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Effect of biochar on the fate and transport of manure-borne progesterone in soil

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ABSTRACT

The sorption affinity and desorption resistance of two types of biochars as soil amendments was evaluated in laboratory. The softwood and hardwood-biochars demonstrated a high sorption affinity for progesterone. The effective distribution coefficient (K_d^{eff}) of soil-soft wood-derived biochar (SBS_{450}) was significantly higher (H0: $P < 0.05$) than soil-hardwood-derived biochar (SBH_{750}), indicating its stronger sorption affinity for progesterone. Accordingly, a field-lysimeter study was conducted to elucidate the fate and transport of manure-borne progesterone in soil matrix and aquatic media in the presence of 1% softwood-biochar (BS_{450}) in upper 0.1 m layer of soil. The spatial–temporal stratification of progesterone was monitored at four depths over a 46-day period where two different types of manures (swine and poultry) were applied to the topsoil of lysimeters under two treatments, soil (S) and SBS_{450}. The progesterone concentrations in SBS_{450} were significantly higher (H0: $P < 0.05$) and persisted for a longer period in the surface soil than in the control (S); however, the concentration was significantly lower in the deeper profile and in leachates. The results clearly showed that the application of biochar as a soil amendment can be used in alleviating the threat of pollution from manure borne progesterone.

1. Introduction

Over the last decade, several cases of biological abnormalities, including sexual, developmental and reproductive disorders, have been reported in the aquatic environment; these abnormalities are linked to the occurrence of a new paramount class of emerging contaminants with endocrine disrupting properties (Söffker and Tyler, 2012). These biologically active, organic micro pollutants are classified as Endocrine Disrupting Chemicals (EDCs). The EDCs are natural and synthetic steroid hormones, possessing the potential to modulate the functions of the endocrine system by mimicking, counteracting, altering or interfering with the metabolism and biosynthesis of endogenous hormones (Colucci et al., 2001). Androgens, estrogens, and progestin are classified as the three main categories of steroid sex hormones. Recently, advances in analytical techniques have made it possible to detect these pollutants at low concentrations in soil and water systems (Pignatello et al., 2010). However, the high chronic toxicity causing adverse long-term biological development and health issues (e.g. carcinogenicity, mutagenicity or teratogenicity) of these organic contaminants at concentrations as low as ng L^{-1} (Choi et al., 2004), has highlighted the need for studies on their fate and transport in the soil-water system.

Agricultural and land management practices, such as the application of biosolids and animal manure and wastewater treatment plant discharges, frequently have been identified as the major sources of environmental female sex hormone pollutants (Bartelt-Hunt et al., 2012; Ho et al., 2014). Poultry and liquid swine manure are the most widely applied organic fertilizers in North America. They are used to boost soil fertility; however, from the environmental and health safety perspective, these manures are major sources of bioactive levels of natural steroidal sex hormones, including 17β-estradiol (E2), estrone (E1), testosterone and progesterone. The frequent contamination of surface water and ground water from manure-borne steroid hormones through surface runoff from agricultural fields receiving livestock and poultry manures has been reported in several studies (Jacobsen et al., 2005; Shore and Shemesh, 2003; Soto et al., 2004).

The environmental occurrence and detection of estrogens, above their lowest observation effect level (LOEL), 10 ng L^{-1} (Shore and Shemesh, 2003), have been reported (Casey et al., 2003; Colucci et al., 2001; Jacobsen et al., 2005; Lee et al., 2003; Yu et al., 2004); however, the environmental behavior and fate of progesterone are not well-known. Progesterone has a direct reproductive role as

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an early precursor in the formation of other steroid hormones; it is produced by both sexes, with a significantly higher concentration in females. Consequently, a large fraction of this hormone is excreted by livestock, leading to significant environmental exposure (Bevacqua et al., 2011).

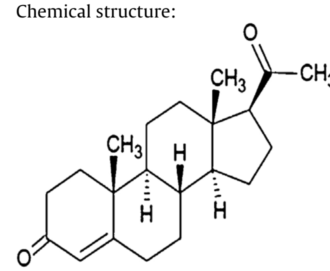
The potential stability of progesterone is expected following the previous detection of the compound in surface water resources (Kolpin et al., 2002), however, a limited number of studies have reported on the occurrence of biologically active progesterone in surface soil and runoff from agricultural fields treated with manure. Kolpin et al. (2002) reported the contamination of 4.3% of streams in the United States with average progesterone concentrations of 0.11 $\mu g L^{-1}$ and a maximum concentration of 0.199 $\mu g L^{-1}$. Detection of biologically active concentrations of progesterone, in beef cattle feedlot soil and in runoff from simulated rainfall were reported by Mansell et al. (2011). In a similar survey, Bartelt-Hunt et al. (2012) reported the presence of progesterone in both soil and manure samples. They also detected progesterone in runoff having an average concentration of 59.5 $ng L^{-1}$ with a maximum concentration of 570 $ng L^{-1}$. Given the limited understanding of the environmental pathways and ecotoxicology of high-toxicity-at-low-concentrations of manure-borne steroid hormones in soil and water media, there is inadequate knowledge to address the remediation of manure-borne steroid hormones in the environmental matrix. As a result, there is a pressing need to conduct detailed studies with the objective of developing feasible remediation techniques in order to reduce the environmental and biological consequences of hormonal pollution.

