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Sorption of four estrogens by surface soils from 41 cultivated fields in Alberta, Canada

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ABSTRACT

Estrogenic compounds in livestock manure are also present in soils because manure is land applied on account of its value as an important nutrient source in agricultural production. This is the first study to compare the sorption of 17β-estradiol, estrone, estriol and equol in a wide range of soils. Specifically, for each of these four estrogens, the soil sorption coefficient (K_d) and the sorption coefficient per unit organic carbon (K_{oc}) were determined in 121 surface soils (0–15 cm) obtained from upper-slopes, mid-slopes, and lower-slopes in agricultural fields across seven ecoregions in the Province of Alberta, Canada. Soil organic carbon content (SOC), texture, pH, carbonate content, electrical conductivity and cation exchange capacity were also determined on the air-dried and sieved (2 mm) soil. Both K_d and K_{oc} values significantly increased in the order of K_d-estriol (23 L kg^{-1} soil and 1059 L kg^{-1}, respectively) = K_d-17β-estradiol (23 L kg^{-1} soil and 1082 L kg^{-1}, respectively) < K_d-estrone (33 L kg^{-1} soil and 1557 L kg^{-1}, respectively) < K_d-equol (42 L kg^{-1} soil and 2080 L kg^{-1}, respectively). For each estrogen, SOC was the strongest significant factor explaining variations in K_d values among soils and particularly small K_d values were observed when SOC was below a threshold value of 10 g C kg^{-1}. Regardless of the estrogen, the Mixed Grassland ecoregion characterized by Brown Chernozem soils, as well as upper-slopes in general, demonstrated lesser K_d values because of reduced SOC. However, regardless of the estrogen, the soils with reduced SOC displayed greater K_{oc} values. Equations to predict 17β-estradiol, estriol, estrone or equol K_d or K_{oc} values at the regional level were established using either soil properties (Partial Least Squares (PLS) regression) or one single estrogen (ordinary least squares regression). Regardless of the estrogen or the regression used, the strength of the prediction model, as determined by the coefficient of determination (r^2) and other factors, was always better for K_d than K_{oc} values. Regardless of the regression used, the r^2 of the prediction models exceeded 0.70 for K_d-17β-estradiol and K_d-estriol, but r^2 was below 0.52 for K_d-equol. For both K_d and K_{oc} values, the prediction using soil properties (ranging from a r^2 of 0.51 to 0.87 for K_d and from a r^2 of 0.32 to 0.44 for K_{oc}) always provided better prediction models than using a single estrogen (ranging from a r^2 of 0.38 to 0.71 for K_d and from a r^2 of 0.18 to 0.40 for K_{oc}). We conclude that data on basic soil properties are good tools for estimating K_d values of 17β-estradiol, estrone and estriol in western Canadian soils. Additional studies are required to seek better prediction models at the regional scale for estimating K_d-equol and for estimating K_{oc} values of estrogens, particularly because such information could be important for agri-environmental policy analyses in Canada and elsewhere.

1. Introduction

Livestock excrete a considerable amount of estrogens (Lange et al., 2002) and elevated levels of estrogens have been detected in soils following the application of manure onto agricultural land (Shore et al., 1995). Estrogens may move from agricultural fields to the broader environment by processes such as runoff and leaching (Nichols et al., 1997; Finlay-Moore et al., 2000; Kjær et al., 2007). Estrogens in stream water and lakes affect aquatic organisms by reducing their sperm count, elevating their blood vitellogenin, as well as inducing male feminization, poor offspring development and unusual behavioural effects (Purdom et al., 1994; Lai et al., 2002). Most environmental and toxicological studies have focused on steroidal compounds such as 17ß-estradiol, estrone, estriol and estradiol.

