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Fate of 17 beta-estradiol-3-glucuronide Conjugate in Soils

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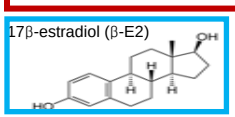
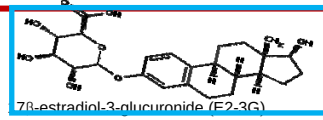
Introduction

In the United States the majority of the more than 2 billion farm animals are raised in confined animal feeding operations (CAFOs), resulting in concentrations of large quantities of animal waste in small land areas. In fact more than 500 million tons of animal waste is generated annually in the 238,000 CAFOs in the United States and typically this waste is stored on site for an extended period before being applied on land as fertilizer. Hormones associated with manure from concentrated animal feed operations (CAFOs) are of concern for both surface and groundwater quality, driving the need to monitor their occurrence, input, and subsequent fate in the environment. Previous investigation has shown significantly higher levels of hormone sulfate and/or glucuronide conjugates compared to that of hormones in animal waste. Compared to their parent compounds, the conjugated hormones are less estrogenic, however, are more water soluble and therefore, more mobile in the environment. Although the environmental fate of hormones is well understood, little information is available on the fate of their conjugates in animal waste and animal waste-applied soil. De-conjugation of hormone conjugates back to their parent compounds could significantly enhance the levels of hormones in the environment. Hence, a better understanding of hormone conjugate transformation in soils will help predict the environmental exposure to hormones in animal waste-affected environment.

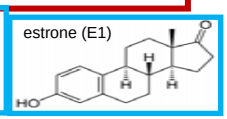
17β-estradiol (β-E2)



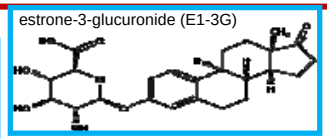


7β-estradiol-3-glucuronide (E2-3G)

estrone (E1)



estrone-3-glucuronide (E1-3G)



Objectives

- To investigate biotic and abiotic degradation kinetics of 17β-estradiol-3-glucuronide (E2-3G) and formation of metabolites in two different soils using laboratory microcosms.
- To understand how temperature affects E2-3G transformation.

Materials and Methods

- Surface layer (0 – 20 cm) of Mcgary and Purdy silt loam (fine, mixed, active, mesic Aeric Epiaqualfs) and Hayter loam (fine-loamy, mixed, active, mesic Ultic Hapludalfs) were collected. The properties of the two soils are listed in Table 1.
- The collected soils were transported to the laboratory immediately, air-dried for 48h, sieved (2 mm), and stored in the dark at 4ºC until use.
- 200 g of air-dried sterilized and non-sterilized soil was spiked with E2-3G to achieve an initial concentration of 5mg kg^{-1}. The water content of each soil was re-adjusted to the 60% of its maximum water holding capacity (-0.33 bar) and maintained at this level through out the incubation experiment.
- The E2-3G-spiked soils were incubated in Mason jars in darkness at 5 and 22ºC.
- Subsamples were collected after each targeted incubation period.
- Both E2-3G and its metabolites were extracted from each subsample using methanol/acetone (1/1, v/v) and methanol/water (1/1, v/v) on a pressurized solvent extractor (SpeedExtractor, E-916, BÜCHI), cleaned up using solid phase extraction cartridges (Oasis HLB,60mg, 3ml; Waters), and analyzed on a HPLC-DAD-FLD.
- The linear first order model was used to fit the E2-3G transformation (Microsoft Excel 2010).

Table 1. Physical and chemical properties of the two soils tested

Soil	Organic matter (wt%)	pH (1:1 soil:water)	CEC (meq 100 g^{-1})	sand (wt%)	silt (wt%)	clay (wt%)
McGary and Purdy	2.35	6.7	14.0	19.6	54.1	26.3
Hayter	2.00	5.8	10.6	43.0	39.5	17.5

