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Evaluation of phosphorus in thermally converted sewage sludge: P pools and availability to wheat

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Abstract *Aims* Dried sewage sludge (SS) and the by-products of four SS thermal conversion processes (pyrolysis, incineration and two types of gasification) were investigated for phosphorus (P) availability.

Methods A sequential extraction was used to determine the distribution of P among different P pools. After mixing materials with soil, availability of the P was determined with soil P extractions and in a growth experiment with wheat.

Results Thermally converted SS contained a greater proportion of P within recalcitrant pools than dried SS. Despite having very different P pool distributions, the incinerated and raw SS provided similar amounts of P to plants. Plant P supply from raw and incinerated SS was lower than the comparable soluble P treatment (50 mg P kg^{-1}), but higher than a soluble treatment at a lower rate (20 mg P kg^{-1}). Plant P uptake in gasified and pyrolysed treatments was only marginally greater than uptake in a control (no P) treatment. Plant P uptake correlated most closely with diffusive gradients in thin films (DGT) P analysis of soil-material mixes. Phosphorus availability in the dried and incinerated SS treat-

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ments increased over time.

Conclusions We propose that the dried and incinerated SS have potential as slow release P fertilisers in low pH soils.

Keywords Biochar · Bioash · Sequential phosphorus extraction · Diffusive gradients in thin films (DGT) · Wheat · Sewage sludge

Introduction

Most P fertilisers currently used come from phosphate rock, which is a finite resource (Scholz and Wellmer, 2013). Alternatively, sewage sludge (SS) can provide crops with P (Metson and Bennett, 2015). However SS has a much lower P concentration compared to conventional P fertilisers (e.g. 3-39 g kg^{-1} reported by O'Connor et al, 2004) and therefore large amounts of SS need to be transported to and applied on farms, which will have higher economic costs compared with conventional P fertilisers. Processing of SS in such a way that the P concentration is increased could lead to it becoming a more viable P amendment.

There is growing interest in thermally converting waste materials to create bioenergy (Müller-Stöver et al, 2012; Kauffman et al, 2014). Bioenergy can be generated by pyrolysis, gasification or incineration. Sewage sludge could potentially be used as a feedstock for bioenergy generation (Wang et al, 2014) from which the by-product is a biochar (from pyrolysis) or a bioash (from gasification/incineration). Thermally converted SS (biochar/bioash) can have a higher P concentration compared with the initial SS due to a decrease in the concentration of carbon (C) and other elements. These processes also destroy organic pollutants, which can be an issue in SS (Harrison et al, 2006). Additionally, biochars can provide soil with many benefits including increased soil aggregate stability, water availability and soil C (Ma et al, 2016). Therefore, thermally converted SS has a great potential to be used as a soil P amendment.

While conventional P fertilisers contain mainly soluble P that is readily available to plants, thermally converted materials can contain a range of P species with varying availability to plants (Wang et al, 2014; DeLuca et al, 2015). Availability of P in biochars and ashes is mostly influenced by the cations present in the feedstock, with most of the P being associated with calcium (Ca), aluminium (Al) and iron (Fe) (Wang et al, 2012; Wilfert et al, 2015; Smith et al, 2002). Generally, biochars made from manures, sewage sludges and grasses have higher P concentrations than wood-based biochars (Singh et al, 2014; Zhao et al, 2013). However, thermal conversion temperature, duration and type (e.g. pyrolysis vs. gasification) can influence P availability. While P availability has been shown to be related to pyrolysis temperatures in some studies (Zheng et al, 2013; Ippolito et al, 2015), in others it has not (Gaskin et al, 2008). Slow pyrolysis can lead to higher P availability compared with fast pyrolysis (Ippolito et al, 2015). Incinerated SS has been found to have less available P compared with raw SS (Jakobsen and Willett, 1986); however, Viader et al (2016) found that the P in incinerated SS was more easily extractable than the P in gasified SS. Alternatively, Kuligowski et al (2010) found little difference in P availability between gasified and incinerated pig manure slurry. There has yet to be a study comparing all three thermal conversion processes (pyrolysis, gasification and incineration) of SS in which plant-available P is determined both indirectly, with soil P extractions, and directly, by measuring plant P uptake.

In this study, the effect of four thermal conversion processes (pyrolysis, incineration and two types of gasification) on P in samples from the same batch of SS was examined and compared with SS which had been thermally dried. The materials were analysed chemically in order to ascertain their total P and C concentrations, and also to determine the size of P pools of different bioavailablity. Then, they were used in a plant growth experiment in order to determine P availability to plants. It was hypothesised that thermally converted SS would have a higher P concentration compared with dried SS; however, much of this P was anticipated to be unavailable to plants in the short term.

