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

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\textbf{Article info}

\textbf{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\textsubscript{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 17\textbeta-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.

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\textbf{Keywords:}

17\textbeta-estradiol
Estrone
Tropical soils
Transport
Recycled-water
Macropores

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.
stand in Mayberg relate to the variety and nature of experiments in previous studies were sandy (Das et al., 2004; Sangsupan et al., 2006) collected between 0 and 20 cm (Das et al., 2004; Kjaer 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 CaCl₂ 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 conditions.
irrigation for crop production, and at 210–240 cm depth to simulate leaching occurring from cesspools, septic tanks and leaky sewers. To evaluate the impact of the nature of the aqueous matrix on transport of estrogens, DI water with calcium chloride ($\text{CaCl}_2$) and recycled water (i.e., sewage effluent subjected to standard activated sludge treatment followed by filtration and UV disinfection) were used in all experiments.

2. Materials and methods

2.1. Chemicals

We used E1 (99% pure) and E2 (97% pure) (Sigma-Aldrich, St. Louis, MO), HPLC-grade methanol, acetone and acetonitrile (EMD Chemicals Inc., NJ). Milli-Q (Billerica, MA) reagent grade DI water with a resistivity of 18.2 MΩ cm (at 25 °C) was used.

2.2. Soils

Disturbed soil samples were collected from sites located at the University of Hawaii (UH) Poamoho Experimental Station (21°32′16.81″N, 158°05′21.3′′W) and at the UH Waimanalo Experimental Station (21°20′18″N, 157°42′53″W) on Oahu, Hawaii, while an intact soil core was collected from the UH Poamoho Experimental Station. The Poamoho (P) soil is classified as an Oxisol (Waialua series, vertic Haplustolls very-fine, kaolinitic and isohyperthermic) (Ikawa et al., 1985). A slightly weathered substrate, referred simply as cinder (C), having particles smaller than 2 mm, was collected from a mountain slope along Tantalus drive (21°19′57.58″N, 157°48′53.34″W) close to UH’s main campus in Honolulu, Hawaii.

Bulk soil samples from P and W were excavated using hand augers at 60–90 cm (top) and 210–240 cm (bottom) depths. Henceforth, the top and bottom of Poamoho and Waimanalo soils are referred to as Pt, Pb, Wt and Wb, respectively. Surface cinder was collected using a hand shovel at 5–10 cm depths. These soil samples were air-dried, ground with a pestle to break the aggregates, sieved (<2 mm), and stored at 4 °C until use.

The structured soil column was only collected at the Poamoho Experimental Station by pressing the sharpened edge of a stainless steel cylinder (14 cm inner diameter, 20 cm length) into the soil between 10 and 50 cm with a truck-mounted hydraulic mechanism (Ray et al., 2007). The soil column was extracted and both ends of the column were sealed to minimize further disturbance to the soil structure during transport to the laboratory where it was stored at 4 °C until use. Sobotkova et al. (2011) used a computed tomography (CT) scanner to examine the pore structure of this core. Results from the CT scanner revealed the presence of macropores (0.5–2.0 mm in diameter) as well as larger cavities (approximately 10 mm; see Sobotkova et al., 2011).

2.3. Recycled water

Fresh recycled water was collected from the Honolulu Wastewater Treatment Plant in Ewa Beach, Oahu, Hawaii. This recycled water is wastewater or sewage influent that has been subjected to standard activated sludge treatment followed by filtration and UV disinfection. The water was collected and stored at 4 °C in the dark. The recycled water was filtered through 0.45 μm GHP filters (Life Science PALL, West Chester, PA) before use in the experiments. The concentrations of E1 and E2 added to the feed water in this study (70 μg/L) were higher than those typically observed in recycled water (Campbell et al., 2006; Ying et al., 2002). Higher concentrations were selected as our aim was to understand the processes involved in transport. Keeping the concentrations at these levels allowed us to analyze for E1 and E2 without any pre-concentration efforts.