The in-situ incorporation of carbon-rich organic amendments on contaminated soils has been deployed as a financially-feasible approach to engineer the natural process to fulfill an environmental remediation requisite (Beesley et al., 2011). Known as a byproduct of the thermo-chemical conversion of biomass and biological residues in the absence of oxygen (pyrolysis), biochar possesses an amorphous structure, containing nano-scale condensed aromatic rings with a crystalline structure and high specific surface area, which provides strong sorption sites in order to fulfill an environmental remediation of inorganic contaminants (e.g. heavy metals) and hydrophobic organic contaminants (Beesley et al., 2011). Based on the pyrolysis conditions, including different heating rates, various types of biochars with specific structural and physio-chemical properties are produced. Slow pyrolysis biochar is the final by-product of pyrolysis at relatively low temperatures (300–500 °C) with a long heating time and a heating rate less than 10 $K min^{-1}$, consisting of higher proportions of aliphatic carbons and functional groups. Whereas fast pyrolysis takes place over a short time at a high temperature (700–900 °C) with a heating rate of more than 1000 $K min^{-1}$, thus resulting in a structure higher in micro porosity and with more poly aromatic carbons (Jung et al., 2013).

Although, the retention capacity of biochar for different types of pesticides, including triazine and acetamiprid (Zheng et al., 2010), herbicides and heteroaromatic amines (Xiao and Pignatello, 2015), aminocyclopyrachlor, bentazone and fungicide pyraclostrobin (Cabrera et al., 2014) and endocrine disrupting compounds (Jung et al., 2013), have been determined using batch sorption-desorption experiments, there is a paucity of knowledge regarding the environmental remediation behavior of biochar under field conditions. Therefore, detailed spatio-temporal investigations of the in situ field-scale retention ability of biochar are needed.

The primary objective of this study was to evaluate the feasibility of incorporation of two types of biochars (soft-wood and hard-wood derived biochars, produced at 450 °C and 750 °C, respectively) as a novel approach for reducing soil and water pollution of progesterone. A laboratory batch equilibrium study was conducted to determine the progesterone retention ability of these biochars. To validate the lab results, a field lysimeter study was conducted to elucidate the fate and transport of the manure-borne progesterone in sandy soil. The specific objective was to study the fate and transport of progesterone in outdoor lysimeters, filled with a sandy soil, at different depths over a 46-day period, and to compare it with the lysimeters where the upper 0.1 m layer was amended with biochar, equivalent to 1% by weight, where two different types of manures (swine and poultry) were incorporated and applied with simulated rainfall.

Table 1
Physical and chemical characteristics of soil (ElSayed and Prasher, 2014), and progesterone (Colucci et al., 2001; Hao et al., 2013; Yu et al., 2004).

Soil	Progesterone
Sand (%): 92.2	Molecular weight: 314.46 ($g mol^{-1}$)
Silt (%): 4.3	Water solubility@ 20 °c: 8.81 ($mg L^{-1}$)
Clay (%): 3.5	Vapor pressure: 1.3×10^{-6} mm Hg at 25 °C
Organic matter (%): 2.97	log K_{OW}: 3.67-3.87
Bulk density (kg m[3]): 1350	log RBA([#]): −0.7
Hydraulic conductivity (m d^{-1}): 1.67 ± 0.45[*]	Chemical structure: 
CEC ($cmol kg^{-1}$)[@]: 4.9	
pH: 5.5	

[@] Cation exchange capacity.
[*] Average saturated hydraulic conductivity ± standard deviation.
[#] RBA: relative binding affinities for androgen and estrogen receptors.

2. Materials and methods

2.1. Analytical chemicals

The analytical chemical standards for progesterone (>98% purity) was purchased from Sigma Aldrich (St. Louis, MO, USA). The physiochemical properties and the chemical structure of progesterone are summarized in Table 1. The anhydrous calcium chloride standard was provided by Science lab, Houston, Texas, USA. High performance liquid chromatography grade acetonitrile, used both as a solvent and for the mobile phase, was purchased from Fisher science. The de-ionized water was used as the mobile phase in the analytical analysis of samples, as a solvent in desorption bath equilibrium experiments and in all steps of the Standard solution preparation.

2.2. Soil characteristics

The soil chosen for the laboratory batch equilibrium study was a sandy soil (with 92.2% sand content) of the Ste-Amable complex, Ferro-Humic podzol (ElSayed and Prasher, 2014), collected from the outdoor lysimeters assigned for the field evaluation. The physical characteristics of the soil are presented in Table 1. The lysimeters were located at the Macdonald campus of McGill University, Ste-Anne-De-Bellevue, Quebec.

2.3. Biochar characteristics

Two types of biochars were provided by BlueLeaf Inc, Drummondville, Quebec, Canada. The main feedstock for the production of both biochar was spruce trees. Softwood-derived biochar (BS_{450}) was produced by slow-pyrolysis of spruce tree bark, at 450 °C for 2.5 h. Hard wood of spruce trees was processed under fast pyrol-