al., 2016) that can be present in plant-available form (Mercl et al., 2021; Wu et al., 2012). Application of untreated or insufficiently treated sewage sludge and manures on land to enable P-recycling can therefore pose an ecological and human health concern. There is a need to establish methods that enable safe and efficient recycling of P from P-rich residues.

Thermo-chemical conversion processes, in an oxygen-rich atmosphere (incineration) and oxygen-poor atmosphere (pyrolysis), remove organic contaminants from sewage sludge and related materials (Buss, 2021). However, the P availabilities in the products from pyrolysis (biochar) and incineration (ash) are lower than in the feedstock materials (Adhikari et al., 2019; Herzel et al., 2016; Xiao et al., 2018). Efficient P recycling requires new approaches to increase the plant-P availability and has been a focus of past research.

Several methods for increasing the P availability have been proposed. In case of incineration residues, P can be extracted from ash via acid washing, a process comparable to conventional P fertiliser production. However, the method also dissolves heavy metals (Fang et al., 2018) and is typically less efficient when high amounts of Fe and Al-phosphates are present, which is the case for many sewage sludge ashes (Kratz et al., 2019). An alternative approach used temperatures of 800-1000°C to treat a blend of sodium sulphate, sewage sludge ash and sewage sludge at a ratio of 2:5:1 at partial reducing, then oxidizing conditions, which resulted in full extractability of P in neutral ammonium citrate (NAC) (Herzel et al., 2021b). The approach was also successful when a mixture of sodium sulphate and potassium sulphate was used (Herzel et al., 2021a).

The described methods increase P availability in incineration ashes but are energy-intensive and require significant modifications to the existing sewage sludge treatment process. Unlike incineration, pyrolysis treatments operate at lower temperatures and additionally retain around half of the carbon present in the feedstock material. Therefore, pyrolysis significantly reduces the environmental impact of P-recycling (Buss, 2021). We previously demonstrated that doping of sewage sludge with a potassium acetate solution prior to pyrolysis at 700°C converts phosphate minerals of low solubility (Al-, Ca-, Fe- and Mg-phosphates) into highly available K-phosphates (Buss et al., 2020).

In this study, we conducted two sets of experiments with the aim to optimise P availability in P-rich residues through doping with potassium acetate followed by pyrolysis. In the first experimental series, sewage sludge was doped with 0.5% and 5% K and pyrolyzed in a micro-scale pyrolysis unit (thermogravimetric analyser) at 100°C intervals between 400-900°C (full-factorial design; 21 biochars and 3 feedstocks). In the second series, swine manure and a second sewage sludge (with ~3-times higher P-content than the one in the first experimental series) were doped with 2% and 4% K and pyrolyzed in a lab-scale, continuous pyrolysis unit

between 500-700°C (selected conditions; 11 biochars in total) to reflect conditions comparable to commercial pyrolysis operations. We performed water-extractions for short-term P availability (biochars from both sets of experiments) and NAC extractions for longer-term P availability (only biochars from continuous unit) (Kratz et al., 2019).

The objectives were to (i) optimise the pyrolysis temperature for maximum P availability in biochars derived from different P-rich feedstocks and doped with potassium acetate, (ii) assess compliance of the (doped) biochars with guidelines and regulations (P content and availability, polycyclic aromatic hydrocarbon (PAHs) content, and heavy metals contamination), and (iii) evaluate the economics and scalability of the process.

## **2 Materials and Methods**

### **2.1 Feedstock preparation and pyrolysis**

#### **2.1.1 Micro-scale biochar production – Thermogravimetric analyser (TGA)**

Sewage sludge provided by Scottish Water (undigested, dried, and granulated) was soaked in potassium acetate solution (Sigma-Aldrich,  $\geq 99.0\%$  purity) to achieve uptake of K equivalent to 0.5% and 5% (weight %) of the material. The pre-dried sewage sludge granules and potassium acetate solution were occasionally stirred until the solution was taken up. The total K contents were measured as described under section 2.2 to determine the effectiveness of K doping. The K contents in the control, 0.5% and 5% K-doped samples were 0.15, 0.74 and 4.5%, respectively, equivalent to an addition of 0.58 and 4.3% K in the 0.5% and 5% K treatments (SI Table 1). The P content in this first type of sewage sludge (SS I) was  $\sim 1.1\%$  (Buss et al., 2020).

SS I was pyrolyzed in a thermogravimetric analyser (Mettler-Toledo TGA/DSC1) at  $100^\circ\text{C}$  intervals from  $400\text{-}900^\circ\text{C}$  at a heating rate of  $50^\circ\text{C min}^{-1}$  and a residence time at highest treatment temperature (HTT) of 10 min. Approximately 80-100 mg of (doped) SS I was pyrolyzed per run. Several (typically 15) runs were performed, and the biochars were pooled for the extractions and digestions.

#### **2.1.2 Continuous pyrolysis unit**

The second sewage sludge (SS II) was provided by the wastewater treatment plant in Linz-Unkel (Germany), where the material was anaerobically stabilised, followed by Fe(III)chloride addition for precipitation of phosphates. The anaerobically digested sewage sludge was subsequently dried. It comprised small granules of max  $\sim 0.5$  cm diameter and had a P content of  $\sim 3.2\%$ .

We further used swine manure from a farm where the pigs were fed with dried feed. The manure was separated into liquid and solid fractions through an initial release of ~1/3 of the liquid within the swine manure, followed by centrifugation. After centrifugation, the material had dry matter, ash, nitrogen and carbon contents of 27.2%, 34.8%, 3.1% and 35.6%, respectively. Before pyrolysis, the material was further dried to ~65% dry matter content. The particle size was comparable to both sewage sludges (<0.5 cm). The swine manure had a P content of 4.1%.

Potassium acetate (purity  $\geq 99\%$ , Roth, Karlsruhe, Germany) was dissolved in water and the solution was applied onto the dry SS II material and swine manure with a spray bottle, while the material was manually stirred with a whisk. Afterwards the materials were dried at 105°C in an oven.

The pyrolysis was performed in a PYREKA lab-scale, continuous pyrolysis unit (Pyreg, Dörth, Germany). A schematic can be found in Hagemann et al. (Hagemann et al., 2020). The feedstock was placed in a feed hopper where it was transported by a screw feeder to a rotary valve that seals the furnace from the ambient atmosphere. The unit uses nitrogen carrier gas to create an inert atmosphere in the reactor. Subsequently, the material is transported through an electrically heated furnace (length: ~1 m). We used residence times in the heated zone of ~20 min and 27 min (details in Table 1) and a throughput of ~2 kg h<sup>-1</sup> and ~0.75 kg h<sup>-1</sup> for SS II and swine manure, respectively, and HTTs of 500-700°C.

## **2.2 Analysis of biochars from microscale pyrolysis unit**

All biochar samples produced in the micro-scale pyrolysis unit and the respective sewage sludge feedstock (SS I) were digested using the modified dry ashing method described previously (Buss et al., 2016a).



We also conducted deionised water extractions in 50 mL centrifuge tubes using 100 mg manually ground (mortar and pestle) SS I or biochar and 10 mL of water. We used the same water-to-liquid ratio as recommended in the EU fertiliser regulation for water-extractable P (The European Parliament and the Council of the European Union, 2003) and reagent blanks were included as appropriate. The samples were shaken on a reciprocal shaker at 150 rpm for 2 hours, followed by filtration with Whatman No. 1 filters.

The digests and water-extracts were analysed via ICP-OES (Varian Vista Pro) for 19 elements, including P, K, Ca, Mg, Al, Fe, Cu and Cr using 6-point calibrations from 0.01 to 25 ppm. Further information on the protocol can be found in Buss et al. (2016a).

## **2.3 Analysis of biochars from continuous pyrolysis unit**

### **2.3.1 Fertiliser potential**

The SS II and swine manure biochar samples pyrolyzed in the continuous unit were analysed for their P fertiliser potential by a commercial lab (Eurofins Umwelt Ost, Jena, Germany).