Materials and methods

Materials: sources and analysis

Five materials were used in this experiment: a dried SS and four thermally converted SS. Sewage sludge was from the wastewater treatment facility Bjergmarken Renseanlæg in Roskilde, Denmark. Sludge had been processed into three forms: dry pellets, dry granules and dewatered sludge. Pellets differed to granules in that pellets were larger and cylindrical (ca. 0.6 mm diameter and 5-10 mm long) whereas granules were smaller and more spherical (ca. 2-3 mm diameter). More information on the wastewater treatment is provided in the supplementary material. A sample of the dry granules had been further dried at 104°C to almost 100% dry matter. This sample is hereafter referred to as ‘dried SS’. A sample of the dry pellets had been converted in a Two Stage Fixed Bed Gasifier (2S gasifier; Ahrenfeldt et al, 2006; Henriksen et al, 2006) to produce 2S gasified SS. A sample of the dry granules had been processed in a Low Temperature Circulating Fluidised Bed Gasifier

(LT gasifier; Ahrenfeldt et al, 2006; Thomsen et al, 2015) to produce LT gasified SS. Another sample of the dry granules had been pyrolysed using a slow pyrolysis process with a maximum temperature of 600°C, producing pyrolysed SS. The dewatered SS was transported directly from the wastewater treatment facility to an incineration facility, where it was incinerated at 850°C. More detailed descriptions of the thermal conversion processes are given in the supplementary material.

Once the materials were obtained, their chemical properties were analysed. The incinerated SS was already a very fine powder with a particle size of less than 0.4 mm. A subsample of the other materials was ground to a fine powder using a ball mill for elemental analysis, while another sample was ground using a mortar and pestle to less than 2 mm for the sequential P extraction, pH and electrical conductivity (EC) determination, and for the plant growth experiment. Total P concentration (and concentrations of a range of other elements) was determined following digestion of materials (100 mg for dried sludge, 25 mg for other amendments) with nitric acid and hydrogen peroxide in an UltraWAVE (Milestone Inc. Milan, Italy). After digestion, 200 μl of 49% hydrofluoric acid (HF) was added to the samples which were then analysed using ICP-OES (Agilent Technologies, Manchester, UK). The concentrations of nitrogen (N) and C in the materials were determined by Dumas combustion using a vario Macro cube elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The P pools in the materials were analysed in triplicate using the sequential extraction procedure of Hedley et al (1982a) with some modifications. Phosphorus was sequentially extracted from 0.5 g of materials using 30 ml of deionised H_2O, 30 ml of 0.5 M sodium bicarbonate ($NaHCO_3$, pH = 8.5), 30 ml of 0.1 M sodium hydroxide (NaOH), and 30 ml of 1 M hydrochloric acid (HCl). Each extraction was conducted with continuous shaking for 16 hr at 25°C. After each extraction, inorganic P concentration of the supernatant was determined colorimetrically (FIAstar 5000 Analyzer). In this study, the organic P concentrations were not determined as it is expected that most of the P in the materials will be present in an inorganic form (Huang and Tang, 2015; Qian and Jiang, 2014). Moreover, some of the organic P will likely have been hydrolysed in the NaOH and HCl treatments. The ‘residual’ pool of P was determined by subtracting the sum of the P extracted in each extraction from the total P, which was measured on a different subsample. Therefore, the residual P accounts for the proportion of organic P which was not hydrolysed (but potentially extracted) and the proportion of inorganic P that could not be extracted with any of the extractants. The pH and EC of materials were determined on 1:25 and 1:75 material:H_2O extracts, respectively.

Plant growth experiment

The soil was taken in 2014 from the upper layer of a nutrient depletion trial at the University of Copenhagen’s experimental research farm in Tåstrup, Denmark, from a treatment receiving neither P nor potassium (K) for more than 50 years. This soil is a sandy loam (16.5% clay) and has a pH of 5.3 measured in a 1:2.5 soil:0.01M CaCl2 suspension. The soil was air-dried, passed through a 5 mm sieve and stored in a dark, cool room before use. The soil was mixed with sand (1:1, w:w). This mix (hereafter referred to as soil) had a water holding capacity (WHC) of 18% gravimetric water content.