Equol is a nonsteroidal compound produced by gastrointestinal bacteria in mammals from isoflavones such as formononetin and daidzein. Isoflavones are present in a range of crops and food products. Equol has been associated with reproductive disorders in ewes feeding on clover (Mustonen et al., 2006) but also to lower incidences of prostate cancer in humans favouring a diet of soybean based products (Akaza et al., 2004). Equol is excreted in the urine and can dominate estrogenic activity in manure (Lorenzen et al., 2006). To

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our knowledge, there have been no studies on the fate of equol in agricultural soils.

Sorption often controls the fate of organic compounds in agricultural soils. Sorption is generally defined by sorption coefficients, which are measured using batch-equilibrium experiments. For most estrogens, equilibrium is usually reached within 24 h (Lai et al., 2000; Ying and Kookana, 2005; Hildebrand et al., 2006). However, equilibrium times vary among estrogens (Lee et al., 2003) with reported equilibrium times ranging from 1 h for 17ß-estradiol, estrone and estriol (Lai et al., 2000) to 168 h for 17ß-estradiol (Casey et al., 2003). Equilibrium times in the same soil ranged from 42 h for 17β-estradiol to 72 h for 17α-ethynyl estradiol. (Lee et al., 2003). Using 17ß-estradiol, Yu et al. (2004) reported that the equilibrium time of an estrogen in soil is also dependent on the estrogen concentration used.

Batch-equilibrium studies using estrogens have been conducted on a limited number of soils and no information on soil-landscape or regional-scale variations have been reported. Previous studies demonstrate that estrogen sorption is predominantly influenced by soil organic carbon content (SOC) (Yu et al., 2004; Hildebrand et al., 2006; Loffredo and Senesi, 2006), but specific surface area and hence soil texture can also affect estrogen sorption (Yu et al., 2004; Loffredo and Senesi, 2006).

At a regional scale spanning the provinces of Alberta, Saskatchewan and Manitoba, Canada, Anderson (1979) reported that SOC increases in the order of Dark Brown < Black < Dark Gray Chernozem soil great groups. In the Province of Alberta, Gaultier et al. (2008) quantified that SOC and 2,4-dichlorophenoxyacetic acid (a herbicide) sorption was significantly smaller in the Mixed Grassland ecoregion that contains Brown Chernozems than in five other ecoregions with different soil great groups. Farenhorst et al. (2008) concluded that SOC and 2,4-D sorption typically increase in the order of upper < mid < lower slope positions in agricultural fields. There are no data on spatial variations of estrogen sorption within and between fields, soil great groups or ecoregions. Such information can be useful for defining beneficial land management practices for manure disposal and for agri-environmental policy analyses in Canada (Lefebvre et al., 2005).

The Province of Alberta is an important contributor to agricultural production in Canada with more than 96,000 km^2 devoted to annual cropping (Alberta Agriculture and Food, 2006). The Alberta livestock industry accounts for more than 6 million cattle and calves and more than 2 million hogs, directly contributing to the Province of Alberta economy and generating manure to enhance the fertility of Alberta's crop land (Alberta Agriculture and Food, 2006). Manure applications introduce estrogens in agricultural soils but there have been no studies on the fate of estrogens in the Province of Alberta agricultural soils.

The objectives of this study were to determine K_d and K_{oc} values of 17β-estradiol, estrone, estriol and equol in 121 soil samples collected throughout the Province of Alberta and relate these values to variations in soil properties, soil-landscape position, soil great groups and ecoregions.

