Journal of Environmental Management 150 (2015) 39–47

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Bioenergy crops grown for hyperaccumulation of phosphorous in the Delmarva Peninsula and their biofuels potential☆

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ARTICLE INFO

Article history:
Received 19 August 2014
Received in revised form
20 October 2014
Accepted 28 October 2014
Available online

Keywords:
Bioenergy
Phytoremediation
Poultry manure
Potassium
Pyrolysis

ABSTRACT

Herbaceous bioenergy crops, including sorghum, switchgrass, and miscanthus, were evaluated for their potential as phytoremediators for the uptake of phosphorus in the Delmarva Peninsula and their subsequent conversion to biofuel intermediates (bio-oil) by fast pyrolysis using pyrolysis-gas chromatography/mass spectroscopy. Four cultivars of sorghum, five cultivars of switchgrass and one miscanthus (*Miscanthus × giganteus*) were grown in soils with two different levels of poultry manure (PM) applications. Little variation was seen in phosphorus uptake in the two different soils indicating that the levels of available phosphorus in the soil already saturated the uptake ability of the plants. However, all plants regardless of trial took up more phosphorus than that measured for the non- PM treated control. Sorghum accumulated greater levels of nutrients including phosphorus and potassium compared to switchgrass and miscanthus. The levels of these nutrients in the biomass did not have an effect on carbohydrate contents. However, the potential yield and composition of bio-oil from fast pyrolysis were affected by both agronomics and differences in mineral concentrations.

1. Introduction

The Delmarva Peninsula, situated between the Chesapeake Bay and the Delaware Bay, has been home to most of the United States poultry industry since the early 20th century. With over 568 million birds produced annually and manure production exceeding 700,000 Mg, the Chesapeake Bay has suffered from excessive eutrophication from leaching of phosphorus (P) and nitrogen (N) at high levels into the water supply (Feyereisen et al. (2010); Kibet et al., 2013). While the booming Delmarva poultry industry is economically lucrative, it has significantly degraded the water quality of the Chesapeake Bay and its surrounding waters, exemplifying a scenario where a finite ecosystem can be overpowered by continuous economic growth and rendering it unsustainable (Boesch et al., 2001). The enormous quantities of manure generated from concentrated animal feeding operations has overwhelmed the ability of crops to absorb manure as fertilizer thereby resulting in a flow of excess nutrients, particularly P in the soil and into the Bay (Boesch et al., 2001; Kleinman et al., 2002). Phosphorus management is required to reduce agricultural runoff and improve soil and water quality.

Phosphorus is a major nutrient for plants, vital to cellular function and metabolic regulation. Most natural soils are P deficient, since the majority of P is in organic forms unavailable for plant uptake, which is a limiting factor in plant growth (Holford, 1997). The utilization of manure to increase crop production and the availability of P in the soil has led to soils with P surpluses, including the watershed region for the Chesapeake Bay (MacDonald et al., 2011). One way to mitigate P accumulated soils is to utilize plants that can hyperaccumulate P and act as a method of phytoremediation. Several perennial grasses have been identified as P hyperaccumulators, such as Duo grass (*Lolium × Festuca*),

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http://dx.doi.org/10.1016/j.jenvman.2014.10.030
0301-4797/Published by Elsevier Ltd.

Lolium multiflorum, rice cutgrass (*Leersia oryzoides* Sw.) and tall fescue (*Festuca arundinacea* Schreb.) (Klaber and Barker, 2014; Padmanabhan et al., 2013; Sharma and Sahi, 2011). In addition, recent studies have shown that the perennial grass elephant grass (*Pennisetum purpureum* Schumach.) developed as a dedicated energy crop has P hyperaccumulation properties (Silveira et al., 2013). Both bioenergy crops miscanthus (*Miscanthus* × *giganteus*) and switchgrass (*Panicum virgatum* L.), have been studied as hyper-accumulators of heavy metals (Chen et al., 2011; Pidlisnyuk et al., 2014).

The use of bioenergy crops with P hyperaccumulation properties in the Delmarva Peninsula would have multiple environmental benefits for this region. The successful identification of plant genotypes with the potential to produce high biomass yield while possessing high energy conversion efficiency and high P extraction potential from P enriched soils could create a complementary bioenergy industry to be co-located with and mitigate the effects of the poultry industry in the Delmarva Peninsula. Fast pyrolysis of P laden biomass would be advantageous since the P in the biomass would accumulate in the bio-char in a concentrated form and be easily transported out of the watershed at a lower cost than that of the manure. However, there are concerns related to the effects of P and other trace metals in the biomass on conversion efficiency of the biofuels production process. For example, trace metals and other inorganic material found in the ash portion of the biomass have been found to have a catalytic effect on pyrolysis and bio-oil production (Carpenter et al., 2014; Wilson et al., 2013).

