Combustion and pyrolysis as potential ways of recycling Phosphorus from agricultural residues as fertilizers for plant production

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Abstract
Separation enriches the solid fraction of pig slurry with the essential nutrient Phosphorus (P). By incinerating or pyrolyzing the fibres, the P concentration in the ash and char is enhanced, but nutrient plant availability is also altered. This study introduces the DGT-technique ("Diffusive gradient in thin films"), compared with chemical extractions, as a new method for the assessment of plant P availability. Plant P availability generally decreased with rising processing temperatures (ranging from 300 to 1000º Celsius) during thermal treatment. DGT-application and water-extraction result in similar qualitative tendencies. Higher extractability of the total P was observed from the chars after pyrolysis than from the combusted products. No P is expected to be plant available from the combusted and pyrolyzed products after thermal treatment above 500 and 700º Celsius, respectively. With respect to P recycling, pyrolysis is consequently the preferred thermal treatment.

Introduction
Large amounts of agricultural wastes accrue in areas of intensive livestock production, making them "hot spots" of nutrient surplus, scattered around Europe. Due to the risk of severe environmental consequences, governmental regulations increasingly limit the allowed application rates of manure on agricultural land. To sustain animal production in these areas under these regulations, innovative technologies have been developed to facilitate the separation of manures into a liquid and solid fraction. The liquid fraction with its easily available nitrogen (N) is a valuable fertilizer for local use. The considerable volume reduction of the fibrous fraction, which is enriched in phosphorus (P), enables long-distance transportation [1]. This means that the vast majority of the essential - but increasingly scarce - nutrient P can be transported to regions where agricultural land is P-deficient.

Before application, the solid fraction can be used for energy production, via either combustion or pyrolysis. In addition, thermal processing reduces the volume of the fibres significantly. In addition the complete removal of water prohibits potentially occurring biological activity and hence increases stability of the product during storage. However, thermal treatment under different conditions, such as processing temperature, might also alter chemical P speciation and hence affect plant availability [2].

In order to estimate potential plant uptake, conducting growth experiments is time-consuming, while chemical extraction methods are less laborious, but correlate only poorly with actual plant availability. An alternative method to predict the nutrient release capability of a soil amendment is the application of the "diffusive gradient in thin films" (DGT) technique. The DGT mimics some of the key processes in the root zone, where it acts as an 'infinite' sink for the nutrient and transport to the sink is limited by diffusion through a well-defined gel. This method has recently been successfully used to assess the P status of different agricultural soils [3, 4].

This study investigates the effect of incineration or pyrolysis temperature of the solid fraction of pig slurry on the plant availability of the contained P. By applying both, chemical extraction methods and the DGT technique, the value of the resulting product as P fertilizer is estimated quantitatively.

Material and Methods
The solid fraction of pig slurry and its derived ash- & char-products
A decanter centrifuge (GEA Westfalia) separated solid fraction from a pig breeding farm in Sæby, Denmark was dried at 80ºC before further thermal processing at lab scale. For combustion, the dried fibres were placed in open crucibles, whereas they were - in order to limit oxygen supply during

thermal treatment - tightly packed into stacked crucibles for pyrolysis. The temperature of the thermal processing was varied between 300 and 1000ºC (in 100°C intervals). As soon as desired peak temperature was reached, treatment continued for 1h.

The feedstock fibres and the products from incineration (referred to as "ashes") as well as from pyrolysis (referred to as "chars") were analysed for their elemental composition using isotope ratio mass spectrometry (SerCon Callisto CF-IRMS) for Carbon (C) and Nitrogen (N) and inductively coupled plasma atomic emission spectroscopy (ICP-OES, Perkin Elmer Optima 5300 DV) after microwave digestion (Milestone UltraWave) for P.

Estimation of plant availability by chemical extraction & application of the DGT-technique

For extraction, three extraction liquids with increasing strength were applied: Deionised water (DIW), 2% citric acid (CA) and 1 molar hydrochloric acid (HCl). The extractants were added to the products at a solid-liquid-ratio of 1:100 and shaken overhead for 16 hours at room temperature. Subsequently the liquid was filtered at 0.45 µm and stored at 4°Cbefore phosphate analysis.

For DGT-application, the products were amended to an inert sand matrix at a product-sand-ratio of 1:100. Water (DIW) was added to the mixture up to saturation. After 24 hours of equilibration, a DGT-device, equipped with a ferrihydrite-containing binding gel (DGT Research Ltd, Lancaster, UK), was applied to the surface for 24 hours at room temperature. The resin-gel was extracted with 1 molar nitric acid (HNO_3) and stored at 4°C before phosphate analysis. After DGT-application, pH was measured in the product-sand mixes at a solid-water-mass-ratio of 1:2.5.