2.4. Column experiments

Vertical flow-through columns (stainless steel; 4.75 cm inner diameter, 7.60 cm height) were used for the packed soil column experiments. Soil was added in increments of 5 mm to each column and compacted using a vortex mixer (VWR, Thorofare, NJ) before use in the experiments. The concentrations of E1 and E2 were selected as our aim was to understand the processes involved in transport. Keeping the concentrations at these levels allowed us to analyze for E1 and E2 without any pre-concentration efforts.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characteristics of granular porous media used for experiments.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid properties</strong></td>
<td><strong>Pt</strong></td>
</tr>
<tr>
<td>Particle size distribution (%)</td>
<td></td>
</tr>
<tr>
<td>Sand [0.05–2.0 mm]</td>
<td>2</td>
</tr>
<tr>
<td>Silt [0.002–0.05 mm]</td>
<td>18</td>
</tr>
<tr>
<td>Clay [&lt;0.002 mm]</td>
<td>80</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>1.17</td>
</tr>
<tr>
<td>pH</td>
<td>6.08</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>54.8</td>
</tr>
<tr>
<td>TOC (%)</td>
<td>0.57</td>
</tr>
<tr>
<td>Mn (μg/g soil)</td>
<td>8772</td>
</tr>
<tr>
<td><strong>Liquid properties</strong></td>
<td><strong>Recycled water</strong></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>7.7</td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Note: * = data not available.

* Particles range between 0.25 mm and 2 mm.
Flow interruption was used to investigate the impact of non-equilibrium flow (Jardine et al., 2001) on the transport of the estrogens. Flow interruption is a technique that is often used to reveal the presence of advection-dominated (during the displacement of the chemicals) as well as diffusion-dominated flow paths (upon flow interruption) within the porous media. During the injection of E1 and/or E2, flow was interrupted for approximately 30 h and the outlet and inlet tubes were sealed to prevent possible evaporation.

A steady water flow rate of 18.7 cm/day (~1 PV/day) was established through the structured soil column. This flow rate is higher than the infiltration rate typically used in landscape areas with high irrigation water requirements (USDOE, 2010), as well as the typical water application rate used on golf courses (Walker and Balogh, 1990). NaN₃ was not used in the experiments with high irrigation water requirements (USDOE, 2010), as well as the typical water application rate used on golf courses (Walker and Balogh, 1990). NaN₃ was not used in the experiments with high irrigation water requirements (USDOE, 2010), as well as the typical water application rate used on golf courses (Walker and Balogh, 1990).

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Effluent from the structured soil column, was passed through solid-phase-extraction (SPE) cartridges (Waters, Milford, MA) prior to the analysis of E1 and E2 with an HPLC system (Thermo Finnigan, Waltham, MA) coupled with a photo diode array (PDA) detector and a fluorescence detector (Shimadzu, Columbia, MD). The two chemicals were separated using a reverse phase column (100.0 mm × 2.1 mm, 3.0 μm; Restek, Bellefonte, PA) protected by a guard column with a matching stationary phase. Both columns were kept at 30 °C during analysis. Acetonitrile and DI water were used as the mobile phase. Bromide concentration was measured with an ion chromatography (IC) system (Dionex, Bannockburn, IL). Total organic carbon (TOC) in the recycled water was determined using a TOC analyzer (Shimadzu, Columbia, MD), while the surface area of the soils was measured with a surface area analyzer (Micrometrics, Norcross, GA). Pore structure of the soil samples was characterized by a scanning electron microscope (SEM) (Hitachi, Schaumburg, IL). Acceleration voltage, magnification and working distance were set at 5000 V, 4500 and 10.9 mm, respectively. The SEM was coupled with an energy dispersive X-ray (EDX) spectroscopy system for elemental analysis (Oxford Instruments, Scotts Valley, CA). Detailed information on soil characterization can be found in the Supplementary Information.

3. Results

3.1. Soil and liquid properties

Soil and liquid properties are provided in Table 1. The P soil was highly aggregated and had higher clay content (68–80%) and lower sand content (2%) than the other two soils. Particles in C ranged between 0.25 mm and 2.0 mm. The P soil has moderate and fine subangular blocky structure, and higher iron oxide (11% as Fe and 15.7% as Fe₂O₃) compared to W soil (7.7% as Fe and 11.0% as Fe₂O₃) (Ikawa et al., 1985). Both P and W samples had few roots, fine and very fine pores (Ikawa et al., 1985).