The samples were digested via aqua regia (method DIN 51729-11: 1998-11) and analysed for P via ICP-OES following method DIN EN 11885:2009-09. The P contents analysed in the digest were referred as “total P contents” and determined in three SS II biochar samples and the swine manure feedstock sample. Assuming 100% P retention at typical pyrolysis temperatures ( $\leq 700^{\circ}\text{C}$ ) as reported in the literature (Yuan et al., 2015), the total P content of all biochars was calculated based on the respective biochar yields (Table 1).

The water-extractable P contents were determined in all biochar samples according to DIN EN 15958:2012-02, followed by analyses of the extracts via ICP-OES (method DIN EN 11885:2009-09). The extractions were performed in 500 mL beakers using 5 g of biochar and 450 mL of water. The samples were mixed for 30 min in a rotary shaker, then 50 mL of water was added, and the samples were subsequently filtered and analysed.

In addition, the NAC-soluble P content was determined. NAC is typically used to assess the fertilizer potential of recycled materials and is considered a good indicator for longer-term plant P-availability (Kratz et al., 2019; Krüger and Adam, 2017). NAC-soluble P was extracted according to DIN EN 15957:2011-12 and the extracts were also analysed via ICP-OES (DIN EN 11885:2009-09). In short, the NAC solution was prepared by dissolving 370 g crystallised citric acid in 1,500 mL deionised water and by addition of 345 mL of ammonium hydroxide solution (28% NH<sub>3</sub>). The solution was adjusted to pH 7 and water was added up to a total volume of 2,000 mL. The NAC-extraction was performed in a beaker using 1 g of biochar and 100 mL of NAC-solution. The NAC-biochar blend was gently shaken for 1 hour on a rotary shaker and subsequently filtered and analysed via ICP-OES.

### **2.3.2 Contaminants**

The sum of 16 US EPA PAHs and the content of potentially toxic elements (PTEs) were determined in one K-doped sewage sludge biochar sample (i.e., SS II 600°C + 4% K). For PAH extraction, the biochar was extracted with toluene following the protocol DIN EN 16181:2019-08. The PAH analysis was performed by Eurofins Umwelt Ost (Jena, Germany). The same biochar sample was digested via aqua regia followed by ICP-OES analysis of Cr, Cu, Ni and Zn, ICP-MS analysis of As, Pb, Cd and Tl and CV-AAS analysis of Hg. The PTE analyses were performed by the Landeslabor Hessen (Kassel, Germany)

## 3 Results and Discussion

### 3.1 Sewage sludge temperature series in micro-scale pyrolysis

#### 3.1.1 Phosphorus availability

The water-extractable of the total P content in the undoped sewage sludge (SS I) prior to pyrolysis was 3.7%, and in the 0.5% and 5% K-doped samples 3.3% and 4.9%, respectively (Figure 1; SI Table 2). After pyrolysis, the extractable P content decreased in undoped SS I substantially to 0.1-0.4% of the total content, a 17-fold decrease across the six pyrolysis temperatures (Figure 1; SI Table 2). Other studies also report dramatic declines in P availability after sewage sludge pyrolysis, e.g., Zhang et al. (2015) found a 7-fold decrease for sewage sludge biochar produced at 400°C relative to unpyrolyzed sewage sludge (Zhang et al., 2015).

Doping of SS I with 0.5% K increased the water-extractable P content relative to undoped biochar 3-fold to 0.4-0.8% (mean: 0.5%) (Figure 1; SI Table 2). Doping with 5% K further increased the water-extractable P content to an average of 27% of total P across the six pyrolysis temperatures (400-900°C). This is equivalent to a 200-fold increase relative to the undoped biochar control and is even a 5.5-fold increase relative to the SS I prior to pyrolysis. Our results highlight that K-treatment can substantially increase P-availability in sewage sludge biochar across the whole temperature range tested (Figure 1).

The water-extractable P content in undoped and 0.5% doped biochar did not change consistently with pyrolysis temperature (Figure 1; SI Table 2) in contrast to other studies that reported decreasing P extractability with increasing pyrolysis temperature (Liang et al., 2018; Zhang et al., 2015). However, we did see such effect in the 5% K doped biochar where the water extractable P fraction decreased from ~43% in biochar produced at 400°C to 6% in the 900°C-biochar (Figure 1). The relative change in P-availability due to K-doping was also

highest at lower pyrolysis temperatures; K-doping increased the P-extractability 700-fold and 17-fold in biochars produced at 400°C and 900°C, respectively. It highlights that lower pyrolysis temperatures are more suitable for K-doped sewage sludge biochar pyrolysis.

### **3.1.2 Fate of added potassium**

In addition to studying phosphorus availability, we also conducted K mass balances from feedstock to biochar. Interestingly, the results did not reveal any clear effect of temperature on K retention during pyrolysis (Figure 2B), although K can volatilise during pyrolysis at >400°C (Okuno et al., 2005). K retention was high across all pyrolysis temperatures: 86±2.4%, 92±8.4% and 85±6.1% for undoped, 0.5% and 5% K-doped biochars, respectively. There was no significant difference in K retention between the doped and undoped treatments (one-way ANOVA,  $p = 0.175$ ). This demonstrates that K doping of biomass boosts the K content in the biochar without elevated K losses during pyrolysis, which is a significant and novel finding.

All the added K was recovered in one water extraction step in unpyrolyzed SS I doped with 5% K (Figure 2A). A high water-extractable K content in unprocessed sewage sludge or biochar can be problematic as excess K can cause salinity issues and hence inhibit plant growth (Buss et al., 2016b). In contrast, in the 5% K-doped biochar, 40-60% of the total K was water-extractable across all pyrolysis temperatures (mean: 50%), with a slight decrease at the highest pyrolysis temperatures (Figure 2A). This buffered release of K could help provide K to plants in more moderate quantities. Previously, we showed that repeated water extractions (6-steps), simulating medium-term availability, recovered 100% of K in a K-doped sewage sludge biochar (Buss et al., 2020).

Overall, the total K contents in the 5% K-doped SS I biochars were 8-11% (SI Table 2) with ~50% immediately available (one-step water-extraction) and the second proportion likely

plant-accessible throughout the growing season. This makes K-doped sewage sludge biochar a promising K fertiliser.

### **3.2 Sewage sludge and manure treatment in continuous unit**

In the second set of experiments, we investigated whether the effects observed in the microscale pyrolysis are (i) transferrable from a batch process to a continuous pyrolysis process, (ii) scalable from a microscale reactor (milligram scale) to a small pilot reactor (kilogram scale), and (iii) transferrable to feedstocks with higher P contents and different composition (swine manure ~4% P and second sewage sludge (SS II) ~3.2% P).

We produced two K-doped biochar temperature series from 500-700°C using 2% K-doped SS II (Figure 3A) and 4% K-doped swine manure (Figure 4A). The data confirmed the results from the microscale pyrolysis; the water-extractable P content decreased with increasing pyrolysis temperature, so did the percentage of NAC-extractable P, though to a lesser extent. Subsequently, we investigated the effect of 2% and 4% K-doping in both feedstocks produced at 600°C (Figure 3B; Figure 4B). The water-extractable P content in the SS II biochar doped with 2% and 4% K increased 9 and 31-fold relative to an undoped control to 1.1 and 3.7%, respectively (Figure 3B; Table 1). In the same biochars, the NAC-extractable P content increased from 21% in the undoped control to 24% and 30% with 2% and 4% K-addition (Figure 3B; Table 1). In the swine manure samples, the 4% K-doping nearly tripled the NAC-extractable P content from 17% to 48% of the total P. This demonstrates that the effect of K-doping is not feedstock-specific and can also effectively increase the P-availability in materials with higher P content.

We then produced an improved SS II biochar via doping with 4% K and pyrolysis at 500°C. In this biochar, 67% of P was NAC-extractable and 4.1% water-extractable (Figure 3B). Only very few other studies showed similar increases in P availability, and only by using more complex treatment options (Steckenmesser et al., 2019; Vogel et al., 2017). Our results are

very promising for the fertiliser potential of K-doped biochar, but still need confirmation in plant trials (currently being conducted in Hessen, Germany using the “SS II 600°C + 4% K”-biochar sample).