The objective of the research was to evaluate the dual use of energy crops to absorb and manage P and harvested biomass as a biofuels feedstock for both biochemical and thermochemical conversion technology platforms. The specific goal was to test the ability of a set of select bioenergy grasses including forage sorghum (*Sorghum bicolor* AL. Moench), sorghum-sudangrass hybirds (*S. bicolor* × *S.* × *drumondii*), switchgrass (*P. virgatum* L.), and miscanthus (*Miscanthus x giganteus*) for their hyperaccumulation of P and the efficiency of the P-laden feedstocks for biochemical conversion (estimated as theoretical ethanol yield) and thermochemical conversion through fast-pyrolysis. In this study five cultivars of switchgrass, four cultivars of sorghum, and miscanthus were grown in replicated trials on a high poultry manure (HPM) site and a low poultry manure (LPM) site to evaluate their potential to uptake minerals, changes in plant cell wall composition, and subsequent conversion into bio-oil through fast pyrolysis.

2. Materials and methods

2.1. Field trial and source material

Ten different bioenergy grasses were planted in replicated trails at the Agricultural Experiment Station at the University of Maryland Eastern Shore, Princess Anne, MD (Tables 1 and 2). The two locations were UMES 1 with a history of low poultry manure (LPM) application and Bozman II with a history of high poultry manure (HPM) applications. Both UMES I and Bozman II sites are well drained and flat land. Both sites were in corn/soybean rotations previously. Soil physical and chemical analyses were performed on samples obtained from 15.0 cm to 25 cm depths. Samples from the two depths were air dried, ground, and mixed prior to submission to A & L Eastern Laboratories, Inc. for analyses. The HPM site had 2.6 times greater levels of P in the soil compared to the LPM site. The switchgrass and miscanthus were planted in June of 2011 and allowed to go through one growing cycle and winter dormancy. In June of 2012, the sorghum was planted amongst the miscanthus and switchgrass.

At each location, cultivars were randomized in a complete block and each block replicated four times with 10 plots per block and one cultivar per plot. Soil preparation comprised regular plowing and harrowing. Planting was done manually. No fertilizer or herbicide was applied to the field. Weed control consisted of hoeing until the crop canopy closed up. A plot consisted of four rows each, six meters in length and 0.75 m between rows. Within row spacing of seedlings, already raised in the greenhouse, was 20 cm. Plants were harvested when they turned brown and dry in the field between mid-November and December of 2012. At dry maturity, 1.0 m of each of the two center rows was harvested by cutting the plant at soil level. These were oven dried in a forced-air oven at 60○C for 72 h. Dried samples of the same cultivars from each of the four blocks from each trial were combined and ground for chemical analysis. A switchgrass sample of the cultivar ‘Carthage’ grown on a site without high phosphorus in Pennsylvania was incorporated into the analyses for comparison purposes. The grasses used for the Maryland trials were four switchgrass cultivars, ‘Alamo’, ‘Blackwell’, ‘Kanlow’, and ‘Nebraska 28’, an Iowa ecotype of switchgrass, two sorghum/sudangrass hybrids, ‘4Ever Green’ and ‘Megagreen’, a sweet sorghum hybrid, a forage sorghum ‘Millenium’, and miscanthus (*Miscanthus* × *giganteus*).

Table 1
Soil characteristics for the high-poultry manure (HPM) and the low-poultry manure (LPM) trials.

Soil characteristics	Trial HPM	 LPM
Sand (%)	57	64
Silt (%)	27	22
Clay (%)	16	14
P (kg ha^{-1})	517	198
K (kg ha^{-1})	197	186
Mg (kg ha^{-1})	250	334
Ca (kg ha^{-1})	1982	2412
pH	6.4	7.1

2.2. Moisture and ash content

Percent moisture content was determined by drying 1.5 g of biomass in a muffle furnace for 3 h at 105 °C. The same samples were subsequently used to calculate percent ash after heating in a muffle furnace at 650 °C for 6 h.

2.3. Elemental analysis

Ultimate analysis (C, H, N, and O) was performed on 2 mg of biomass using a ThermoFlash EA1112 CHNS/O analyzer (Thermo Fisher Scientific, Waltham, MA) with complete combustion of the sample followed by GC quantification. Oxygen is determined by difference on a dry-ash free basis.

2.4. Determination of mineral content

Acid digestions were performed by digesting 100 mg of ash from each sample in 10 mL of HCl at room temperature overnight. Each sample was diluted to 100 mL with double distilled water. After the settling of particulates, 10 mL of sample was transferred to auto-sampler tubes for analysis by inductively-coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo Scientific iCAP 6300 (Waltham, MA). Quantitation of Al, Ca, Cu, Fe, K, Mg, Na, and P in the biomass was determined by external standards using the instrument software.