3.2. Case 1: Effect of soil types when E1 and E2 were individually applied in disturbed (packed) soil columns

BCTs of E1 (when only E1 was injected) and BCTs of E1, E2 and bromide (when only E2 was injected) are shown in Fig. 1a–d. In experiments when only E1 or only E2 was injected, bromide appeared earlier (within 1 PV) than E1 and E2 (~3 PV) in the P and W soils (Fig. 1a–d). BCTs of bromide when only E1 was injected (curves not shown) were similar to those

Table 2

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Poamoho</th>
<th>Poamoho</th>
<th>Waimanalo</th>
<th>Waimanalo</th>
<th>Volcanic ash</th>
<th>Poamoho</th>
<th>10–50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60–90</td>
<td>210–240</td>
<td>60–90</td>
<td>210–240</td>
<td>60</td>
<td>10–50</td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions

Case 1: Effect of different soil types when E1 and E2 are individually applied in disturbed (packed) soil columns

E1 only
DI water with 1.0 mM CaCl₂ for all soil columns except the structured soil column
E2 only
DI water with 1.0 mM CaCl₂ for all soil columns except the structured soil column

Case 2: Effect of different soil types and different aqueous matrices when E1 and E2 are simultaneously applied in disturbed (packed) soil columns

E1 + E2
DI water with 1.0 mM CaCl₂ for all soil columns except the structured soil column
Recycled (R1) water for all soil columns except the structured soil column

Case 3: Effect of different aqueous matrices on transport of E1 and E2 in the structured soil column

E1 + E2
–
–
–
–
DI, R1 water

Note: Bromide was added in all case studies.
observed in Fig. 1d (when only E2 was injected). Additionally, the depth from which the sample was taken had no significant impact on bromide breakthrough in either soil (Fig. 1d). E1, E2 and bromide appeared almost simultaneously (after 0.6, 0.7 and 0.75 PV, respectively) in C soil (Fig. 1a–d). In all soils except Wb when only E2 was introduced, concentrations of its degradation product, E1, were consistently higher than E2 concentrations. When only E1 was introduced, the early appearance of E1 (<1 PV) was observed in C and Wb soils, while E1 appeared after 3 PV in the remaining soils.

High mass recovery (mass recovered in the effluent compared to the mass injected) between 95% and 100% of bromide was observed in all three soils (Table 3). The mass recovery of both estrogens was lower (16–46% for E2 and 48–82% for E1) than that of bromide in W and P soils. When E2 alone was introduced, greater recovery of E2 was observed in W soil compared to P soil. For both the W and P soils, recovery was greater from the deeper soils (Table 3). Flow interruption caused a decrease in the concentrations of bromide and E2 and an increase in the concentration of E1. The impact of flow interruption was more evident in Wb (Fig. 1b, c).

3.3. Case 2: Effect of soil types and aqueous matrices when E1 and E2 were simultaneously applied in disturbed (packed) soil columns

The BTCs of bromide, E2 and E1 in the CaCl2 solution (Fig. 2a, c, e) and recycled water (Fig. 2b, d, f) are plotted as a function of the number of PVs passing through the columns. Bromide appeared within 1 PV in both W and P soils, taken from both depths, and for both aqueous matrices (Fig. 2a). E1 and E2 appeared earlier in W soil than in P soil (Fig. 2c, e). In the presence of CaCl2 solution, BTCs of E1 and E2 were nearly identical (Fig. 2c, e). When recycled water was used, the shape of the tails of the BTCs for Wb and Wt were similar, while relatively longer tailing was observed in Pt compared to Pb. Early appearance of both estrogens was also observed (Fig. 2d, f).

High recovery of bromide was observed with CaCl2 solution (~95%) and recycled water (~88%). The highest recovery of both E1 and E2 was seen in the P soil (Table 3). In the recycled water, the recovery of E1 was greater than 100%, while 40% to 60% of E2 was recovered.