A plant growth experiment was conducted to determine the availability of P in the materials. Nutrients were added to the soil (to ensure the only nutrient limiting plant growth was P) as follows: 370.31 mg K_2SO_4, 7.5 mg $CaCl_2.2H_2O$, 10.5 mg $MnSO_4.H_2O$, 5.4 mg $ZnSO_4.7H_2O$, 2.1 mg $CuSO_4.5H_2O$, 0.18 mg $Na_2MoO_4.2H_2O$, 285.71 mg NH_4NO_3 and 405.43 mg $MgSO_4.7H_2O$ per kg soil. After 40 days of plant growth, a further 285.71 mg of NH_4NO_3 per kg soil was added to all pots to ensure N would not limit plant growth. Each of the materials (dried, 2S gasified, LT gasified, pyrolysed and incinerated SS) were mixed into soil at a rate of 50 mg P kg^{-1}, which equated to between 520 and 1310 mg of material per kg soil. Additionally, two soluble P treatments were included in which monopotassium phosphate (KH_2PO_4) was mixed into soil at a rate of 50 (P50) or 20 (P20) mg P kg^{-1}. Also, a control was included in which no P was added to soil.

Once materials were mixed with soil, 2.5 kg soil was filled into pots (bottom capped PVC pipes, 10 cm diameter x 28 cm height, 13 pots per treatment) and watered to 60% of WHC (10.8% gravimetric water content). Soil was kept at this moisture content for an incubation period of 8 days as sowing in the field often does not occur immediately following application of SS. Following the incubation, one pot from each treatment was kept aside and after a further 5 days, soil from these pots was analysed for plant-available P using two different methods: Colwell P (Colwell, 1963) and DGT P (Mason et al, 2010). Two different methods for analysing plant-available P were used in order to determine which method was most appropriate for soils amended with thermally converted materials. Additionally, the pH and EC of the soil were determined in a 1:5 soil:H_2O extract.

Three pre-germinated seeds of spring wheat (*Triticum aestivum* L. var. Axe) were sown in each remaining pot (12 pots per treatment). After four days, seedlings were thinned to two per pot. There were three sampling times: 26, 40 and 55 days after sowing. At each sampling time four pots from each treatment were destructively harvested. For the duration of the plant growth experiment, pots were kept in a growth chamber with a day/night temperature of 25°C/18°C and day/night length of 14/10 h. Pots were watered 3-4 days per week to 80% WHC throughout the plant growth experiment.

At each harvest, aboveground plant material was collected, oven-dried (at 60°C until constant mass was reached), and analysed for total P concentration colorimetrically using a FIAstar 5000 Analyzer following digestion in nitric acid in an UltraWAVE (Milestone Inc.). From the concentration and biomass, plant P uptake was determined. The amount of P taken up between each harvest (that is, for the time periods: 0-26 days, 27-40 days, and 41-55 days) was determined by subtracting the average P uptake of the previous harvest from P uptake of each replicate of the corresponding treatment in the current harvest. Then, the plant P uptake rates were determined for the time periods: 0-26 days, 27-40 days, and 41-55 days, by dividing the amount of P taken up in each time period by the number of days in each time period.

Statistical analysis

All statistical analyses were conducted in R (version 3.2.3) with α level of 0.05. A principal component analysis (PCA) was performed to identify differences in physicochemical properties among materials using the ‘prcomp’ function with standardisation of variances. Generalised Linear Models (GLMs, family = gaussian) were used to determine differences among materials for each P pool; differences among treatments for soil pH, EC, Colwell P and DGT P; differences among treatments and harvests (and the interaction between treatment and harvest) for plant aboveground biomass and aboveground P uptake; and differences among treatments and time periods (and the interaction) for plant P uptake rate. All interactions were significant, so GLMs were used to analyse results from each harvest or time period separately. When GLMs were significant, they were followed up with a Tukey's test. Pearson's correlations were performed to explore relationships between amendment and soil analyses and mean plant P uptake for each treatment at each harvest time. Two sets of correlations were performed. One set included P pool data (as determined by sequential extraction), soil P data and P uptake only in treatments where SS was applied (i.e. excluding P50, P20 and control, as there was no P pool data for these treatments). The second set included soil P data and P uptake in all treatments.