### **3.3 Mechanisms responsible for unlocking P availability and optimisation potential**

In sewage sludges and manures, P is present in organic form, and as pyrophosphate and orthophosphate (Liang et al., 2018; Qian and Jiang, 2014; Uchimiya and Hiradate, 2014).

With increasing pyrolysis temperature, organic-P and pyrophosphate peaks disappear, leaving orthophosphate as the sole P component (Liang et al., 2018; Qian and Jiang, 2014; Uchimiya and Hiradate, 2014). Pyrolysis in particular fosters the formation of insoluble P-Ca orthophosphates, which substantially decreases P availability in biochar (Liang et al., 2018; Qian and Jiang, 2014; Uchimiya and Hiradate, 2014).

Previously, we performed P K-edge X-ray absorption near-edge spectroscopy (XANES) on 5% K-doped sewage sludge biochar (700°C) and the equivalent undoped biochar sample produced from the same SS I feedstock as in the current study and compared the results to various reference materials containing Ca-, Al-, Fe- and K-P compounds (Buss et al., 2020). The results indicated that hydroxyapatite and aluminium phosphate were still present in the K-doped biochar, however, in addition a potassium hydrogen phosphate was formed due to the interactions between K and phosphates during pyrolysis of K-doped sewage sludge. Such potassium hydrogen phosphate is much more soluble ( $K_2HPO_4$ ; 168 g/100 g water) than Ca, Mg, Al and Fe phosphates typically present in undoped sewage sludge biochar (Liang et al., 2018), which resulted in the increased extractability of P in the K-doped biochar samples. K needs to be present in excess of P in the biomass/biochar to meet the 2:1 molar ratio required for  $K_2HPO_4$  formation. Herzel et al. (2016) found P-extractability in sewage sludge incineration ash increased linearly with K and Na addition until a K:P or Na:P ratio of 2 was

reached (Herzel et al., 2016). This is further evidence for the formation of  $K_2HPO_4$  and related compounds of similar K:P or Na:P ratios during thermochemical conversion of doped biomass.

In our study, the contents of water-extractable P in biochars produced from undoped SS I and SS II were comparable (SS I: 0.22% across the temperatures, SI Table 2; SS II: 0.12% at 600°C, Table 1). On the other hand, the amount of water-extractable P in biochars doped with the upper level of K (4% and 5%) was higher in the biochars produced from SS I compared to SS II (e.g., 33% vs. 4.1% in the 600°C biochars). This result can be explained by the respective K:P ratios. The P content in SS I was ~3-fold lower than in SS II and we added less K to SS II (4% vs. 5% K), resulting in K:P ratios of 3 and 1 in SS I and SS II biochars, respectively. The swine manure biochar had an even lower K:P ratio of only 0.8. This highlights potential for further optimisation of P-availabilities in SS II and swine manure biochars in which we already detected up to 2/3 and 1/2 NAC-extractable P, respectively.

We further discovered that lower pyrolysis temperatures promoted P-availability in K-doped biochar. Many studies report highest P-availability in the unpyrolyzed feedstock material and subsequently decreasing P-availability with pyrolysis temperature (Dai et al., 2016; Liang et al., 2018; Uchimiya and Hiradate, 2014). With K-doping, however, pyrolysis conditions are clearly required to increase P-availability. Simple addition of K acetate to sewage sludge without pyrolysis of the material did not increase P availability (Figure 1). During pyrolysis metal acetates typically start to decompose at temperatures of ~350°C (Cheng et al., 2019; McAdie and Jarvis, 1970; Patil et al., 1968) and between 200-400°C the reactivity of K increases as it volatilises without loss (Jensen et al., 2000; Tian et al., 2017). This fosters interactions of K and P, which enable the formation of K-P compounds of high solubility. Our discovery that pyrolysis temperatures at the lower to medium end of pyrolysis (400-600°C)

are particularly effective at increasing P availability is an interesting and novel finding of great significance.

Liang et al. report that Na-P compounds, which, as shown in Herzel et al., form under similar conditions as K-P compounds (Herzel et al., 2016), peaked at a pyrolysis temperature of 400°C in undoped swine manure biochar (pyrolysis range 300-700°C). At higher pyrolysis temperatures Na-P (and likely K-P) compounds were replaced by Ca-P compounds (Liang et al., 2018) that display lower solubility and higher thermal stability. This shift towards more thermally stable compounds at the upper temperature range of pyrolysis, which fosters the formation of Ca-P species could explain the decrease in P-availability with temperature in undoped and K-doped biochars samples.

Application of  $K^+$  ions to the feedstock material in a reactive form is the key step to ensure enhanced P recovery in biochar. To effectively increase P availability,  $K^+$  ions need to get into contact with the entire amount of P present in the feedstock. Via synchrotron X-ray fluorescence (XRF), we showed previously that soaking sewage sludge granules (~0.5 cm in size) in potassium acetate solution overnight did not result in full penetration of K into the interior of the sewage sludge pellet (Buss et al., 2020). Using finer sewage sludge particles or enhanced application of the potassium acetate solution, e.g., via a pressure sprayer, might enable deeper penetration of K into the sewage sludge matrix. We tried mixing solid, undissolved potassium acetate salt with sewage sludge prior to pyrolysis. As expected, the P extractability after pyrolysis was lower compared to wet application as the K was not incorporated into the sewage sludge matrix as fully as during wet application (SI Table 5). However, the differences in NAC-extractabilities between wet and dry K-doped samples were small and hence dry doping, which has the advantage of not adding moisture to the feedstock, is an option that needs further investigation.



In summary, to maximise P availability in biochar (i) mineral addition should be done in a way that ensures full contact of K with P in the feedstock material to maximise P-availability and (ii) adjusts the K:P ratio to ~2, and (iii) the material should be pyrolyzed at 400-600°C.

### **3.4 Contaminants in K-doped sewage sludge biochars**

This work demonstrated that K doping can dramatically increase the P availability in biochar derived from P-rich feedstock. Alkali metals, such as K, can also promote biochar formation and hence increase the carbon sequestration potential of biochar by changing the dynamics during thermochemical conversion, which also affects the formation of polycyclic aromatic hydrocarbons (PAHs) (Buss et al., 2020; Giudicianni et al., 2021; Mašek et al., 2019). Since PAHs are contaminants of concern in biochar (Hale et al., 2012), we analysed the PAH content in one of the doped biochars, the “SS II 600°C 4% K”-biochar produced in the continuous unit. The sum of 16 US EPA PAHs was only 1.6 mg kg<sup>-1</sup> with 1.2 mg kg<sup>-1</sup> attributed to NAP (Table 2), the least hazardous of the 16 US EPA PAHs (Delistraty, 1997). Therefore, the biochar meets the PAH limit value of the International Biochar Initiative (IBI) (International Biochar Initiative, 2011) and additionally achieves the highest biochar grade of the European Biochar Certificate (EBC) (animal feed) (EBC, 2012), with limits of 6 and 4 mg kg<sup>-1</sup> respectively. It demonstrates that K doping does not pose a concern for PAH levels in biochar.

The “SS II 600°C + 4% K”-biochar also meets the potentially toxic element (PTE) limit values of phosphorus fertilisers in the German fertiliser ordinance (SI Table 4) (Düngemittelverordnung, 2012). PTE contents in sewage sludges vary substantially depending on their origin (Herzel et al., 2016). Legal limits in different countries and jurisdictions are also inconsistent and therefore, whether the biochar meets local threshold values for total PTEs needs to be evaluated on a case-by-case basis.

While regulation threshold values are still mostly based on total contents of PTEs, in terms of an actual environmental impact the more relevant parameter is the availability of PTEs, i.e., the amount that is taken up and affects plants and soil organisms. Therefore, we investigated whether the water-extractable fraction of PTEs in biochar was influenced by K addition in the SS I biochars (Figure 5). Of the 8 PTEs assessed (As, Cd, Co, Cr, Hg, Ni, Pb, Zn), only the water-extractable levels of Cr and Cu were above the detection limit in the biochar from undoped sludge. The availability of both PTEs increased markedly in the 5% K-doped biochars relative to the undoped biochars and the sewage sludge prior to pyrolysis when produced at temperatures above 500°C and reached 10% and 40% of the total levels in the biochar produced at 900°C, rendering high temperatures undesirable (Figure 5). It is unclear why K-doping increased Cr and Cu availability at elevated pyrolysis temperatures, and this should be part of future investigations. Importantly the water-extractable levels in the 400°C and 500°C biochars were below the limit of detection and therefore much lower than in the sewage sludge prior to pyrolysis.