3.4. Case 3: Transport of E1 and E2 in structured soil column

BTCs of bromide, E1 and E2 passing through the structured soil column are presented in Fig. 3. Peak breakthrough occurred earlier for the bromide than for E1 and E2. Bromide appeared at around 0.5 PV and reached a plateau within 1.2 PV (Fig. 3a). Peak breakthrough for both estrogens was at 12 PV. The increase in concentration of E1 was higher than that of E2 (between 12 and 28 PV), after which concentrations of both estrogens reached a plateau (Fig. 3a). After resuming flow after the 30 h interruption, bromide and estrogen concentrations decreased between 39 and 41 PV, after which concentrations of

![Fig. 1. Breakthrough curve of E1 when only E1 was introduced (a) and breakthrough curves of E1, E2, and bromide when only E2 was introduced (b, c, and d). In all columns, the aqueous solution was 1.0 mM CaCl2 and bromide (at 15 mg/L) was also introduced. The vertical arrows indicated the starting of flow interruption.](image-url)
Table 3
Recovery (%) of bromide, E1 and E2 from soils under experimental conditions.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Bromide (%)</th>
<th>E1 (%)</th>
<th>E2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Pb</td>
<td>Pt</td>
</tr>
<tr>
<td>Disturbed – E1 only in 1 mM CaCl₂ solution</td>
<td>95</td>
<td>96</td>
<td>97</td>
</tr>
<tr>
<td>Disturbed – E2 only in 1 mM CaCl₂ solution</td>
<td>100</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>Disturbed – E1 &amp; E2 in 1 mM CaCl₂ solution</td>
<td>–</td>
<td>95</td>
<td>96</td>
</tr>
<tr>
<td>Disturbed – E1 &amp; E2 with R1 water</td>
<td>–</td>
<td>88</td>
<td>89</td>
</tr>
<tr>
<td>Structured – E1 &amp; E2 in 1 mM CaCl₂ solution</td>
<td>–</td>
<td>–</td>
<td>97</td>
</tr>
<tr>
<td>Structured – E1 &amp; E2 with R1 water</td>
<td>–</td>
<td>–</td>
<td>95</td>
</tr>
</tbody>
</table>

Note: – = data not available. The recovery of E1, E2 and bromide in the presence of the structured soil was calculated between 0 (starting of the injection of the solution) and 86 PV (ending of the flushing period).

Fig. 2. Breakthrough curves of bromide, E2 and E1 in the presence of 1.0 mM CaCl₂ solution (a, c, and e) and R1 water (b, d, and f), respectively.
all increased continuously (Fig. 3a). The column was flushed (between 66 and 86 PV) with CaCl₂ solution. During this period, bromide was completely removed, while 75% of E1 and 42% of E2 were removed. A longer flush-out (>22 PV) period was needed to fully remove E1 and E2 from the structured soil column.

In the presence of recycled water (Fig. 3b), earlier breakthrough peaks of E1 were observed compared to the CaCl₂ solution (Fig. 3a). Higher recovery of E1 and lower recovery of E2 were observed in the recycled water (Fig. 3b).

4. Discussion

4.1. Influence of compound structure and soil organic matter on E1 and E2 transport

In the different soils examined here, the breakthrough of estrogens occurred after that of bromide, suggesting sorption of estrogen during transport through the soil. E1 and E2 breakthrough generally mirrored soil organic carbon content, with the estrogens appearing last in Pt with the highest organic carbon content, and earliest in C and Wb, with the lowest organic carbon content. In addition, based upon the molecular structure of E1 and E2 and their relative extents of sorption, we suggest that the sorption capability of both estrogens is a function of organic matter rather than pH.

It is established that hormones primarily interact with soil organic matter via hydrogen bonding interactions that occurs between hydrogen donors and acceptors (Yamamoto et al., 2003). The relatively higher sorption of E1 compared to E2 in soils with similar properties may be related to the differences in capacity for hydrogen bonding with sites on soil organic matter. Significantly, E1 possesses a ketone group instead of a hydroxyl group at C-17, as is the case for E2. Ketone groups are monopolar strong H-acceptors while the hydroxyl group is a bipolar, weaker H-acceptor. As such, the ketone group on E1 is likely to exhibit a more favorable interaction with phenolic hydroxyl groups present on organic matter, which in turn results in a higher sorption capacity (Neale et al., 2009), as noted in our study. Consequently, pH is unlikely to influence sorption since E1 and E2 are neutral at environmentally relevant pH values. Furthermore, changes in pH do not alter the driving force of neutral compounds that sorb primarily via hydrophobic exclusion and hydrogen bonding. As such, we find that soil organic carbon content likely has a greater influence of E1 and E2 transport than pH. This is consistent with earlier studies by Yamamoto et al. (2003) and Van Emmerik et al. (2003).