Results

Material analysis

All thermally converted SS were considerably different compared with the dried SS and each other in terms of the physicochemical properties measured (Figure 1, Table 1 and 2). Principle component analysis revealed that LT gasified, 2S gasified and incinerated SS were associated with higher total P, K and Ca, and lower N, NaOH-P and $NaHCO_3$-P compared with dried SS (Figure 1). It also found that pyrolysed SS was associated with higher residual P compared to dried SS (Figure 1). The C concentration of the dried SS was 267 mg g^{-1}, which was 1.2 fold greater than pyrolysed SS, 3.7-4.5 fold greater than gasified SS and 53.4 fold greater than incinerated SS. Thermally converted materials had 0.9-1.5 fold greater P concentration compared to the dried SS, which had a P concentration of 38.3 mg g^{-1}. The C:P ratios of the materials was highest for the dried SS (7.0) and lowest for the incinerated SS (0.1; Table 1). Therefore, less of the incinerated than of the dried SS was needed in order to provide the same amount of P to the soil. The N concentration was lower in thermally converted SS compared to dried SS, while the concentrations of K and Ca were higher compared to dried SS (Figure 1, Table 1). There were negligible differences in P:K (6.9-7.9) and P:Ca (0.6-0.7) ratios among materials. The pH of the dried SS was higher than the raw SS, while the EC varied among materials (Table 1).

The distribution of P among chemical pools differed among the different materials (Table 2, Figure 1) with thermally converted SS generally containing lower P in the H2O-, NaHCO3- and NaOH-extractable P pools and greater P in the HCl-extractable P pool compared with dried SS (Table 2, Figure 1). Most of the P in all materials being present in the HCl-extractable pool (51.5% - 91%; Table 2). For all materials, the H2O-extractable P pool was the smallest, containing only 1.7% of the P in the dried SS and less than 0.15% of the P in the other materials (Table 2). The NaHCO3-extractable pool was also small for all materials, containing 5.2% of the P in the dried SS and less than 1.8% of the P in the other materials (Table 2). While thermally converted SS generally had a greater percentage of P in the residual pool than dried SS, this was not the case for the incinerated SS, which had the lowest percentage of P in the residual pool of all materials (Table 2). Principle component analysis revealed that the residual P pool was an important factor distinguishing materials from each other (Figure 1).

Plant growth experiment

After the materials had been mixed with soil, there were differences in some soil properties but not in others (Table 3). The pH and EC of the soils were similar regardless of treatment, with addition of materials only marginally increasing pH (< 0.1 units) and EC (< 0.2 mS cm^{-1}) of soil (Table 3). Colwell P was higher in the dried SS treatment and in the P50 and P20 treatments compared with the control. However, the remaining treatments had less Colwell P than the control (Table 3). All SS treatments had between 1.3 and 3 fold greater DGT P compared to the control (Table 3). The highest plant-available P (both Colwell and DGT P) was measured in the P50, P20 and dried SS treatment (Table 3).

There were a number of differences among treatments in aboveground biomass (Figure 2a), P uptake (Figure 2b) and P uptake rate (Figure 3). The P50 treatment had the largest aboveground biomass and the largest aboveground P uptake at each harvest, with 1.6-7.9 fold greater biomass and 1.4-6.0 fold greater P uptake than other treatments at 55 days. While at 26 and 40 days after sowing the P20 treatment had larger aboveground biomass than the dried and thermally converted SS, at 55 days there was no significant difference between P20 and dried SS. At 26 days, aboveground P uptake was greater in P20 compared with all SS treatments. However, at 40 days there was no difference between P20 and dried SS and at 55 days both dried and incinerated SS had 1.3 fold greater P uptake compared with P20. Moreover, in the third time period (41-55 days) dried and incinerated SS had significantly higher P uptake rates compared with all other treatments (617.9 μg day^{-1} and 573.7 μg day^{-1} compared with less than 355.0 μg day^{-1}). The P uptake rates in dried and incinerated SS treatments were more than 10 times higher in the third growing period compared with the first growing period. Of the SS, the raw and incinerated SS resulted in the largest biomass and P uptake at the final harvest followed by the LT gasified SS. At 55 days after sowing, the amount of P that incinerated SS provided to plants was 69% of the P which was provided by P50, while the amount of P that 2S gasified SS provided was only 21% of the P which was provided by P50. The 2S gasified SS and the pyrolysed SS were not different from the control at the final harvest in both biomass and P uptake. In the third growing period there were no significant differences in P uptake rate among P50, P20, LT gasified SS, 2S gasified SS, pyrolysed SS and the control.