We recommend ~500°C for pyrolysis of K-doped, P-rich feedstocks that also contain increased levels of PTEs and organic contaminants because (i) the availability of P decreases with pyrolysis temperature, (ii) the availability of PTEs increases with pyrolysis temperature and (iii) organic contaminants present in the feedstock material are almost completely removed at temperatures of  $\geq 500^\circ\text{C}$  as demonstrated previously (Buss, 2021).

### **3.5 Environmental, agricultural and economic relevance**

Commercial single and double super-phosphate fertilisers contain 8.8% and 17% P, respectively. Our SS II and swine manure biochars have levels of P (9-12%) comparable to such fertiliser of which up to 2/3<sup>rd</sup> was NAC-extractable (Table 1). In addition, the materials contain ~10% K (SI Table 3) in a partially immediately, partially medium-term available

form. Our biochars clearly contain P and K levels of agronomical relevance and could replace PK fertilisers as a climate-friendly alternative.

According to the new EU Fertilising Product Regulation, mineral fertilisers defined as materials with <1% organic carbon content, require a minimum NAC-P-extractability of 75% (The European Parliament and the Council of the European Union, 2019). However, for recycled P-fertilisers, the STRUBIAS report (Precipitated Phosphate Salts & Derivates, Thermal Oxidation Materials & Derivates and Pyrolysis & Gasification Materials) suggests that at least 25% of P should be water-extractable or 30% NAC-extractable (Huygens et al., 2019). All our biochars treated with the higher K-application rates (4% / 5%) and produced  $\leq 700^{\circ}\text{C}$  satisfy the requirement suggested in the STRUBIAS report. It is very likely that our process can even exceed the higher limit for P-NAC-extractability of 75% with further optimisation, such as higher K:P ratio and more efficient K-doping.

Drying is the most energy-intensive step of the sewage sludge-pyrolysis operation (Cheng et al., 2020; McNamara et al., 2016; Miller-Robbie et al., 2015) and therefore, adding potassium acetate solution after sewage sludge drying should be avoided as additional energy is needed to subsequently drive off the added moisture. The potassium acetate solution could be added after dewatering (pressing) and before full thermal drying. Movement during the drying operation should ensure mixing, homogenous K application and hence maximum effectiveness. Dry mixing of potassium acetate should also be further investigated. In contrast to currently used techniques that increase the P availability in conversion products of sewage sludge (mainly incineration ashes) (Kratz et al., 2019), potassium acetate doping prior to pyrolysis does not need any process modifications and additional costs are limited to costs for the potassium acetate.

To amend biomass with 4% K, 10% potassium acetate needs to be added as it contains 40% K. This treatment incurs costs of US\$ 60-80 per tonne of dry sewage sludge at potassium

costs of US\$ 600-800 (Alibaba.com, 2021). Our feedstock pre-treatment further supplies K and therefore the extra costs for K doping could be partially offset by its obtained K fertiliser value. The price for potash is ~US\$ 300-600 t<sup>-1</sup> K<sub>2</sub>O (US\$ 250-500 t<sup>-1</sup> K), resulting in a K-value of US\$ 25-50 per tonne K doped sewage sludge biochar (10% K), which is ~US\$ 10-20 per tonne processed sewage sludge (at 40% biochar yield). The extra K-fertiliser value therefore reduces potassium acetate doping costs to US\$ 40-70 per tonne of dry sewage sludge. Ultimately, K-doped sewage sludge biochar will display increased agronomical value due to enhanced P-availability, a property challenging to convert into monetary value as there is no universal standard to assess and hence put a price on P-availability.

Current sewage sludge incineration costs in the EU are estimated at US\$ 90-500 per tonne processed sewage sludge (Capodaglio and Olsson, 2020) and proposed methods that increase the P-availability in sewage sludge ash need additional processes, such as a second stage ~1000°C-treatment after sodium sulphate addition (Steckenmesser et al., 2019; Vogel et al., 2017). This would incur significant additional costs to the existing sewage sludge processing expenses. In contrast, our simple potassium acetate addition utilises a single-step process that does not require extra energy inputs or process modifications and therefore, is considerably more cost-efficient and practical. Importantly, our method is based on pyrolysis, which retains and stabilises a significant part of the carbon within the biomass and incidentally, K-doping can further increase the carbon sequestration potential of biochar by boosting carbon retention and stability (Buss et al., 2022, 2020; Mašek et al., 2019).

## **4 Conclusions**

We showed that K-doping coupled with pyrolysis converts sewage sludges and manures of different composition into valuable resources with enhanced total and available P and K levels. Our process can be optimised for different types of P-rich residues. A cost-benefit

analysis should be conducted on a case-by-case basis to decide on the most-efficient level of K addition considering the costs of potassium acetate and residue composition (i.e., mainly P content). The method described here paves the way for using sewage sludge and manure biochar as sustainable fertilisers that recycle nutrient at a competitive price while simultaneously providing long-term carbon sequestration. Pyrolysis of K-doped sewage sludge has distinct potential to be applied as a cost-effective, P-recycling technology.

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## Reference

- AbfKlärV, 2017. Verordnung über die Verwertung von Klärschlamm, Klärschlammgemisch und Klärschlammkompost (Klärschlammverordnung - AbfKlärV). Germany.
- Adhikari, S., Gascó, G., Méndez, A., Surapaneni, A., Jegatheesan, V., Shah, K., Paz-Ferreiro, J., 2019. Influence of pyrolysis parameters on phosphorus fractions of biosolids derived biochar. *Sci. Total Environ.* 695, 133846. <https://doi.org/10.1016/j.scitotenv.2019.133846>
- Alibaba.com, 2021. [www.alibaba.com/showroom/potassium-acetate-price.html](http://www.alibaba.com/showroom/potassium-acetate-price.html) [WWW Document]. accessed 26/10/2021.
- Buss, W., 2021. Pyrolysis solves the issue of organic contaminants in sewage sludge while retaining carbon – Making the case for sewage sludge treatment via pyrolysis. *ACS Sustain. Chem. Eng.* 9, 1048–1053. <https://doi.org/10.1021/acssuschemeng.1c03651>
- Buss, W., Bogush, A., Ignatyev, K., Mašek, O., 2020. Unlocking the fertilizer potential of waste-derived biochar. *ACS Sustain. Chem. Eng.* 8, 12295–12303. <https://doi.org/10.1021/acssuschemeng.0c04336>
- Buss, W., Graham, M.C., Shepherd, J.G., Mašek, O., 2016a. Suitability of marginal biomass-derived biochars for soil amendment. *Sci. Total Environ.* 547, 314–322. <https://doi.org/10.1016/j.scitotenv.2015.11.148>
- Buss, W., Graham, M.C., Shepherd, J.G., Mašek, O., 2016b. Risks and benefits of marginal biomass-derived biochars for plant growth. *Sci. Total Environ.* 569–570, 496–506. <https://doi.org/10.1016/j.scitotenv.2016.06.129>
- Buss, W., Wurzer, C., Manning, D.A.C., Rohling, E.J., Borevitz, J., Mašek, O., 2022. Mineral-enriched biochar delivers enhanced nutrient recovery and carbon dioxide removal. *Commun. Earth Environ.* 3, 67. <https://doi.org/10.1038/s43247-022-00394-w>
- Capodaglio, A.G., Olsson, G., 2020. Energy issues in sustainable urban wastewater management: Use, demand reduction and recovery in the urban water cycle. *Sustain.* 12. <https://doi.org/10.3390/su12010266>
- Cheng, F., Luo, H., Colosi, L.M., 2020. Slow pyrolysis as a platform for negative emissions technology: An integration of machine learning models, life cycle assessment, and economic analysis. *Energy Convers. Manag.* 223, 113258. <https://doi.org/10.1016/j.enconman.2020.113258>
- Cheng, S., Qiao, Y., Huang, J., Wang, W., Wang, Z., Yu, Y., Xu, M., 2019. Effects of Ca and Na acetates on nitrogen transformation during sewage sludge pyrolysis. *Proc. Combust. Inst.* 37, 2715–2722. <https://doi.org/10.1016/j.proci.2018.08.018>
- Clarke, B.O., Smith, S.R., 2011. Review of “emerging” organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environ. Int.* 37, 226–247. <https://doi.org/10.1016/j.envint.2010.06.004>
- Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Glob. Environ. Chang.* 19, 292–305. <https://doi.org/10.1016/j.gloenvcha.2008.10.009>
- Dai, L., Li, H., Tan, F., Zhu, N., He, M., Hu, G., 2016. Biochar: a potential route for recycling of phosphorus in agricultural residues. *GCB Bioenergy* 8, 852–858. <https://doi.org/10.1111/gcbb.12365>
- Delistraty, D., 1997. Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Toxicol. Environ. Chem.* 64, 81–108.
- Düngemittelverordnung, 2012. Verordnung über das Inverkehrbringen von Düngemitteln, Bodenhilfsstoffen, Kultursubstraten und Pflanzenhilfsmitteln (Düngemittelverordnung — DüMV) - Düngemittelverordnung vom 5. Dezember 2012 (BGBl. I S. 2482), die zuletzt durch Artikel 3 der Verordnung v.
- EBC, 2012. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar - Version 9.4E, 19th of July 2021. <https://doi.org/10.13140/RG.2.1.4658.7043>
- Fang, L., Li, J., Shan, Donatello, S., Cheeseman, C.R., Wang, Q., Poon, C.S., Tsang, D.C.W., 2018. Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. *Chem. Eng. J.* 348, 74–83. <https://doi.org/10.1016/j.cej.2018.04.201>