4.2. Degradation of E2

In the packed columns, the presence of E1 in the effluent, even when only E2 was applied, indicates the degradation of E2 to E1 despite the addition of 1.5 mM NaN₃. This degradation in the presence of NaN₃ was also observed by Mansell and Drewes (2004). We suspect the concentration of NaN₃ (1.5–2.0 mM) may not have been high enough to inhibit all biological degradation, or possibly E2 was degrading abiotically. Colucci et al. (2001) was among the first to observe that the degradation of E2 did not require the presence of living organisms. In addition, this study did not observe a consistent effect of soil properties (i.e., soil pH, organic matter and soil texture) on the degradation behavior of E1 and E2. In fact, in all soils at both depths, except Wb, concentrations of E1, the breakdown product of E2, were consistently higher than E2 concentrations (Fig. 1b, c). The impact of flow interruption on the degradation of E2 was also similar throughout the different soils. During flow interruption, concentrations of E2 decreased, while concentrations of E1 progressively increased (Fig. 1b, c). Sheng et al. (2009) observed that E2 rapidly dissipated in the sterile soil slurry and E1 was simultaneously produced. They attributed this oxidation to the presence of oxidizing soil components, such as metal oxides, which may oxidize the hydroxyl group at position 17 of the E2 molecule to a carbonyl (Sheng et al., 2009; Xu et al., 2008). Among the different metal oxides, manganese showed the highest degradation capacity (Sheng et al., 2009; Zitnick et al., 2011). Studies of biotic degradation have established that more readily available carbon, such as glucose, inhibit the microbial degradation of E2 (Herman and Mills, 2003). In keeping with the findings from these studies, we attribute the degradation of E2 in our system to both biotic and abiotic processes.

![Fig. 3. Breakthrough curves of E1, E2, and bromide when E1 and E2 were introduced into the structured soil column where the aqueous solution was either (a) 1.0 mM CaCl₂ or (b) R1 water. The vertical arrows indicate the starting of flow interruption.](attachment:image)
4.3. Physical non-equilibrium: Presence and impact on E1 and E2 mass recovery and transport

P soil has high clay content and water-stable aggregates, holds substantial amounts of immobile water and exhibits channelized flow due to macropores when re-wetted (Uehara and Gillman, 1981). W soil has lower clay content, higher sand content and larger surface area compared to the other soils (Table 1). Results obtained using the particle size analyzer revealed the presence of colloidal particles with an average size of approximately 380 nm in the recycled water used in this study.

Mass recovery of the estrogens was lower than that of bromide. This was related to irreversible sorption and degradation of the estrogens in the soil. In our experiments, the recovery of E2 was lower than the recovery of E1, due to the breakdown of E2 to E1. Among the different soils, the recovery of E1 and E2 was greatest in Pb and Wb. This could be because of the reduced interaction of estrogen compounds with the soil due to lower TOC, possibly less developed soil and the presence of macropores in the deeper soils, as well as higher rates of degradation of E2 and consequent production of E1.

Enhanced transport was more evident in the structured soil column than in the packed columns where soil macropores are usually reduced due to packing (Fig. 3 vs. Fig. 2). Early appearance and faster increase in bromide, E2 and E1 was observed in the structured soil column (Fig. 3).

Macropores are characterized by higher flow velocity and less tortuosity and they also enhance the movement of colloids (Grolimund et al., 1998). The presence of macropores as well as larger cavities (approximately 10 mm) in P soil, were also confirmed by Sobotkova et al. (2011) from a CT scan of our column. These macropores could be the result of biological activity or physicochemical processes, and could be responsible for the preferential non-equilibrium transport of solutes in soils (Ghodrati et al., 1999). The size of most macropores detected by CT was in the range of 0.5–2.0 mm in diameter and several centimeters in length. Some of these pores were also vertically interconnected (Sobotkova et al., 2011).

