



## Assessment of the abiotic transformation of 17 $\beta$ -estradiol in the presence of vegetable matter – II: The role of molecular oxygen

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### ABSTRACT

This study characterizes the effect of oxygen in the abiotic transformation of estrogens when they are contacted with a surrogate of the vegetable wastes found in sewage. 17 $\beta$ -Estradiol (E2) and 17 $\beta$ -<sup>14</sup>C<sub>4</sub>-estradiol (<sup>14</sup>C-E2) were utilized as model compounds. Batch experiments were run under both oxic and anoxic conditions. In order to accomplish an accurate mass balance of the target estrogen, two analyses were performed simultaneously: first, radioactivity counting, and second, quantitation of E2 and <sup>14</sup>C-E2, as well as their transformation product estrone and <sup>14</sup>C<sub>4</sub>-estrone, by Liquid Chromatography tandem Mass Spectrometry. Under oxic conditions, the total concentration of <sup>14</sup>C-E2 was found to decrease by 78% in 72 h (15% and 7% remained in the liquid and solid phases, respectively). Conversely, when the estrogens were contacted with the synthetic influent under anoxic conditions, E2 was quantitatively recovered after 72 h (70% and 22% in aqueous and solid matrices, correspondingly). These results suggest that when the concentration of dissolved oxygen is null or limited, catalysis through an oxidative coupling mechanism is halted. Moreover, it was confirmed that the catalytic reaction occurred solely in the presence of the solid phase of the model vegetable matter.

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### 1. Introduction

Endocrine Disrupting Chemicals (EDCs), along with pharmaceuticals and personal care products, have become a major concern in the past decade and still constitute an emerging topic for the scientific community and the general public. Estrogens are among the most studied EDCs due to their potent disrupting effect and, in most cases, their natural origin in animal and human excretions. The significance of understanding the fate of estrogens in the environment is not limited to the necessity of their attenuation in the environment, it also resides in their chemical structure, which is commonly found in steroidal natural products, consumer products, and pharmaceuticals. The structure of estrogens consists of a sterane-type backbone and a phenolic group in ring A (Fig. SI-1 in Supporting Information (SI)); the presence of this phenolic group makes estrogens an ideal surrogate for predicting how other micropollutants will behave in the environment.

In recent years, extensive research has been performed to determine the fate of estrogens in different environmental matrices (Kolpin et al., 2002; D'Ascenzo et al., 2003; Hanselman et al., 2003; Casey et al., 2005; Khanal et al., 2006). Additionally, several studies have been conducted to assess the efficiency of wastewater treatment technologies in attenuating estrogens in wastewater streams (Joss et al., 2004; Suidan et al., 2005; Esperanza et al., 2007; Bolong et al., 2009; Janex-Habibi et al., 2009). Overall, conventional wastewater treatment plants have not been found to adequately attenuate these compounds (Khanal et al., 2006) and advanced treatment systems seem to only provide short-term solutions (Joss et al., 2008). Furthermore, the economic and energy requirements of these processes need to be carefully assessed (Lundstrom et al., 2010) to determine the sustainability of these solutions, as well as their application at a global scale.

A common flaw in the early work in this field is the assumption that only biodegradation and adsorption processes are involved in the elimination and transportation of estrogens in the environment. This was partially caused by the lack of sensitive analytical instrumentation and the exclusive application of indirect mass balances, where only liquid phases were considered.

The occurrence of catalytic reactions, such as oxidative coupling, which eliminate phenolic chemicals (such as estrogens) and anilines from the environment is well documented in soils, aquifer materials and other environmental matrices and systems (Vidic et al., 1993; Huang et al., 1995; Li and Lee, 1999; Colarieti et al., 2002; Hanselman et al., 2003; Lee et al., 2003; Sheng et al.,

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2009). Although this reaction may occur spontaneously in soils in the presence of oxygen at neutral and alkaline pH, the presence of a catalyst is normally required (Sorial et al., 1993; Huang et al., 1995). These catalysts can be separated into two groups: biotic and abiotic. Laccases and peroxidases are ligninolytic enzymes identified as biotic catalysts (Gianfreda and Rao, 2004). Abiotic catalysts include metal oxides, clays, and organomineral complexes (Huang et al., 1995). Copper, manganese, and iron oxides or complexes are reported as major species involved in the polymerization of phenolic compounds (Huang et al., 1995; Liyanapattirana et al., 2010) in environmental samples.

However, little attention has been devoted to these reactions in wastewater transport and treatment. These abiotic processes may play a key role in the elimination of estrogens from the environment, but only a few studies (on their role during wastewater treatment) have been published to date under laboratory conditions (de Rudder et al., 2004; Forrez et al., 2009; Sheng et al., 2009). Moreover, the use of biogenic manganese and other metals has recently been proposed as a potential alternative for wastewater treatment (Hennebel et al., 2009). The implementation of these reactions in engineered systems or their enhancement in natural scenarios will possibly be an aid in the minimization of economic and energy costs of the different treatments. Assessment of the impact of environmental variables on these catalytic reactions is required for a more comprehensive understanding of the fate of estrogens in natural and engineered systems. The outcomes from this study could aid in the development of novel technologies for control of these compounds during wastewater treatment.

