Journal of Contaminant Hydrology 166 (2014) 1–10

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

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

Fate and transport of selected estrogen compounds in Hawaii soils: Effect of soil type and macropores

Matteo D'Alessio [a,b], Dharni Vasudevan [c], Joseph Lichwa [a], Sanjay K. Mohanty [b,1], Chittaranjan Ray [a,b,*]

[a] Water Resources Research Center, University of Hawaii at Manoa, Honolulu, HI 96822, United States
[b] Department of Civil and Environmental Engineering, University of Hawaii at Manoa, Honolulu, HI 96822, United States
[c] Department of Chemistry, Bowdoin College, Brunswick, ME 04011, United States

ARTICLE INFO

Article history:
Received 27 October 2013
Received in revised form 10 July 2014
Accepted 18 July 2014
Available online 25 July 2014

Keywords:
17β-estradiol
Estrone
Tropical soils
Transport
Recycled-water
Macropores

ABSTRACT

The fate and transport of estrogen compounds in the environment is of increasing concern due to their potential impact on freshwater organisms, ecosystems and human health. The behavior of these compounds in batch experiments suggests low mobility, while field studies indicate the persistence of estrogen compounds in the soil with the possibility of migration to surface water as well as groundwater. To better understand the movement of these chemicals through soils, we examined their transport in three different Hawaiian soils and two aqueous matrices. The three different soils used were an Oxisol, a Mollisol and a cinder, characterized by different mineralogical properties and collected at depths of 60–90 cm and 210–240 cm. Two liquid matrices were used; deionized (DI) water containing calcium chloride ($CaCl_2$), and recycled water collected from a wastewater treatment facility. The experiments were conducted in packed and structured columns. Non-equilibrium conditions were observed during the study, especially in the structured soil. This is believed to be primarily related to the presence of macropores in the soil. The presence of macropores resulted in reduced contact time between soil and estrogens, which facilitated their transport. We found that the organic carbon content and mineralogical composition of the soils had a profound effect on the transport of the estrogens. The mobility of estrone (E1) and 17β-estradiol (E2) was greater in cinder than in the other soils. In column experiments with recycled water, earlier breakthrough peaks and longer tails of estrogens were produced compared to those observed using DI water. The use of recycled water for agricultural purposes and the siting of septic tanks and cesspools should be critically reviewed in light of these findings, especially in areas where groundwater is the primary source of potable water, such as Hawaii.

1. Introduction

Estrogen compounds in the environment are receiving significant attention due to their potential impact on freshwater organisms, ecosystems, and human health (Bolong et al., 2009; Corcoran et al., 2010). Estrogens naturally occur and are synthetically produced for use in oral contraceptives and hormonal therapy as well as in veterinary treatment of domestic and farm animals (Wise et al., 2011). Natural estrogens, E2 and E1 are excreted by women (2–12 and 3–20 μg/person/day, respectively) and female animals, as well as by men (E1 5 μg/person/day; see Ying et al., 2002).

These compounds, at low concentrations, are capable of disrupting the endocrine systems of many organisms (Bolong et al., 2009). For example, exposure to estrogens at levels as low as 1 ng/L has been shown to cause feminization of male trout

* Corresponding author at: Department of Civil and Environmental Engineering, University of Hawaii at Manoa, Honolulu, HI, 96822, United States. Tel.: +1 808 956 9652; fax: +1 808 956 5014.
E-mail address: cray@hawaii.edu (C. Ray).
[1] Current affiliation: Department of Civil and Environmental Engineering, Stanford University, Stanford, CA, 94305, United States.

http://dx.doi.org/10.1016/j.jconhyd.2014.07.006
0169-7722/

(Hansen et al., 1998; Purdom et al., 1994) and Japanese medaka fish (*Oryzias latipes*) (Metcalfe et al., 2001). Therefore, the presence of these compounds in surface water is a matter of concern. Because traditional wastewater treatment does not remove these compounds, they are frequently detected in treated wastewaters (Desbrow et al., 1998; Jiang et al., 2005; Ternes et al., 1999) as well as in animal waste lagoons (Kjær et al., 2007; Khan and Lee, 2012; Laegdsmand et al., 2009; Thompson et al., 2009) and in septic tanks (Drewes et al., 2003; Swartz et al., 2006). In a study by Kolpin et al. (2002), detectable concentrations of reproductive hormones were found in approximately 21% of 139 streams surveyed across the United States. Groundwater in some areas is similarly contaminated. For example, 17β-estradiol (E2), at concentrations between 13 ng/L and 90 ng/L, was detected in the Ozark Plateau Aquifer, a karstic area in southwest Missouri, USA (Wicks et al., 2004).

To minimize environmental exposure to estrogens, it is important to understand their fate and transport in the environment. Our review of the literature, detailed below, indicates that there is no clear understanding about the fate of natural estrogens in the soil environment. This lack of understanding may be related to the variety and nature of experiments conducted (batch, packed columns and field studies), as well as the solid and liquid matrices used.