- Giudicianni, P., Gargiulo, V., Grottola, C.M., Alfè, M., Ferreiro, A.I., Mendes, M.A.A., Fagnano, M., Ragucci, R., 2021. Inherent Metal Elements in Biomass Pyrolysis: A Review. *Energy and Fuels* 35, 5407–5478. <https://doi.org/10.1021/acs.energyfuels.0c04046>
- Goss, M.J., Tubeileh, A., Goorahoo, D., 2013. A Review of the Use of Organic Amendments and the Risk to Human Health, in: *Advances in Agronomy*. Elsevier, pp. 275–379. <https://doi.org/10.1016/B978-0-12-407686-0.00005-1>
- Hagemann, N., Schmidt, H.P., Kägi, R., Böhler, M., Sigmund, G., Maccagnan, A., McArdell, C.S., Bucheli, T.D., 2020. Wood-based activated biochar to eliminate organic micropollutants from biologically treated wastewater. *Sci. Total Environ.* 730, 138417. <https://doi.org/10.1016/j.scitotenv.2020.138417>
- Hale, S.E., Lehmann, J., Rutherford, D., Zimmerman, A.R., Bachmann, R.T., Shitumbanuma, V., Toole, A.O., Kristina, L., Arp, H.P.H., Alling, V., Breedveld, G., Sparrevik, M., 2012. The total and bioavailable fraction of toxic contaminants in biochar.
- Herzel, H., Aydin, Z., Adam, C., 2021a. Crystalline phase analysis and phosphorus availability after thermochemical treatment of sewage sludge ash with sodium and potassium sulfates for fertilizer production. *J. Mater. Cycles Waste Manag.* 23, 2242–2254. <https://doi.org/10.1007/s10163-021-01288-3>
- Herzel, H., Krüger, O., Hermann, L., Adam, C., 2016. Sewage sludge ash - A promising secondary phosphorus source for fertilizer production. *Sci. Total Environ.* 542, 1136–1143. <https://doi.org/10.1016/j.scitotenv.2015.08.059>
- Herzel, H., Stemann, J., Simon, S., Adam, C., 2021b. Comparison of thermochemical treatment of sewage sludge ash with sodium sulphate in laboratory-scale and pilot-scale experiments. *Int. J. Environ. Sci. Technol.* <https://doi.org/10.1007/s13762-021-03252-y>
- Hill, D.N., Popova, I.E., Hammel, J.E., Morra, M.J., 2019. Transport of Potential Manure Hormone and Pharmaceutical Contaminants through Intact Soil Columns. *J. Environ. Qual.* 48, 47–56. <https://doi.org/10.2134/jeq2018.06.0233>
- Huygens, D., Saveyn, H.G.M., Tonini, D., Eder, P., Sancho, L.D., 2019. Technical proposals for selected new fertilising materials under the fertilising products regulation (Regulation (EU) 2019/1009)—Process and quality criteria, and assessment of environmental and market impacts for precipitated phosphate salts & derivatives, EUR 29841 EN. Luxembourg. <https://doi.org/10.2760/186684>
- International Biochar Initiative, 2011. Standardized product definition and product testing guidelines for biochar that is used in soil, v. 2.1, November 23rd 2015.
- Jensen, P.A., Frandsen, F.J., Dam-Johansen, K., Sander, B., 2000. Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis. *Energy and Fuels* 14, 1280–1285. <https://doi.org/10.1021/ef000104v>
- Kratz, S., Vogel, C., Adam, C., 2019. Agronomic performance of P recycling fertilizers and methods to predict it: a review. *Nutr. Cycl. Agroecosystems* 115, 1–39. <https://doi.org/10.1007/s10705-019-10010-7>
- Krüger, O., Adam, C., 2017. Phosphorus in recycling fertilizers - analytical challenges. *Environ. Res.* 155, 353–358. <https://doi.org/10.1016/j.envres.2017.02.034>
- Liang, X., Jin, Y., He, M., Niyungeko, C., Zhang, J., 2018. Phosphorus speciation and release kinetics of swine manure biochar under various pyrolysis temperatures. *Environ. Sci. Pollut. Res.* 25, 25780–25788. <https://doi.org/10.1007/s11356-017-0640-8>
- Mašek, O., Buss, W., Brownsort, P., Rovere, M., Alberto, T., 2019. Potassium doping increases biochar carbon sequestration potential by 45 %, facilitating decoupling of carbon sequestration from soil improvement. *Sci. Rep.* 5514. <https://doi.org/10.1038/s41598-019-41953-0>
- McAdie, H.G., Jervis, J.M., 1970. The pyrolysis of metal acetates. Part 1. Some group ii acetates. *Thermochim. Acta* 1, 19–28.
- McNamara, P.J., Koch, J.D., Liu, Z., Zitomer, D.H., 2016. Pyrolysis of Dried Wastewater Biosolids Can Be Energy Positive. *Water Environ. Res.* 88, 804–810. <https://doi.org/10.2175/106143016x14609975747441>
- Mercl, F., Košnář, Z., Maršík, P., Vojtíšek, M., Dušek, J., Száková, J., Tlustoš, P., 2021. Pyrolysis of biosolids as an effective tool to reduce the uptake of pharmaceuticals by plants. *J. Hazard. Mater.* 405.