Phosphate analysis was conducted on a flow injection analyser (FIA, PerkinElmer). If necessary, the samples were diluted with MilliQ-water.

Results and discussion

With respect to elemental composition, we observed the following tendencies (data not shown):
Carbon content of the chars remained high, well above 35 w/w%, resembling C content of the feedstock fibres. In contrast, C content in the ashes decreased significantly with rising combustion temperature, falling below 10 w/w% from 500ºC and below 1 w/w% from 800ºC and above, respectively. These results prove (apart from visual observation of colour and structure change of the products after thermal treatment) that the lab scale pyrolysis has fulfilled the requirements of limited oxygen supply for incomplete combustion. The high C contents, nearly independent of treatment peak temperature, also highlight the potential of chars for sequestering C in soil, which should be seen as an additional benefit from char-application.

As expected, the Nitrogen content decreased in both, chars and ashes with increasing process temperatures. However, N content of chars was found to be multi-fold higher compared to the respective ashes after processing above 400ºC, which is in line with a study showing the persistence of organic N in plant biomass after natural fires [5] .

Thermal treatment increased total P concentration by up to more than nine-fold compared to dried feedstock (data not shown). Generally we observed highest total P concentration in ashes, processed at high temperatures, as illustrated in Figure 1A. Whereas the char, processed at the lowest temperature had a P concentration of 38.6 mg P g^{-1}, the ash from the highest processing temperature contained 139.2 mg P g^{-1}. The observed P-enrichment can be assigned to the loss of volatile substances during thermal treatment. P-concentration lies within the same order of magnitude as found in related studies [6].

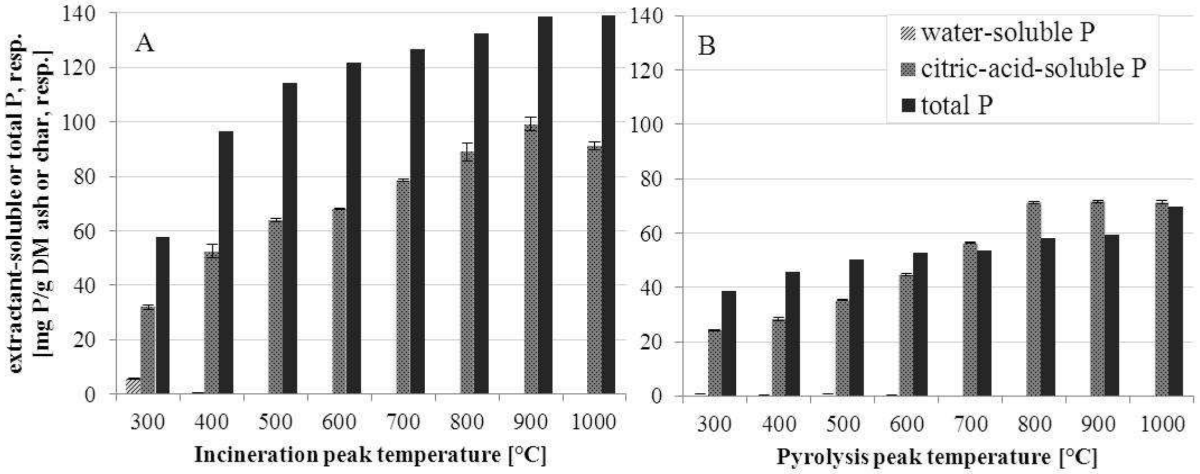

Figure 1. Water-soluble, 2% citric acid-soluble PO_4-P and total P per g dry matter (DM) in ashes after incineration (A) or in chars after pyrolysis (B), depending on peak temperature during thermal treatment (error bars indicate standard errors (for water- and citric acid extractions only))

Extractions with HCl recovered close to 100% of total P in both ash and char products (data not shown). Solubility in citric acid was also found to be high, especially for high temperature processed chars, where total P and citric acid-soluble P laid within the same order of magnitude (slightly higher concentrations in extracts compared to total P content can be assigned to the use of two different analytical methods).

Figure 2 illustrates the effect of peak temperature during incineration or combustion, respectively, on water solubility (Figure 2A) and recovery in the DGT binding gel (Figure 2B) of the P in the ash- and char-products. Water-solubility of P in either ash or char was generally found to be very low. Solely in case of the ash processed at approx. 300ºC 9.6% of the total P was water-soluble. The percentage of recovered P from total P was clearly higher from chars than from ashes, after both, water extraction and DGT application for the temperature range from 400 until 1000ºC.