E2 ($C_{18}H_{24}O_2$) has lower water solubility compared to its degradation product E1 ($C_{18}H_{22}O_2$), 3.85 and 13 mg/L, respectively. Both estrogens have similar pKa (10.3 and 10.23) and log K_{oc} (3.3 and 3.2) values (Lai et al., 2000; Lee et al., 2003). E1 and E2 have similar structures. In fact, both estrogens have a phenolic hydroxyl group at C-3, however E1 has a ketone group at C-17 instead of a hydroxyl group.

Batch and field studies show contrasting mobility in the environment for E1 and E2. Batch experiments, based on equilibrium conditions, suggest moderate mobility (K_d = 17–91 L/kg and 30–93 L/kg for E2 and E1, respectively; Casey et al., 2005; Fan et al., 2008) compared to other organic compounds in which K_d ranged between 0.2, high mobility, to 6000 L/kg, limited mobility (Delle Site, 2000; Tolls, 2001). On the other hand, field studies suggest persistence of E1 and E2 in soils, presenting the possibility of migration to surface water and groundwater (Kjær et al., 2007; Lucas and Jones, 2009; Wicks et al., 2004; Thompson et al., 2009).

Laboratory studies have shown that E2 degrades more rapidly than other natural hormones (Casey et al., 2005; Das et al., 2004; Fan et al., 2007) and therefore its mobility in soil is minimal (Casey et al., 2003; Das et al., 2004; Fan et al., 2008). However, the type of soil, composition of the aqueous matrix and the packing process used during the column studies may affect the degradation and transport of estrogens in soil.

Most of the soils used for batch, column and field experiments in previous studies were sandy (Das et al., 2004; Fan et al., 2008) or sandy loams (Lorenzen et al., 2005; Sangsupan et al., 2006) collected between 0 and 20 cm (Das et al., 2004; Kjær et al., 2007; Lucas and Jones, 2009). Realistic aqueous matrices such as sheep urine (Lucas and Jones, 2009), dairy farm effluent (Steiner et al., 2010), and swine manure (Thompson et al., 2009) contain natural organics and particulate matter that may enhance the transport of trace organic compounds by competitive interactions and colloid-facilitated transport, respectively (McCarthy, 1998; McCarthy and McKay, 2004). In the presence of these realistic aqueous matrices, estrogens were able to persist longer in the aqueous phase as a result of reduced potentials to degrade and/or sorb to soil (Zitnick et al., 2011). Experimental matrices such as DI water and DI water with $CaCl_2$ have been widely used in previous studies (Casey et al., 2003; Das et al., 2004; Fan et al., 2008; Lee et al., 2003) and may have underestimated the potential transport of estrogen compounds through soil because these solutions lack the above-mentioned aqueous constituents that enhance transport.

Most of the previous studies use repacked columns, instead of intact, structured soil columns to investigate the fate and transport of estrogens. Repacking eliminates soil structure and soil macropores, which are typically created by root and earthworm channels, fissures and interaggregate voids. Macropores can result in rapid flow and can reduce the contact time of solutes with adsorption sites. Classical physical non-equilibrium occurs when tracers or chemicals encounter two different flow regimes in the soil, a mobile region (such as macropores) where advection and diffusion/dispersion occurs and an immobile region (the bulk matrix) where diffusion dominates (Coats and Smith, 1964).

The tropical soils in Hawaii are different from the temperate zone soils of the mainland United States and Europe in terms of their structure, texture, charge and metal-oxide content (Teo et al., 2006). Recently, there have been efforts to promote the reuse of wastewater effluent for crop irrigation instead of ocean disposal. Irrigation with recycled water could potentially contaminate groundwater in Hawaii. Groundwater is the primary source of drinking water for the Hawaiian Islands and many small islands in the tropics. On the island of Oahu, nearly all potable water is obtained from underground sources, and is supplied without any treatment except for low-levels of chlorination. Although the depth to groundwater can be hundreds of meters, the rapid transport of chemicals from land surface to groundwater is facilitated by voids in the soil structure and the underlying saprolite and basalt. In the past, groundwater on Oahu and other islands has been contaminated by pesticides such as nematicides (applied in pineapple cultivation) or herbicides (applied mostly on sugarcane crops; see Alavi et al., 2008; Dusek et al., 2010). Other potential sources of groundwater contamination in Hawaii include the significant number of cesspools and septic tanks used by some populations and a small number of animal waste lagoons. In fact, Hawaii has the largest number of cesspools of any state in the US (approximately 100,000), and the greatest number per capita (Fletcher et al., 2010; USEPA, 2004). Of particular relevance to this study is the fact that treated effluent, animal waste lagoons, leaky sewers, septic tanks and cesspools may contain estrogen compounds (Kolodziej et al., 2004; Khan and Lee, 2012); therefore, their transport behavior in Hawaii's tropical soils needs to be elucidated.

The aim of this work was to examine the effect of the substrate type of two highly weathered tropical soils and one slightly weathered cinder as well as the impact of different aqueous matrices on the fate and transport of two estrogens. This work focuses on differences in the transport of two estrogens in packed and intact columns of tropical soils with distinct soil properties and their behavior in the presence of treated wastewater effluent. The soils were collected at 60–90 cm depth in order to simulate leaching under effluent