Aboveground P uptake at all harvests was significantly correlated with both the Colwell P and the DGT P of soil when all treatments were considered; however, the correlations were weaker at the last harvest (Table 4). When just the SS treatments were considered (i.e. excluding P50, P20 and control), DGT P was significantly correlated with plant P uptake at all harvests but Colwell P was only significantly correlated with plant P uptake at the first harvest (Table 5). The H2O-extractable P pool was significantly correlated with plant P uptake at the first harvest, but not at any other harvest (Table 5). None of the other P pools were significantly correlated with plant P uptake at any harvest (Table 5).

Discussion

The P in the thermally converted materials, as analysed by sequential P extraction, was predicted to be largely unavailable. Most of the P in the materials was present in the HCl-extractable pool, which is thought to represent Ca-phosphates (Hedley et al, 1982b) - a common P form in thermally converted materials (Zhao et al, 2013). Calcium phosphates often have a low solubility and therefore low availability to crops. The thermally converted SS also generally had a greater amount of P in the residual pool than dried SS. This is the pool of P which could not be extracted by any of the extractants, and so should be the least available to plants.

As expected based on the sequential P extraction, both the gasified SS and pyrolysed SS provided less P to plants than the dried SS. Nuclear magnetic resonance (NMR) spectroscopy has revealed P components with low solubility in pyrolysed SS, particularly those pyrolysed at high temperatures (Huang and Tang, 2015; Qian and Jiang, 2014). X-ray absorption near edge structure (XANES) spectroscopy has confirmed this for other pyrolysed materials (e.g. Bruun et al, 2017; Zwetsloot et al, 2015). However, there are limited studies which confirm low availability in plant growth experiments. Furthermore, forms of P with low solubility have not been previously reported in gasified materials. On the other hand, the availability of the P in the incinerated SS was not as expected based on P pool analysis. While 91% of the P in the incinerated SS was present in the HCl-extractable P (Table 2), incinerated SS provided plants with similar amounts of P as the dried SS. Jakobsen and Willett (1986) found very low P availability in an incinerated SS, particularly compared with a raw SS. However, our results suggest that, while thermally drying SS and incinerating SS result in very different materials in terms of P speciation, they ultimately have similar plant P availability. Phosphorus in incinerated SS has been found to be more acid-soluble than P in gasified SS, which can give an indication of plant-availability (Viader et al, 2016). Both soil microbe and plant root exudates result in a highly acidic environment (Richardson et al, 2011) and hence solubilisation of the P in the HCl-extractable pool could occur. Moreover, the soil itself was already acidic, which could promote dissolution. Contrasting results have been found regarding the effect of soil pH on availability of P in thermally converted SS. While Cabeza et al (2011) found that a SS ash had greater P availability in a neutral soil compared with an acidic soil, Nanzer et al (2014) found that a SS ash had greater P availability on acidic or neutral soil compared with alkaline soil. In our experiment, solubilisation could have occurred to a greater extent in the treatment with incinerated SS due to the smaller particle size, and hence greater surface area:volume ratio of the incinerated SS compared with the other materials. However, more work is needed to determine the effect of particle size on P availability.

There was clear evidence for P solubilisation over time in the 55 day experiment for dried and incinerated SS treatments, which had more than 10 times higher P uptake rates in the third growing period compared with the first growing period (Figure 3). Increases in P availability over a single growing season have been shown before for a raw SS (McLaughlin and Champion, 1987), but not for dried or thermally converted SS. Biochars have been suggested as slow release P fertilisers (Singh et al, 2014), and likewise incinerated SS could also be used as a slow release fertiliser. However, many crops require large amounts of P in the early stages of their life cycle, with wheat plants taking up 50-60% of their P in the first six weeks of growth (Römer and Schilling, 1986). Without this early P, biomass of crops may not reach optimal levels. While the dried and incinerated SS both eventually provided plants with more P than the P20 treatment (Figure 2b), they still did not result in as much aboveground biomass as P20 (Figure 2a). Dried and thermally converted SS may need to be coupled with a more soluble P fertiliser in order to obtain optimal yields.

The P in the materials which was not taken up by the crops in the first season after application will remain in the soil and may become available to crops in following years. Further investigations are needed to determine how much of this P would become available to plants and over what time scales. Few studies have been conducted in which P uptake from thermally converted materials was measured over multiple growing seasons. While Mellbye et al (1982) found that incinerated SS did not affect plant (corn) P uptake over two growing seasons, they also found no effect of superphosphate, and therefore results are inconclusive. In neutral loamy soil, an incinerated SS was found to provide plants with P over two growing seasons (Cabeza et al, 2011). However, the ash used was a thermochemically treated ash, which would have different P availability compared to the incinerated SS ash used in our study. Moreover, it is possible that thermally converted SS may be modified to provide more P to plants faster, e.g. by adjusting the particle size as mentioned above. Furthermore, there are other emerging techniques which could increase P availability in thermally converted materials (e.g. thermochemical treatment of ash (Herzel et al, 2016)).