<https://doi.org/10.1016/j.jhazmat.2020.124278>

- Miller-Robbie, L., Ulrich, B.A., Ramey, D.F., Spencer, K.S., Herzog, S.P., Cath, T.Y., Stokes, J.R., Higgins, C.P., 2015. Life cycle energy and greenhouse gas assessment of the co-production of biosolids and biochar for land application. *J. Clean. Prod.* 91, 118–127. <https://doi.org/10.1016/j.jclepro.2014.12.050>
- Okuno, T., Sonoyama, N., Hayashi, J.I., Li, C.Z., Sathe, C., Chiba, T., 2005. Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass. *Energy and Fuels* 19, 2164–2171. <https://doi.org/10.1021/ef050002a>
- Patil, K.C., Chandrashekar, G. V., George, M. V., Rao, C.N.R., 1968. Infrared spectra and thermal decompositions of metal acetates and dicarboxylates. *Can. J. Chem.* 46, 257–265. <https://doi.org/10.1139/v68-040>
- Qian, T.T., Jiang, H., 2014. Migration of phosphorus in sewage sludge during different thermal treatment processes. *ACS Sustain. Chem. Eng.* 2, 1411–1419. <https://doi.org/10.1021/sc400476j>
- Schweizer Bundesrat, 2015. Verordnung ueber die Vermeidung und die Entsorgung von Abfaellen (VVEA); Ordinance on Avoidance and Diposal of Waste. Switzerland.
- Steckenmesser, D., Vogel, C., Steffens, D., 2019. Medium-scale Plant Experiment of Sewage Sludge-based Phosphorus Fertilizers from Large-scale Thermal Processing. *Commun. Soil Sci. Plant Anal.* 50, 2469–2481. <https://doi.org/10.1080/00103624.2019.1667373>
- The European Parliament and the Council of the European Union, 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regula. *Off. J. Eur. Union* 62, 1–132.
- The European Parliament and the Council of the European Union, 2003. Regulation (EC) No 2003/2003 of the European Parliament and the council. *Off. J. Eur. Union* 304, 1–194.
- Tian, S., Tan, Z., Kasiulienė, A., Ai, P., 2017. Transformation mechanism of nutrient elements in the process of biochar preparation for returning biochar to soil. *Chinese J. Chem. Eng.* 25, 477–486. <https://doi.org/10.1016/j.cjche.2016.09.009>
- Uchimiya, M., Hiradate, S., 2014. Pyrolysis temperature-dependent changes in dissolved phosphorus speciation of plant and manure biochars. *J. Agric. Food Chem.* 62, 1802–1809. <https://doi.org/10.1021/jf4053385>
- Vogel, C., Sekine, R., Steckenmesser, D., Lombi, E., Steffens, D., Adam, C., 2017. Phosphorus availability of sewage sludge-based fertilizers determined by the diffusive gradients in thin films (DGT) technique. *J. Plant Nutr. Soil Sci.* 180, 594–601. <https://doi.org/10.1002/jpln.201600531>
- Wohde, M., Berkner, S., Junker, T., Konradi, S., Schwarz, L., Düring, R.A., 2016. Occurrence and transformation of veterinary pharmaceuticals and biocides in manure: a literature review. *Environ. Sci. Eur.* 28. <https://doi.org/10.1186/s12302-016-0091-8>
- Wu, C., Spongberg, A.L., Witter, J.D., Sridhar, B.B.M., 2012. Transfer of wastewater associated pharmaceuticals and personal care products to crop plants from biosolids treated soil. *Ecotoxicol. Environ. Saf.* 85, 104–109. <https://doi.org/10.1016/j.ecoenv.2012.08.007>
- Xiao, R., Wang, J.J., Gaston, L.A., Zhou, B., Park, J.H., Li, R., Dodla, S.K., Zhang, Z., 2018. Biochar produced from mineral salt-impregnated chicken manure: Fertility properties and potential for carbon sequestration. *Waste Manag.* 78, 802–810. <https://doi.org/10.1016/j.wasman.2018.06.047>
- Yuan, H., Lu, T., Huang, H., Zhao, D., Kobayashi, N., Chen, Y., 2015. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. *J. Anal. Appl. Pyrolysis* 112, 284–289. <https://doi.org/10.1016/j.jaap.2015.01.010>
- Zhang, J., Lü, F., Zhang, H., Shao, L., Chen, D., He, P., 2015. Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards potential agronomic and environmental implication. *Sci. Rep.* 5, 1–8. <https://doi.org/10.1038/srep09406>



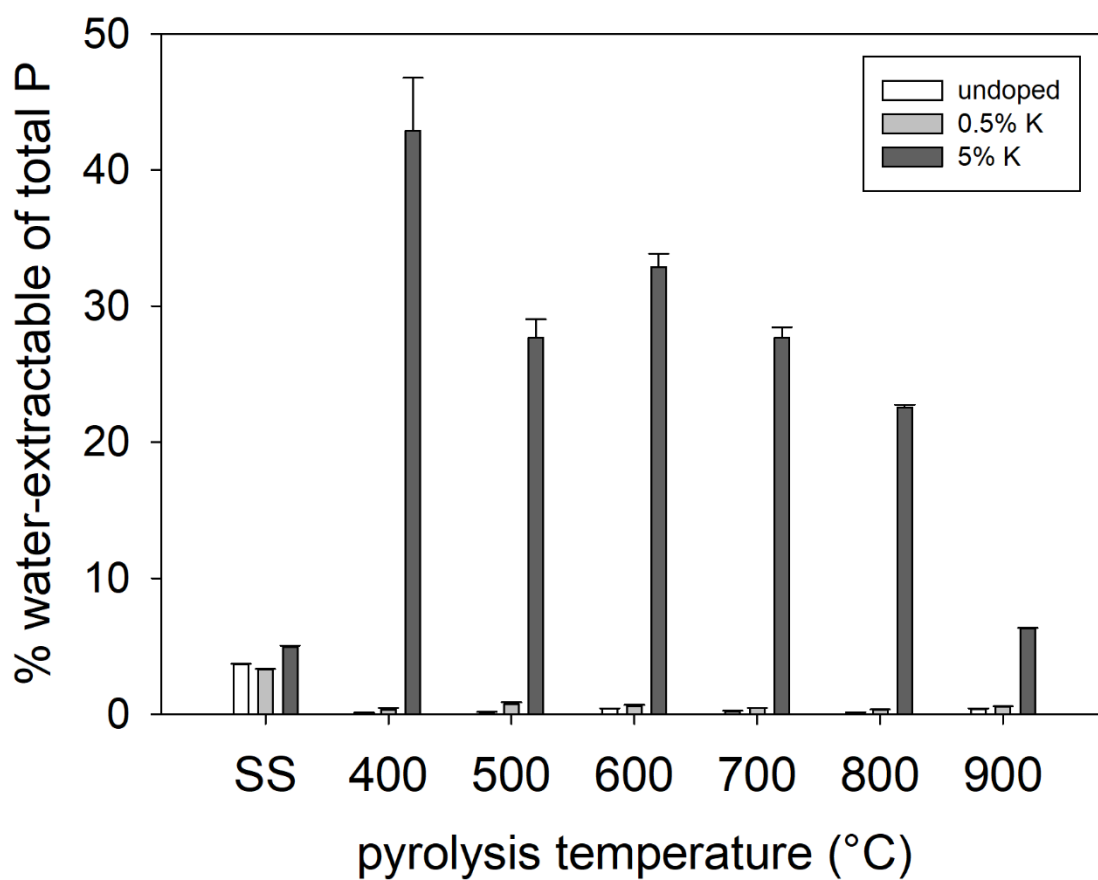


Figure 1: Water-extractable of total phosphorus (P) content in sewage sludge (SS I) and biochars produced in a microscale pyrolysis unit at temperatures of 400-900°C without (undoped) and with 0.5% K and 5% K doping of the feedstock material. Means and standard deviation of three replicate analyses are shown.

