

# Phosphorus forms in soil amended with meat & bone meal ash and dried distillers grain ash

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## Abstract

Biogas production from organic materials via gasification process also generates a valuable byproduct of ash. Ash contains the original nutrient present in organic materials, except carbon, nitrogen and sulfur that are lost as gases during this process. Therefore, the ash is concentrated in the important macronutrient of phosphorus and potassium. If this ash is land-applied, ash phosphorus may reside in soil in different forms. Therefore, to determine the feasibility of land application of ash in providing phosphorus for crops, a study was carried out using Brown chernozemic soil in growth chamber. Specifically, this study aimed to investigate the influence of two ashes applied at three rates of P in comparison with mineral P fertilizer on P species that resided in soil after harvest using a sequential extraction procedure. Plant phosphorus recovery was also investigated. The experimental treatments for the growth chamber study included 3 P sources: dried distillers grain ash (DDGA), meat & bone meal ash (MBMA) and mono-calcium phosphate fertilizer (MP). Each P source was applied at 3 rates: 25, 50 and 100 kg P ha<sup>-1</sup> in addition to a control. Each treatment was supplemented with 200 kg urea-N ha<sup>-1</sup> to ensure that N is not a limiting factor. Analysis of ashes co-produced from gasification of distillers grain and meat & bone meal showed that they are rich in phosphorus, ranging from 18 – 19 % P. A high proportion of residual P from the meat & bone meal ash was present in the form of calcium phosphate in the soil. The most labile forms of P was higher in DDGA treatments compared to MBMA. Phosphorus recovery in DDGA treatments was similar to that of MP treatments, and greater than MBMA.

## Introduction

The gasification process is defined as the thermo-chemical decomposition of organic materials under high temperature (800 – 900 °C) and in presence of oxygen (Ferreira et al., 2009). As shown in Figure 4, this process does not only produce biogas or syngas (CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>), but it also produces ash as another end product. The ash contains all the P and K originally present in the gasified materials (Kuligowski and Poulsen, 2009), and the ash fraction comprises only about 1% of the raw waste mass. As such there is a significant reduction in processed waste volume and nutrient is significantly concentrated (especially P and K) in ash generated, lowering cost of transport. The ash generated from gasification of organic materials contains a relatively high P content. Kuligowski et al. (2008) reported a P content of approximately 5.4% P; however, this is influenced by the type of materials gasified and their original P content. In our laboratory testing, ash from gasification of dried distillers grain and meat and bone meal were found to contain 16% and 13% of total P, respectively.

Growing interest in producing bioenergy from sustainable sources through gasification has led to a large quantity of ash byproduct being generated. In the light of the shrinking global phosphate rock reserves and increasing demand for P fertilizer in agricultural production, recycling P-rich ash would be a better option to replenish P-depleted soil. Therefore, there is a renewed interest in using ash as phosphorus fertilizer source. This study aimed to investigate the effect of ashes generated from different feedstocks applied at different rates on P species that resided in soil after crop harvest.

## Materials and Methods

### Experimental setup

Soil used in this experiment was collected from layer surface (0-20 cm) in fall 2009, from wheat stubble field located near the town of Central Butte, Saskatchewan. Soil was mechanically mixed using a stationary mixer to provide a homogenized sample and then stored under laboratory condition until its use. Ash materials were obtained from biogas production via gasification facility, Agricultural and Bioresource Department, University of Saskatchewan. They were collected in plastic bag and brought to the laboratory. Subsamples were taken from each type of ash to determine their content of nutrient. Then, 1 kg soil was placed into 1-L plastic pot, followed by treatments application. The ashes and mineral fertilizers were mixed with the top 3 cm of the soil. The experimental treatments included: 3 rates (25, 50, 100 kg P ha<sup>-1</sup>) of meat & bone meal ash (MBMA), dried distillers grain ash (DDGA) and mono-calcium phosphate fertilizer (MP). Each treatment was supplemented with 200 kg N ha<sup>-1</sup> as urea, including the control. Each treatment was replicated 4 times. Pots were seeded to canola and grown for 5 weeks.