In future research, it will be helpful to have rapid tools to determine the availability of P in thermally converted materials. It would be most useful if a direct analysis of the materials could be used to assess their P fertiliser value. However, of the P extractions used here, only H_2O-extractable P was correlated with plant P uptake, and only for the first harvest (Table 3). On the other hand, soil parameters largely affect P availability, and therefore it may be necessary to first mix materials with relevant soil types before performing extractions. Following an incubation of incinerated SS and soil, Nanzer et al (2014) extracted P sequentially and found that the combined resin- and $NaHCO_3$-extractable pools were correlated with plant P uptake. We used both Colwell and DGT methods to determine available P in soil. Both methods correlated with plant P uptake for all harvests when all treatments were considered; however, the correlations were weaker at the last harvest (Table 4). Moreover, it is likely that the P50 treatment had a large influence on this model. When only the dried and thermally converted SS treatments were included, DGT P correlated with plant P uptake for all harvests but Colwell P only correlated with plant P uptake for the first harvest (Table 3). Moreover, the Colwell P analysis showed a lower plant P availability after the addition of the thermally converted materials compared to the control. Alkaline extractions, such as Colwell P, have been shown to provide poor estimates of available P when sparingly soluble P is added to soil (Saggar et al, 1992), and hence this extraction may not be appropriate for soil receiving thermally converted materials. The DGT P method has proven successful in fields fertilised with inorganic P (Mason et al, 2010), as well as more recently in pot experiments with organic amendments (Six et al, 2014). The DGT method may be a more sensitive indicator of plant-available P compared with the Colwell method when P is applied in complex forms. After verification using a wider range of soils and crops, DGT P could be used in future soil incubation experiments to gain a general idea of P availability in thermally converted materials, without the need to grow plants.

Conclusion

To summarise, while gasification and pyrolysis of SS had lower availability of P compared with dried SS, this was not the case for incineration. Incinerated SS provided crops with similar amounts of P as dried SS despite the fact that 91% of the P in the incinerated SS was present in the HCl-extractable pool. The plant-availability of the P in the dried and incinerated SS clearly increased throughout the 55 day experiment. Plant P uptake over the time course of the experiment was best correlated with DGT P analysis of the soil-material mixes, and therefore this method could be used to test P availability of other potential P amendments. We suggest that the dried and incineration SS be used as a slow release P fertiliser in low pH soils, and could be coupled with a more soluble P fertiliser for optimal yields.

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Table 1 Chemical analysis of dried and thermally converted sewage sludge. LT = Low Temperature Circulating Fluidised Bed; 2S = Two stage Fixed Bed.

Material	P ($mg\ g^{-1}$)	C ($mg\ g^{-1}$)	C:P	N ($mg\ g^{-1}$)	K ($mg\ g^{-1}$)	Ca ($mg\ g^{-1}$)	pH	EC ($mS\ cm^{-1}$)
Dried	38.3	267	7.0	37	5.4	54.6	7.2	0.35
Incinerated	88.1	5	0.1	n.d.	12.4	139.1	9.2	0.37
LT gasified	94.4	72	0.8	5	13.8	130.0	10.7	0.15
2S gasified	95.8	59	0.6	1	12.4	131.1	9.9	0.05
Pyrolysed	72.3	226	3.2	22	9.2	100.2	11.6	0.36

Table 2 P content (as a percentage of total P) of dried and thermally converted sewage sludge following sequential extraction. LT = Low Temperature Circulating Fluidised Bed; 2S = Two stage Fixed Bed. Values are means ± standard errors. Letters indicate significant differences within columns.