2. Materials and methods

2.1. Estrogens and analytical techniques

Analytical grade 17β-estradiol, estrone, estriol and equol with a purity of 98% or higher were purchased from Sigma-Aldrich Chemical Company, St. Louis, MO. Estradiol [6,7-3H(N)] (99% radiochemical purity, specific activity 40–60 Ci $mmol^{-1}$), estrone [6,7-3H(N)] (99% radiochemical purity, specific activity 40–60 Ci $mmol^{-1}$) and equol [3H(G)] (99% radiochemical purity, specific activity 1–5 Ci $mmol^{-1}$) were purchased from American Radiolabeled Chemicals, St. Louis, MO. Estriol [2,4]3H (99.5% radiochemical purity, specific activity 20–40 Ci/mmol) was purchased from Moravek Biochemicals and Radiochemicals, Brea, CA (Fig. 1). All radiochemicals were delivered in ethanol. The amount of radioactivity in estrogen stock solutions and samples from experiments was determined using Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 7500 Beckman Instruments, Fullerton, CA). Radioactivity was measured using 10 mL of Scintisafe scintillation cocktail (Beckman) and a maximum counting time of 10 min.

2.2. Study area

Alberta Agriculture and Rural Development established a benchmark program in 1997 to monitor soil quality in agricultural fields throughout the Province of Alberta. Detailed site descriptions are given in Leskiw et al. (2000) and Cathcart et al. (2008). The benchmark sites were established with cropping systems being in most cases annual cereal or oilseed crops in an area spanning 49–60°N longitude and 110–120°W latitude thereby including a range of ecoregions.

Forty-one agricultural fields located across seven ecoregions were considered in the present study (Fig. 2). The locations of these sampling locations are described in Gaultier et al. (2008) and Cathcart et al. (2008). Ecoregions constitute units with distinct regional ecological factors (i.e., climate, physiography, vegetation, soil, water, and fauna) and are an entity within a national hierarchy of ecostratification (Ecological Stratification Working Group, 1995). The seven ecoregions in our study are the Peace Lowland (PL), Boreal Transition (BT), Mixed Boreal Uplands (MBU), Aspen Parkland (AP), Moist Mixed Grassland (MMG), Fescue Grassland (FG) and Mixed Grassland (MG) (Table 1). The AP, MMG, and MG also constitute a large part of the agricultural area of the provinces Manitoba and Saskatchewan, Canada and roll up to be a major part of the Prairie Ecozone. The Prairie Ecozone contributes to the majority of the crop production in Canada. Soil great groups in the seven ecoregions included Brown Chernozem, Dark Brown Chernozem, Black Chernozem, Dark Gray Chernozem, Gray Luvisol and Dark Gray Luvisol soils (Soil Classification Working Group, 1998; Cathcart et al., 2008) (Table 1).

2.3. Soil sampling and characterization

Surface soil samples (0–15 cm) were taken from each of three soil-landscape positions (upper-slopes, mid-slopes, lower-slopes) in each of the 41 agricultural fields. SOC, % sand, % clay, pH, $CaCO_3$, CEC and EC were determined on air-dried and sieved (2 mm) soil. SOC was determined by a Leco model CHN 600 C and N determinator (Leco

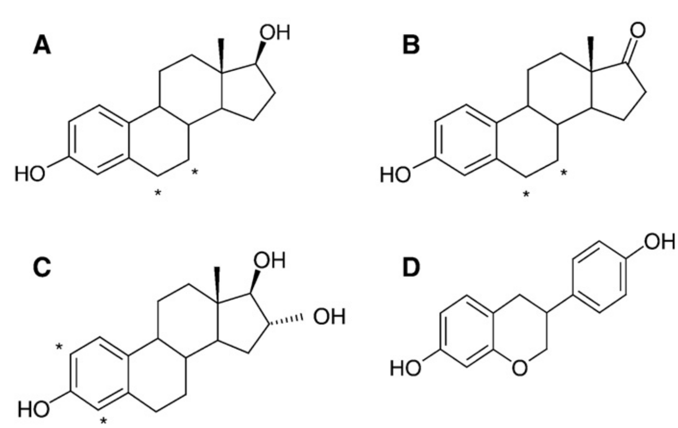

Fig. 1. Structure of the compounds including labeling sites (*): A) Estradiol [6,7-H^3], B) estrone (6,7-H^3), C) estriol (2,4-H^3) and D) equol H^3 (unspecified).