Previous work completed by our research group (Marfil-Vega et al., 2010) identified the occurrence of an abiotic transformation of estrogens in the presence of a model vegetable material that is similar to vegetable residues discharged to the sewer from domestic and natural sources (e.g., humic substances). In the present study, the influence of molecular oxygen on the rate of the abiotic transformation of estradiol (E2) was studied using  $17\beta$ -E2 and  $17\beta$ - $^{14}\text{C}_4$ -estradiol ( $^{14}\text{C}$ -E2) as estrogenic model compounds. Furthermore, an investigation was conducted to determine whether the reaction occurred in the aqueous phase or on the surface of the solid. The use of  $^{14}\text{C}$ -E2 provided the opportunity of detecting and monitoring the presence of estrone (as  $^{14}\text{C}$ -E1) and other unidentified byproducts.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Two estrogens, E2 and  $^{14}\text{C}$ -E2 (structures in Fig. SI-1), were examined in this study. E2 (>98%) was obtained from Sigma-Aldrich (Milwaukee, WI) and  $^{14}\text{C}$ -E2 was purchased from American Radiolabeled Chemicals Inc. (Saint Louis, MO).  $^{14}\text{C}$ -E2 had an activity of 55 mCi mmol<sup>-1</sup> and 98% of it was radiolabelled.  $d_4$ -Ethiny-lestradiol (C/D/N Isotopes Inc., Canada) was utilized as a surrogate to monitor the extraction efficiency in all experiments. Dansyl chloride (from Sigma Aldrich, Milwaukee, WI) and sodium bicarbonate ( $\text{NaHCO}_3$ ) served as derivatization reagents for the Liquid Chromatography/Mass Spectrometry analysis (LC/MS/MS).

### 2.2. Experimental design

The experiment was designed so that sets of batch experiments were performed under oxic, anoxic, and a combination of anoxic-oxic conditions (see Table SI-1 for description). From the comparison of the results obtained under oxic or anoxic conditions, the role of molecular oxygen in our system was investigated. On the other hand, by sequentially combining anoxic-oxic conditions as

detailed in the Supporting Information, the effect of the presence of a solid phase in the system was assessed. In all cases, series of serum bottles were set up in triplicates in a controlled temperature room (at 4 °C), in the dark. E2 or  $^{14}\text{C}$ -E2 was spiked into a synthetic wastewater and the samples were sacrificed at predetermined sampling times. Although the absence of biological activity in our experimental set-up (Marfil-Vega et al., 2010) was confirmed, samples were kept at 4 °C as a precaution. For the experiments that involved anoxic conditions, extra steps were performed to prevent the exposure to oxygen of the samples. E2 and  $^{14}\text{C}$ -E2 were selected as model compounds because of the known transformation to E1 (or  $^{14}\text{C}$ -E1) as a result of biodegradation (Johnson and Sumpster, 2001) as well as other possible chemical transformations (Sheng et al., 2009). The use of  $^{14}\text{C}$ -E2 provided another major advantage; it allowed the simultaneous monitoring of radioactivity (that originated from the parent compound and any other potential byproducts) and the actual concentration of the estrogen measured by LC/MS/MS. Consequently, the fate of E2, as a result of adsorption and chemical transformations, could be accurately determined. A detailed description of how the samples were prepared for each batch (oxic, anoxic, and anoxic-oxic) can be found in the Supporting Information.

### 2.3. Analytical procedure

Fig. 1 represents the different analytical protocols followed in each of the batch experiments. Common to all of the protocols was the individual analysis of aqueous and solid phases, which were performed to accurately estimate the fate of the target compound. At each sampling event, triplicate serum bottles were sacrificed.

The solid line in Fig. 1 represents the standard procedure followed in the batches that were run under oxic conditions and used non-radiolabelled E2. After filtration with glass fiber filters, liquid and solid samples were extracted, cleaned-up, and derivatized with dansyl chloride prior to LC/MS/MS analysis. Briefly, aqueous samples were extracted by Solid Phase Extraction with C-18 cartridges, and cleaned-up prior to derivatization with neutral alumina cartridges. At the same time, the solids were extracted in

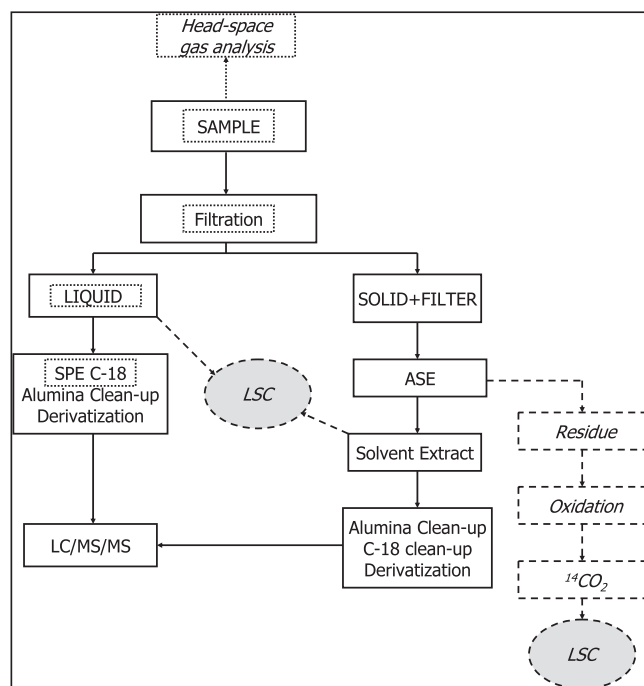


Fig. 1. Analytical protocol.

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