	Percent of total P				
Material	H_2O	0.5M $NaHCO_3$	0.1M NaOH	1M HCl	Residual
Dried	1.66 ± 0.02 a	5.18 ± 0.05 a	37.19 ± 0.49 a	51.50 ± 1.19 d	4.47 ± 0.85 c
Incinerated	0.01 ± 0.00 c	0.53 ± 0.01 c	8.43 ± 0.03 d	90.95 ± 0.29 a	0.07 ± 0.28 d
LT gasified	0.01 ± 0.00 c	0.41 ± 0.01 cd	11.11 ± 0.03 c	80.75 ± 0.10 b	7.72 ± 0.10 b
2S gasified	0.13 ± 0.01 b	0.36 ± 0.03 d	5.97 ± 0.11 e	88.69 ± 0.33 a	4.85 ± 0.43 c
Pyrolysed	0.00 ± 0.00 c	1.79 ± 0.02 b	18.17 ± 0.30 b	68.51 ± 0.08 c	11.53 ± 0.24 a

Table 3 Analysis of soil amended with soluble P, sewage sludge (either dried or thermally converted) or no P (control) following a 13 day incubation. Values are means ± standard errors. Letters indicate significant differences within columns.

Treatment	pH	EC ($mS\ cm^{-1}$)	Colwell P ($mg\ kg^{-1}$)	DGT P ($\mu g\ l^{-1}$)
P50	5.39 ± 0.01	0.31 ± 0.02	10.42 ± 0.45 a	1355.86 ± 89.60 a
P20	5.37 ± 0.00	0.32 ± 0.01	7.12 ± 0.10 a	437.13 ± 3.49 b
Dried	5.46 ± 0.02	0.32 ± 0.00	7.44 ± 1.56 b	150.96 ± 19.14 c
Incinerated	5.43 ± 0.01	0.31 ± 0.01	5.83 ± 0.89 b	133.55 ± 31.90 c
LT gasified	5.42 ± 0.00	0.32 ± 0.03	5.35 ± 0.02 b	87.66 ± 0.91 c
2S gasified	5.44 ± 0.02	0.31 ± 0.01	4.88 ± 0.02 b	57.65 ± 10.60 c
Pyrolysed	5.39 ± 0.06	0.46 ± 0.11	4.79 ± 0.07 b	65.74 ± 5.03 c
Control	5.38 ± 0.01	0.30 ± 0.00	6.00 ± 0.57 b	50.56 ± 1.80 c

Table 4 Results from Pearson's correlation analyses of soil (Colwell P and DGT P) P pools with plant P uptake at three different harvests (26, 40 and 55 days). All treatments in plant growth experiment are included (N=8). Values are correlation coefficients (R values) with P values in parentheses. Significant correlations are indicated in bold.

	P uptake (mg/pot)		
Variable	26 days	40 days	55 days
Colwell P (mg/kg)	**0.96 (<0.01)**	**0.94 (<0.01)**	**0.86 (0.01)**
DGT P (μg/l)	**0.98 (<0.01)**	**0.96 (<0.01)**	**0.78 (0.02)**

Table 5 Results from Pearson's correlation analyses of dried and thermally converted sewage sludge (H_2O-, $NaHCO_3$-, NaOH-, HCl- and Residual-P) and soil (Colwell P and DGT P) P pools with plant P uptake at three different harvests (26, 40 and 55 days). Only data from treatments with dried or thermally converted sewage sludge are included (N=5). Values are correlation coefficients (R values) with P values in parentheses. Significant correlations are indicated in bold.

	P uptake (mg/pot)		
Variable	26 days	40 days	55 days
H_2O-P (%)	**0.90 (0.04)**	0.61 (0.28)	0.55 (0.34)
$NaHCO_3$-P (%)	0.82 (0.09)	0.54 (0.35)	0.49 (0.41)
NaOH-P (%)	0.79 (0.11)	0.53 (0.36)	0.46 (0.43)
HCl-P (%)	-0.63 (0.26)	-0.33 (0.58)	-0.26 (0.67)
Residual-P (%)	-0.49 (0.40)	-0.65 (0.24)	-0.71 (0.18)
Colwell P (mg/kg)	**1.00 (<0.01)**	0.88 (0.05)	0.84 (0.08)
DGT P (μg/l)	**0.93 (0.02)**	**0.99 (<0.01)**	**0.99 (<0.01)**