Results and Discussion

- Within 48 hours, E2-3G transformed completely in both non-sterilized soils at 5 and 22ºC (Figs. 1&2).
- For sterilized soils, insignificant E2-3G transformation was observed at 5ºC within 20-day incubation, however, at 22ºC E2-3G was almost completely transformed during the same incubation period with half life of ~200 hours for both soils (inserts of Figs 1&2).
- Although much slower than biotic transformation, abiotic E2-3G transformation is important at 22ºC compared to at 5ºC (inserts of Figs 1&2).
- E2-3G transformation follows 1st order kinetics (Table 2). Higher temperature enhances transformation rates.
- β-E2 and E1 were major metabolites of E2-3G biotic and abiotic transformation, indicating deconjugation coupled with oxidation of 17th hydroxyl functional group were major mechanisms for E2-3G transformation.
- Small quantity of E1-3G was detected in the unsterilized soils, suggesting oxidation of 17th hydroxyl functional group before deconjugation of E2-3G, however, E1-3G quickly transformed within a few hours, most likely due to further deconjugation to form E1 (Figs 1&2).
- In unsterilized soils, after their concentrations reached to the highest, both β-E2 and E1 transformed rapidly within 24 hours followed by slower transformation. At 5ºC, ~15% of both compounds remained in the McGary and Purdy silt loam at the end of 24-day incubation.
- In sterilized soils, E1 remained stable even after 65-day incubation (inserts of Figs 1&2), indicating that different from β-E2, E1 transformation is mostly biologically-driven.
- This study suggests that conjugated hormones can be a potential source of free hormones in soils with high clay and organic matter contents at low temperature.

Table 2. E2-3G transformation parameters for the McGary and Purdy silt loam and Hayter loam at 5 and 22ºC

Treatment	K((mg kg^{-1})$^{-1}$ h^{-1})	r^2	DT_{50} (h)	DT_{90} (h)
McGary and Purdy				
5ºC	0.125	0.846	5.56	18.5
22ºC	0.354	0.923	1.96	6.50
Hayter loam				
5ºC	0.290	0.939	2.39	7.94
22ºC	0.497	0.810	1.50	4.97

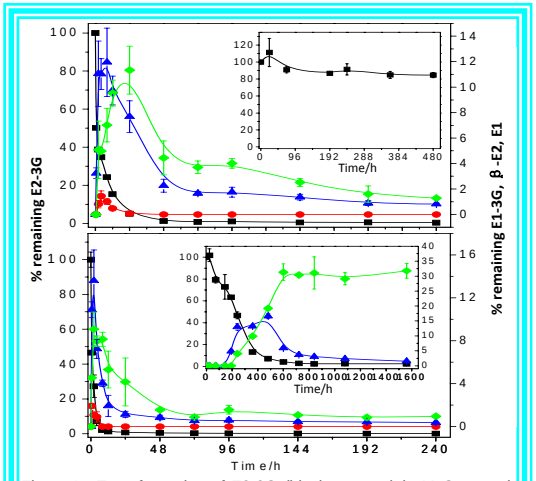


Figure 1. Transformation of E2-3G (black squares) in McGary and purdy silt loam. 5ºC (top) and 22ºC (bottom). Insert boxes are for the sterilized soil. E1-3G (red circle), β-E2 (blue triangle), and E1 (green diamond) are metabolites of E2-3G transformation.

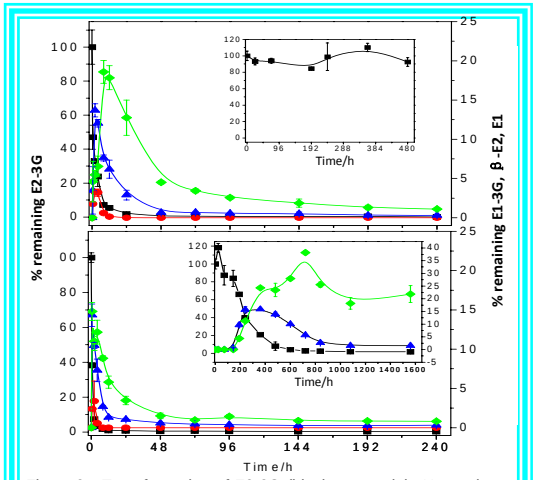


Figure 2. Transformation of E2-3G (black squares) in Hayter loam. 5ºC (top) and 22ºC (bottom). Insert boxes are for the sterilized soil. E1-3G(red circle), β-E2 (blue triangle), and E1 (green diamond) are metabolites of E2-3G transformation.

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