After harvesting, plants were dried at 50 °C and weighed for dry matter determination. Plant phosphorus uptake was determined to allow for plant P recovery calculation. Pots soil was air-dried and ground to pass a 2-mm sieve mesh. Soil samples were sequentially extracted for phosphorous forms characterization. A 0.5 g sample of air-dried and sieved soil collected from the soil in each pot after harvest was sequentially extracted by Hedley procedure as described by Tiessen and Moir (2007) to determine the forms and amounts of P in the different pools as a function of extractant strength according to the following scheme:

1. NaHCO<sub>3</sub>-P (P<sub>inorganic</sub> and P<sub>organic</sub>): 30 mL 0.5 NaHCO<sub>3</sub> (pH 8.5), shaken overnight.
2. NaOH-P (P<sub>inorganic</sub> and P<sub>organic</sub>): 30 mL 0.1 M NaOH, shaken overnight.
3. HCl-P (P<sub>inorganic</sub>): 30 mL 1.0 M HCl, shaken overnight.
4. Conc. HCl (P<sub>inorganic</sub> and P<sub>organic</sub>): 15 mL concentrated HCl, heated for 20 min at 80 °C.

Inorganic P (orthophosphate) in the various soil extracts was measured colorimetrically using an ascorbic acid reduction method (Murphy and Riley 1962). Treatments selected for sequential P extraction were the two ashes at the rate of 100 kg P ha<sup>-1</sup>).

## Results and discussion

Ashes co-produced from gasification of meat & bone meal and dried distillers grain are mainly rich in phosphorus (Table 1). Soil P fractions were significantly affected by ash addition, especially the labile

(bioavailable) P fractions. Addition of both ashes significantly increased the most labile  $\text{NaHCO}_3$  and  $\text{NaOH}$  (inorganic forms) when compared to the control (Table 2). For a given P application rate, MBMA had the lowest labile inorganic P content, followed by DDGA, with MP the highest. This could be explained by the reaction of phosphate with Ca in the meat and bone meal to form calcium phosphate compounds of low solubility. Greater increases in labile inorganic P fractions from DDGA than MBMA, especially at the high rate, may be due to fixation of P with the large amounts of calcium present in the MBMA. Higher content of  $\text{HCl-P}$  in MBMA when applied at the high rate treatment supports this concept. Ash had lower  $\text{NaOH-P}_i$  and  $\text{P}_o$  compared to mineral P treatments and control; this may be related to enhanced dissolution of Al and Fe P containing compounds. The treatments of MBMA had the highest content of  $\text{HCl-P}_i$ , especially when applied at the high rate. This is consistent with MBMA containing and/or producing Ca-P compounds of relatively low solubility in soil. The residual P remaining in soil after previous extractants, considered very recalcitrant and stable P, was similar among treatments. However, MBMA applied at the high rate tended to show higher residual P.

Plant phosphorus recovery decreased with increasing P rate (Fig. 1). Phosphorus recovery in DDGA treatments was similar to that of MP treatments, and greater than MBMA. Greater recovery of DDGA P by canola is consistent with the observed higher content of soil labile P forms compared to MBMA P.

## **Conclusion**

The labile forms of soil P were highest in MP fertilizer treatments, followed by DDGA, and were the least in the soil amended with MBMA. The moderately labile forms of P in MP treatments were higher or similar to that in DDGA and MBMA treatments, when averaged across all treatments. Ca-Mg-associated  $\text{P}_i$  ( $\text{HCl-P}_i$ ) was higher in soil treated with MBMA. This may be related to the presence and formation of Ca-P compounds of low solubility and less availability with this amendment.

Ashes can potentially be a good source of P in a prairie soil. However, differences in behavior and availability may occur related to the elemental composition of the feedstock.

Future work is recommended to corroborate chemical speciation by identifying P forms in ash and amended soils using spectroscopic techniques (XANES synchrotron spectroscopy).