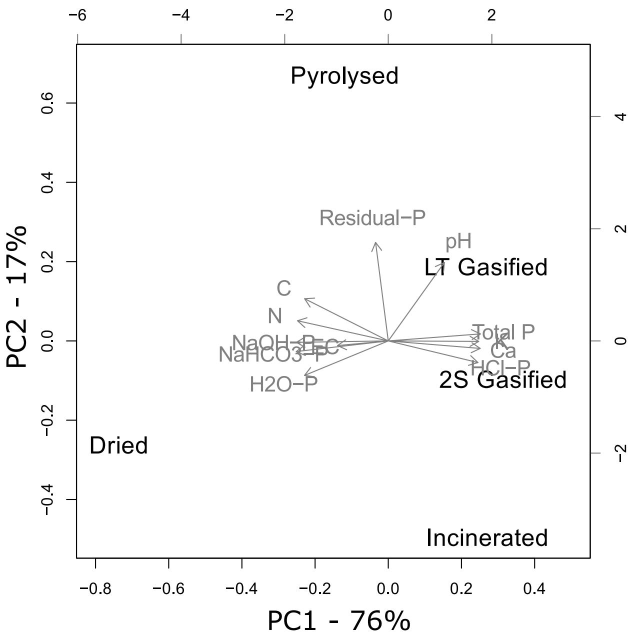

Fig. 1 Biplot showing ordination of dried and thermally converted sewage sludge (black text) based on PCA of their physicochemical properties (grey text). PC1 explains 76% of the variance in the data and PC2 explains 17% of the variance in the data.

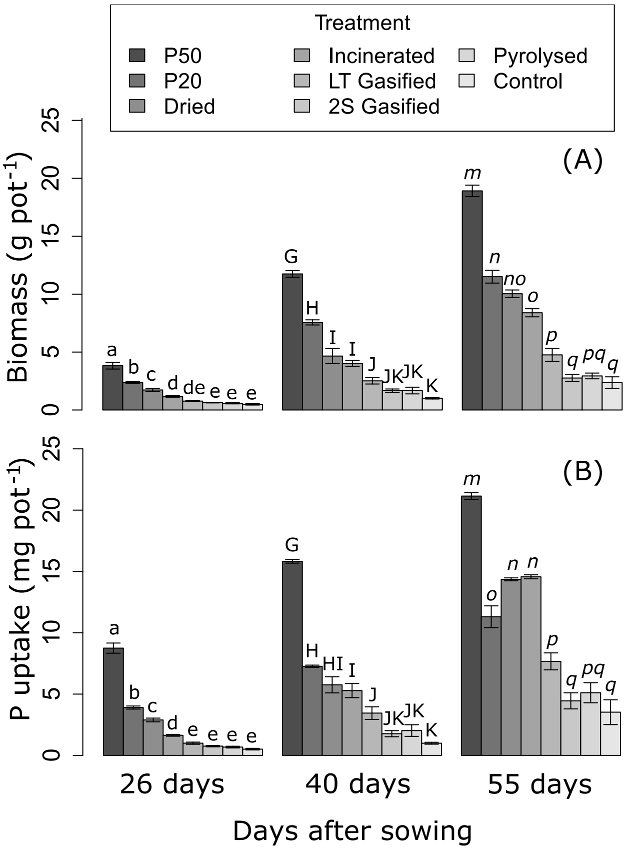

Fig. 2 Aboveground biomass (a) and aboveground P uptake (b) of plants grown in soil which was amended with soluble P, sewage sludge (either dried or thermally converted) or no P (control). Letters indicate significant differences within harvests. Comparisons were not made among harvests and therefore different letter sets (lower case, upper case, italic) were used for each harvest ($p < 0.05$). Error bars indicate standard error. n = 4.

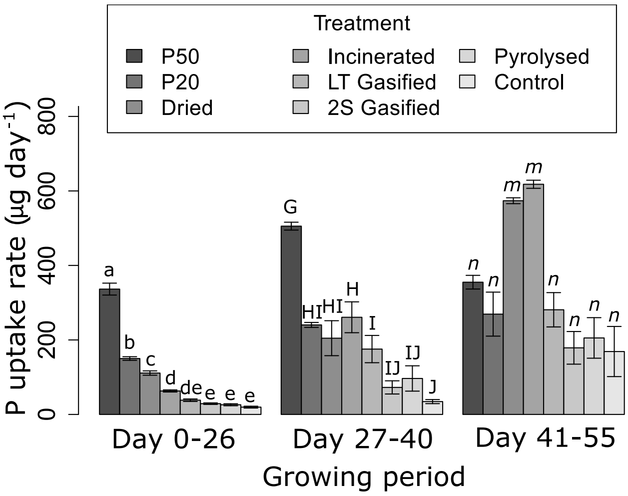

Fig. 3 Aboveground P uptake rate of plants grown in soil which was amended with soluble P, sewage sludge (either dried or thermally converted) or no P (control). Letters indicate significant differences within growing periods. Comparisons were not made among growing periods and therefore different letter sets (lower case, upper case, italic) were used for each growing period ($p < 0.05$). Error bars indicate standard error. n = 4.