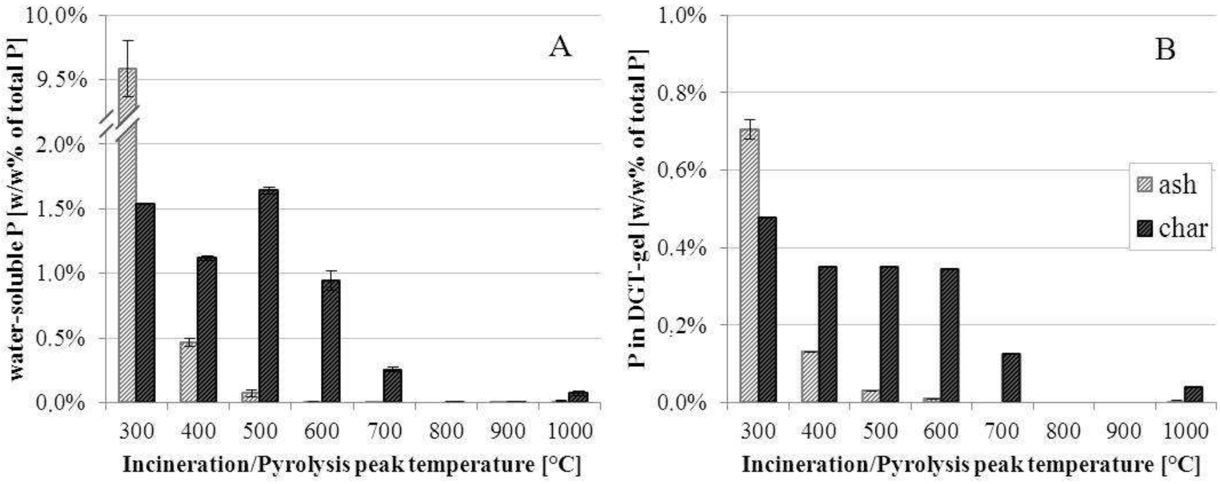

Figure 2. Percentage of total P in water extracts (A) and P eluted from binding gel in DGT-device (B), depending on peak temperature during thermal treatment (error bars indicate standard errors)

Water-solubility of P or P mass recovered in DGT-devices is generally decreasing with rising processing temperatures during thermal treatment. Hence, elevation of processing temperature during thermal treatment will result in significantly lower plant availability. Whereas the detectable percentage of P in chars remained fairly constant up to a pyrolysis temperature of 600ºC, the decrease in extractable P from ashes was much more pronounced along the incineration temperature gradient.

According to results shown in Figures 2A & 2B, no P is expected to be plant available from the combusted and pyrolyzed products after thermal treatment above 500 and 700ºC, respectively.

The assessment of plant availability by water-extraction and DGT-application show similar qualitative tendencies. However, the ratio of P availability from ash to char at a certain process temperature is not identical, when comparing the results from extraction and DGT-technique. In addition, reproducibility is better when applying the DGT technique, as seen from standard errors (Figure 2).

No investigation with regards to chemical speciation of P in the ashes and chars were undertaken. However, we would expect the predominance of highly water-insoluble P compounds, such as hydroxyapatite ($Ca_5(PO_4)_3(OH)$) after high temperature combustion, as shown in previous work [6]. Little is known about the speciation of the P after pyrolysis, but earlier published work on nuclear magnetic resonance (NMR) spectres of biomass after natural fires [5] have indicated that P is also built into polycyclic aromatic structures, which are hardly water-soluble.

In correspondence with earlier findings [7], the addition of all amendments changed the pH of the product-sand-mix to alkaline values between 7.7 (for addition of dried fibres) and 10.5, (ash produced at 800ºC). The products may therefore serve as liming agent for amelioration of acidic agricultural soils, but the pH increase will also affect plant availability of the applied ash or char P.

Conclusion and perspectives

The results from the study provide an indication for most suitable processing conditions during thermal treatment of P-containing agricultural residues with respect to optimal P recycling: Pyrolysis at peak temperatures of max. 600°C is to be preferred compared with incineration. Application of the DGT-technique and water extractions resulted in similar tendencies for P plant availability. The effect of soil characteristics (i.e. texture, pH) on P availability from ash- and char-products are subject to currently on-going experimentation.

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