The presence of physical non-equilibrium was also suggested by the early appearance of bromide (within 1 PV), and asymmetrical BTCs with long tails especially in the structured soil column (Fig. 3a, b). The bromide tracer test, in our structured column, confirmed the presence of more extended physical non-equilibrium and enhanced transport. During flow interruption, after approximately 40 and 105 PV, there was an observed irregularity in the conservative tracer after flow was resumed. More specifically, interruption of the flow, during the leaching experiment conducted with bromide, caused a decrease in bromide concentration ($C_i/C_0$ dropped from 100% to approximately 90%) when flow was resumed. After that, $C_i/C_0$ was stable (approximately 100%). In contrast, interrupting the flow during the tracer flush-out (the solution containing bromide was replaced with DI water alone) caused a small increase in the concentration of bromide ($C_i/C_0$ increased from 32% to 34%) when the flow (DI water alone) was resumed. According to Jardine et al. (2001), during the injection tracer concentrations within the advection-dominated flow paths (e.g., fractures and macropores) are higher than those within the remainder of the soil. Upon flow interruption, the relative decrease in concentration observed indicated that solute diffusion may be occurring from larger, more conductive pores into the smaller pores. During tracer displacement, the concentration within the preferred flow-paths was lower than that within the matrix, and solute diffusion from smaller pores into larger pores may have been occurring (Jardine et al., 2001).

The combined effect of macropores and, to a limited extent, colloid-facilitated transport enhanced the movement of E1 and E2 when recycled water was applied to structured and repacked soil columns. Earlier breakthrough peaks and higher recovery of E1 were observed in the presence of recycled water under structured and packed soil columns.

4.4. Possible impact on the Hawaiian Islands

The enhanced movement of estrogen compounds is of particular concern especially in locations such as Hawaii, where groundwater is the primary source of potable water, or for coastal waters. Considering the low level of estrogen in recycled water (< 10 ng/L), potential water usage for landscape areas and associated meteorological conditions, and the adsorption properties of the different soils, the migration of E1 and E2 is limited to the upper section of each soil (mostly within one meter). Deeper movement can be expected in the presence of macropores, high DOC (dissolved organic carbon), as well as under the influence of natural colloids. Leaching from cesspools may represent a critical environmental issue in areas having shallow groundwater as well as poorly developed soil (such as the island of Hawaii). In Hawaii, many beach front properties located in rural areas are served with cesspools or septic tanks for waste disposal. Depth to groundwater in such areas can be on the order of a few meters. The soils at the bottom of the cesspools are typically low in organic carbon (Ikawa et al., 1985; Miller et al., 1988) and the natural sorption potential for estrogen is low. The high concentration of DOC present in cesspool effluent also enhances transport of estrogens and other chemicals. Aerobic degradation of these chemicals is expected to be low as soil below the bottom of the cesspool is expected to be anoxic. In certain rural areas of Hawaii (e.g., Paradise Park subdivision on the island of Hawaii) where wells and septic/cesspools are used for domestic water supply and waste disposal, monitoring for the presence of these chemicals in well waters is recommended.

5. Conclusion

Our results clearly demonstrated that experimental design (packed vs. structured soil columns), soil type, and the nature of the aqueous matrices highly impacted the behavior of the two estrogens. These factors should be carefully considered before designing a land application system or siting septic tanks/cesspools.

In all the tested soils, breakthrough of the estrogens appeared after the breakthrough of bromide, which suggested sorption during the transport of estrogens through the soil. Non-equilibrium conditions were observed during the study, especially in the structured soil. This was believed to be related to the presence of macropores and other heterogeneities in the soil. The presence of macropores resulted in reduced contact time between soil and estrogens, which facilitated their transport. The mineralogical composition and levels of organic carbon and metal oxides in the soil impacted the transport of...
the estrogens. Rapid transport was mostly observed in soil C, mainly due to the large particles, the limited content of fines and the low TOC. When only E2 was introduced into the columns, E1 was consistently present in the effluent, due to the degradation of E2 despite the addition of NaN₃. Transport of estrogens in all the soils was enhanced in recycled water. In fact, early breakthrough peaks, long tails and full recovery of both estrogens was observed when recycled water was used as the vehicle.

Leakage from septic tanks, cesspools and animal waste lagoons may enhance the movement of estrogen compounds into the soil as well as into surface water and groundwater. At sites where irrigation using 100% recycled water on such soils is practiced, monitoring systems must be in place to track the downward migration of these chemicals.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jconhyd.2014.07.006.

References


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