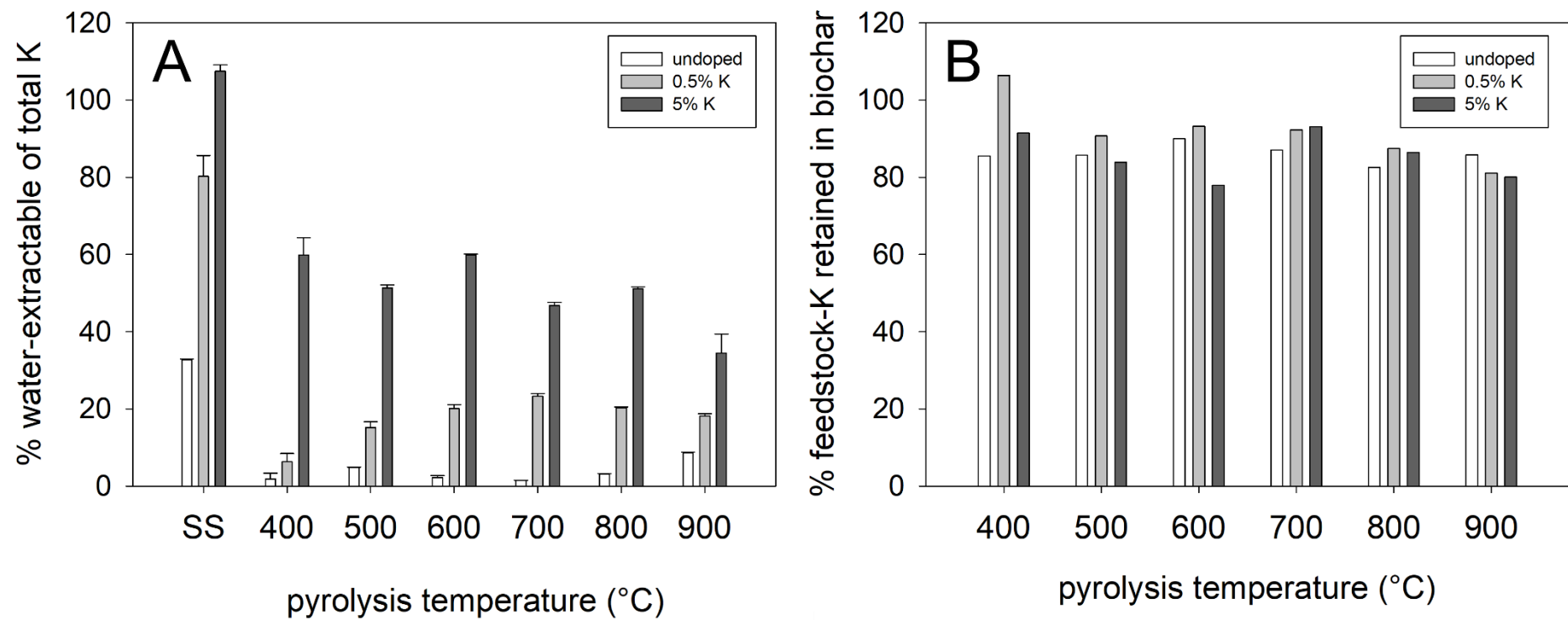


Figure 2: (A) Water-extractable of total potassium (K) content in sewage sludge (SS I) and biochars produced in a microscale pyrolysis unit at temperatures of 400-900°C without (undoped), and with 0.5% K and 5% K doping of the feedstock material. Means and standard deviation of three replicate analyses are shown. (B) Mass balance of K during pyrolysis, from feedstock to biochar (no replication).

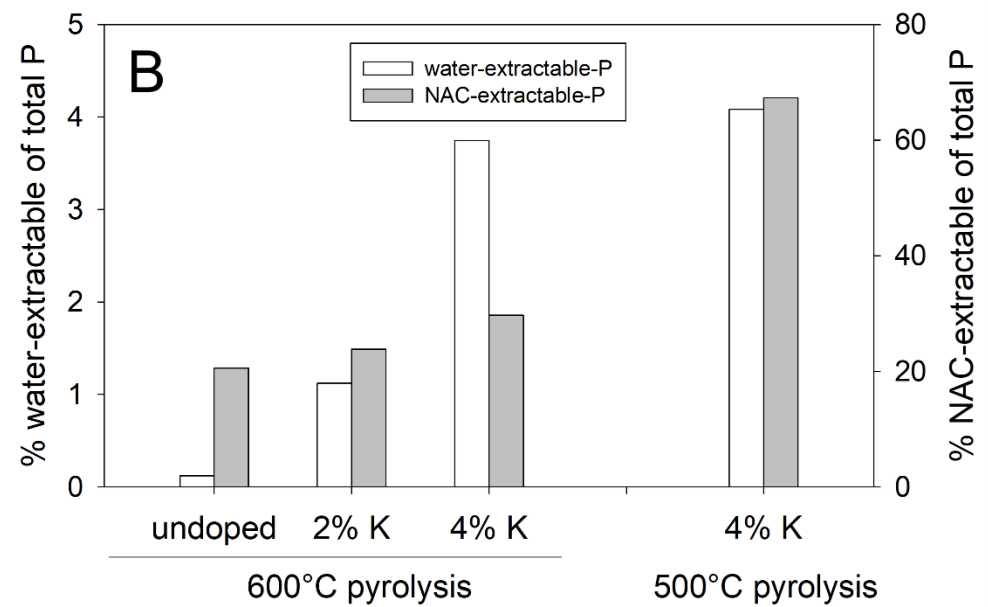
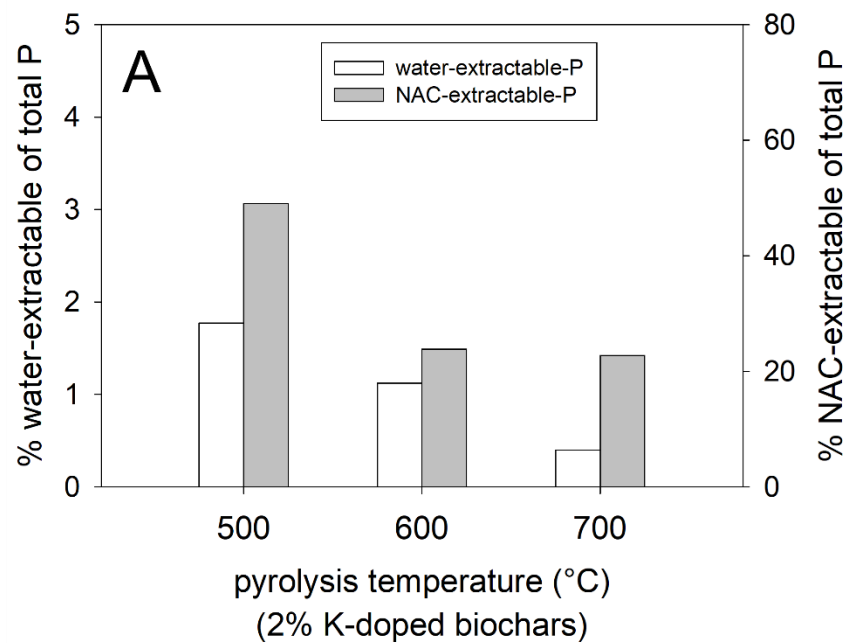


Figure 3: Water-extractable and neutral ammonium citrate (NAC)-extractable of total phosphorus (P) content in sewage sludge (SS II) biochars produced with a continuous pyrolysis unit (PYREKA). (A) SS II biochar produced at 500, 600 and 700°C with 2% K-doping of the feedstock material. (B) SS II biochar produced at 600°C without (undoped), and with 2% K and 4% K doping of the feedstock material, and biochar produced at 500°C with 4% K-doping.