## **Acknowledgement**

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**Table 1. Selected characteristics of dried distillers grain ash (DDGA) and meat & bone meal ash (MBMA) used in the growth chamber study.**

| Parameter                      | Ash Source |       |
|--------------------------------|------------|-------|
|                                | DDGA       | MBMA  |
| Total N (%)                    | 0.135      | 0.235 |
| Total P (%)                    | 18.65      | 17.65 |
| Total K (%)                    | 14.9       | 2.88  |
| Total S (%)                    | <1.0       | 0.425 |
| Total Na (%)                   | 7.45       | 6.55  |
| Total Ca (%)                   | 7.85       | 24.65 |
| Total Mg (%)                   | 5.4        | 1.07  |
| Total Cu (mg g <sup>-1</sup> ) | 0.25       | 0.08  |
| Total Fe (%)                   | 0.62       | 0.358 |
| Total Mn (mg g <sup>-1</sup> ) | 1.68       | 0.09  |
| Total Zn (mg g <sup>-1</sup> ) | 1.19       | 0.69  |
| Moisture (%)                   | <0.10      | <0.10 |

**Table 2. Effect of MP, DDGA and MBMA applied at three rates (25, 50 or 100 kg P ha<sup>-1</sup>) on phosphorus forms in soil after canola harvest.**

| Treatment           | NaHCO <sub>3</sub> -P <sub>i</sub> | NaHCO <sub>3</sub> -P <sub>o</sub> | NaOH-P <sub>i</sub> | NaOH-P <sub>o</sub> | HCl-P <sub>i</sub> | Residual-P       |
|---------------------|------------------------------------|------------------------------------|---------------------|---------------------|--------------------|------------------|
|                     | µg P g <sup>-1</sup> soil          |                                    |                     |                     |                    |                  |
| Control             | 21.86 ± 5.12 c                     | 30.06 ± 4.16 bc                    | 82.45 ± 4.71 abc    | 243.83 ± 11.25 a    | 615.09 ± 22.77 b   | 205.41 ± 7.77 ab |
| MP-25               | 42.26 ± 2.50 ab                    | 25.45 ± 0.52 c                     | 86.38 ± 6.76 abc    | 236.45 ± 5.41 a     | 543.48 ± 74.88 c   | 202.60 ± 6.13 ab |
| MP-50               | 34.23 ± 2.12 abc                   | 27.37 ± 1.69 c                     | 82.04 ± 7.51 abc    | 214.14 ± 7.14 bc    | 619.46 ± 40.66 b   | 204.61 ± 4.20 ab |
| MP-100              | 41.66 ± 4.34 ab                    | 26.40 ± 1.09 c                     | 88.78 ± 6.23 ab     | 219.98 ± 3.30 b     | 632.14 ± 36.41 b   | 200.51 ± 7.82 ab |
| MBMA-25             | 19.29 ± 2.94 c                     | 37.08 ± 2.72 ab                    | 68.66 ± 5.01 bcd    | 189.42 ± 3.84 d     | 698.30 ± 48.23 b   | 207.40 ± 1.19 ab |
| MBMA-50             | 23.31 ± 2.77 c                     | 34.81 ± 1.19 abc                   | 69.40 ± 5.41 bcd    | 195.71 ± 4.83 cd    | 678.57 ± 40.43 b   | 208.69 ± 4.15 ab |
| MBMA-100            | 30.39 ± 4.38 bc                    | 32.70 ± 1.49 abc                   | 67.65 ± 5.53 cd     | 192.85 ± 2.88 cd    | 812.95 ± 37.22 a   | 222.45 ± 8.29 a  |
| DDGA-25             | 22.84 ± 0.46 c                     | 32.92 ± 1.04 abc                   | 61.65 ± 4.08 d      | 184.61 ± 3.66 d     | 658.30 ± 36.15 b   | 190.31 ± 2.01 b  |
| DDGA-50             | 28.22 ± 2.00 bc                    | 38.80 ± 3.16 ab                    | 77.63 ± 21.55 abcd  | 195.29 ± 2.97 cd    | 661.07 ± 15.88 b   | 192.63 ± 7.44 ab |
| DDGA-100            | 44.56 ± 4.88 a                     | 40.78 ± 2.54 a                     | 92.37 ± 20.44 a     | 196.17 ± 4.39 cd    | 699.20 ± 58.90 b   | 201.21 ± 9.69 ab |
| Treatment           |                                    |                                    |                     |                     |                    |                  |
| <i>P</i> > <i>F</i> | ***                                | ***                                | ***                 | ***                 | ***                | .                |
| LSD (0.05)          | 9.98                               | 6.47                               | 13.22               | 15.96               | 61.04              | 18.66            |