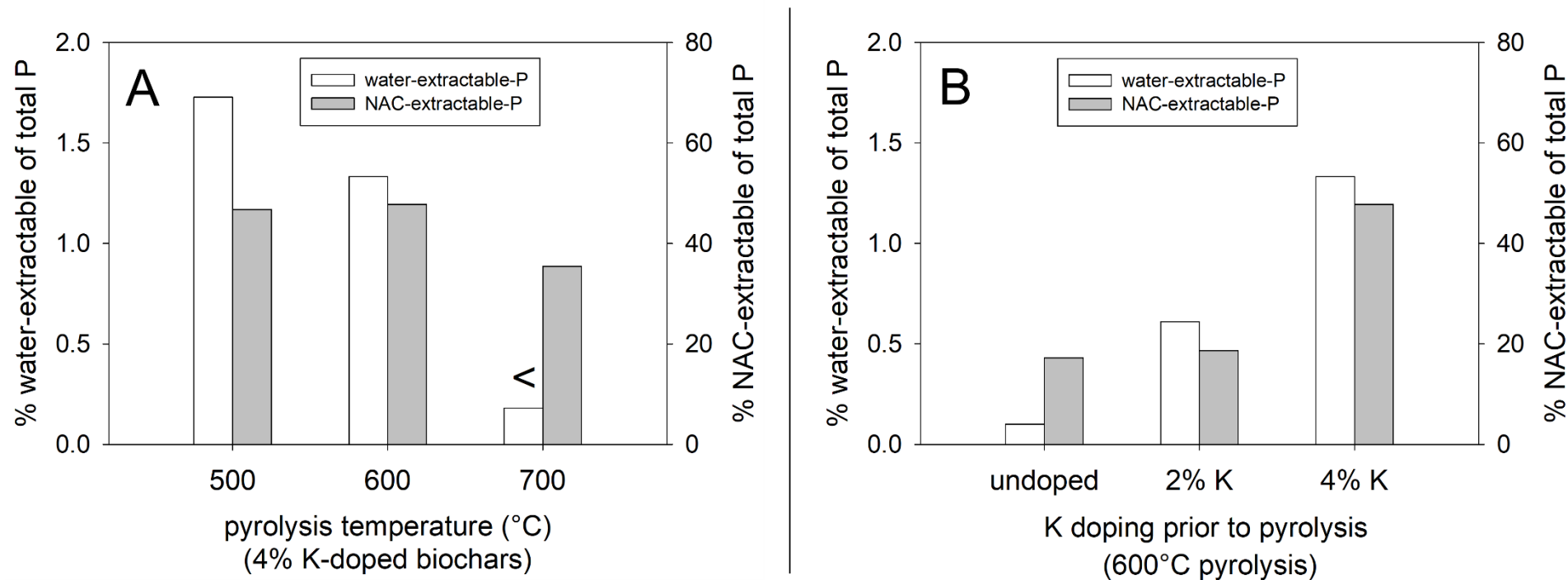


Figure 4: Water-extractable and neutral ammonium citrate (NAC)-extractable of total phosphorus (P) content in swine manure biochars produced with a continuous pyrolysis unit (PYREKA). (A) Swine manure biochar produced at 500, 600 and 700°C with 4% K-doping of the feedstock material. (B) Swine manure biochar produced at 600°C without addition (undoped), 2% K and 4% K doping of the feedstock material.

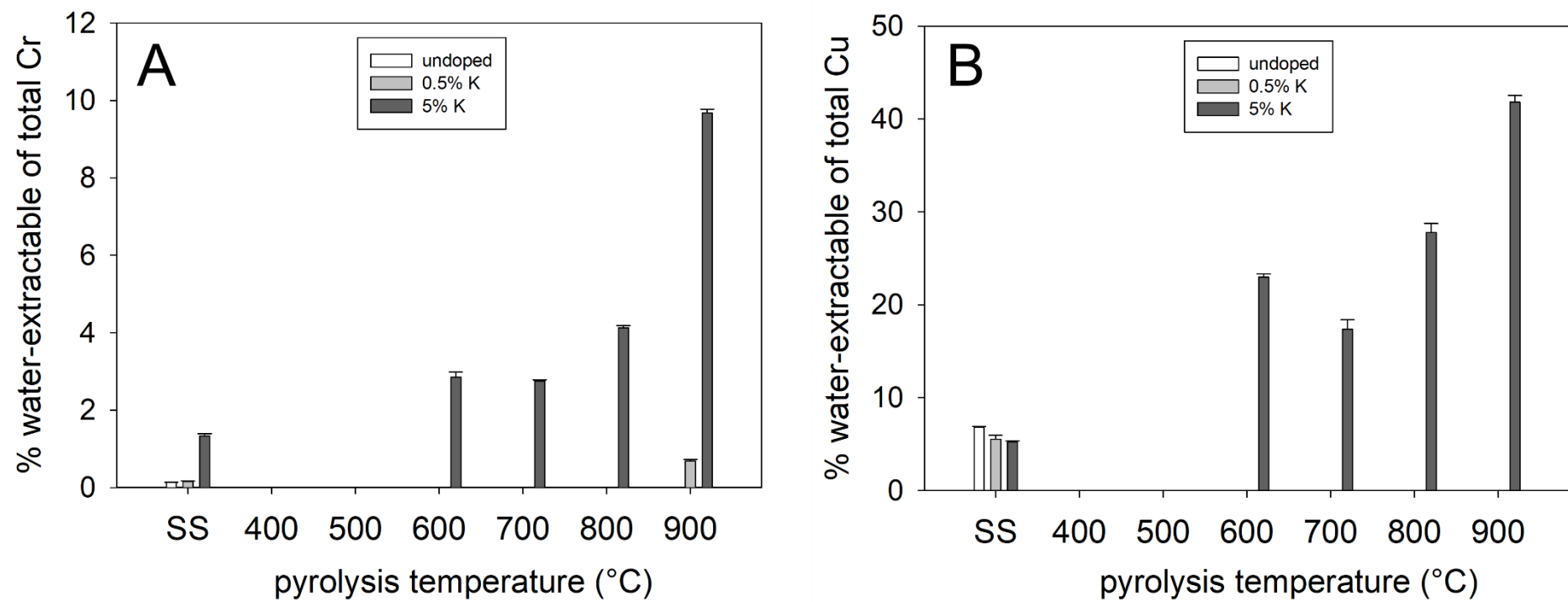


Figure 5: Water-extractable of total Cr (A) and Cu (B) contents in sewage sludge (SS I) biochar produced in the microscale pyrolysis unit at temperature of 400-900°C without (undoped), and with 0.5% K and 5% K doping of the feedstock material. Means and standard deviation of three replicate analyses are shown. Cr and Cu were the only potentially toxic elements out of a set of 8 (As, Cd, Co, Cr, Hg, Ni, Pb, Zn) with water-extractable levels above the detection limit.

Table 1: Characteristics of biochars produced with the PYREKA continuous pyrolysis unit from sewage sludge (SS II) and swine manure at selected conditions. HTT, highest treatment temperature; RT, residence time; NAC, neutral ammonium acetate; SS, sewage sludge

feedstock	HTT °C	feedstock K addition	RT min	biochar yield % dry wt.	P content %	water-extractable P		NAC-extractable P	
						mg kg <sup>-1</sup>	% total	mg kg <sup>-1</sup>	% total
SS II	600	no addition	17-20	38	8.3*	100	0.12	17100	21
SS II	500	2%	17-20	49	5.3	940	1.8	26000	49
SS II	600	2%	17-20	42	7.7*	860	1.1	18300	24
SS II	700	2%	17-20	38	8.5*	340	0.40	19400	23
SS II	500	4%	17-20	50	4.9	2000	4.1	33000	67
SS II	600	4%	17-20	43	7.5	2810	3.7	22300	30
swine manure	600	no addition	27	34	11.9#	120	0.10	20500	17
swine manure	600	2%	27	36	11.3#	690	0.61	21100	19
swine manure	500	4%	27	42	9.8#	1700	1.7	46000	47
swine manure	600	4%	27	45	9.0#	1200	1.3	43000	48
swine manure	700	4%	27	37	11.0#	200	0.18	39000	35

\* calculated based on P content in sewage sludge biochar produced at 600°C, using respective biochar yields and assuming 100% P retention during pyrolysis

# calculated based on P content in swine manure feedstock, using respective biochar yields and assuming 100% P retention during pyrolysis

Table 2: Content of 16 US EPA PAHs in sewage sludge (SS II) biochar doped with 4% K prior to pyrolysis at 600°C in the PYREKA continuous pyrolysis unit (toluene extraction DIN EN 16181:2019-08).

PAH	content (mg kg <sup>-1</sup> )
naphthalene	1.2
acenaphthylene	<0.1
acenaphthene	<0.1
fluorene	<0.1
phenanthrene	0.3
anthracene	<0.1
fluoranthene	0.1
pyrene	<0.1
benz(a)anthracene	<0.1
chrysene	<0.1
benzo(b)fluoranthene	<0.1
benzo(k)fluoranthene	<0.1
benzo(a)pyrene	<0.1
indeno(1,2,3-cd)pyrene	<0.1
dibenz(a,h)anthracene	<0.1
benzo(g,h,i)perylene	<0.1
Σ16 US EPA PAHs	1.6