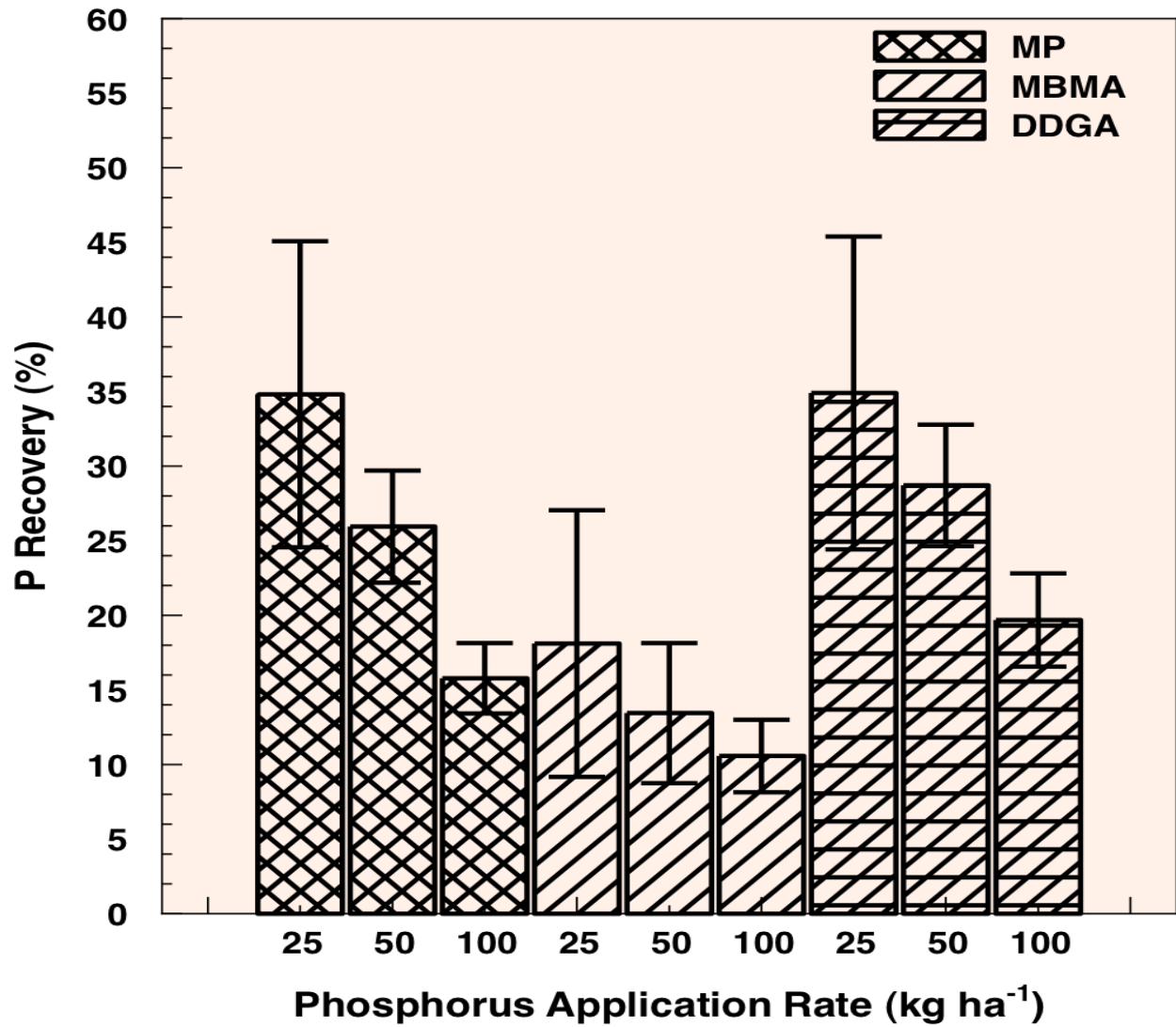


Figure 1. Effect of mineral P, DDGA and MBMA addition on plant P recovery.