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Impacts of Environmental Colloids on the Transport of 17 **β**-estradiol in Intact Soil Cores

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Abstract

Estrogens such as 17-β estradiol (E2) are endocrine-disrupting compounds and can affect the reproductive systems of aquatic organisms. Therefore, it is important to understand the mechanisms of their transport in the environment. E2 and its daughter product estrone (E1) are both strongly adsorbed by soil organic matter and have relatively short half-lives. Reduced contact time with soil make transport of E2 and E1 in soil more likely. In this study, intact soil cores from three soils representing a range of particle size distribution, structure, and organic matter content were used to compare the transport of E2 with and without the presence of colloidal material fractionated from soil or swine manure. In chemical transport experiments conducted with undisturbed soil columns, E2 and E1 were measured both in solution and attached to suspended solids in column effluent. During the transport experiments, colloids passed through, carrying E2, all soils with the exception of the sandy soil. The presence of colloids decreased the first detection time of E2 in the aqueous phase, was correlated with greater peak E2 concentrations in the effluent of both loamy and clayey soils, but not through the sandy soil, and increased mass fractions of the E2 that was transported.

Keywords

estrone, macropore, estrogens, water dispersible colloids

Disciplines

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Comments

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ABSTRACT

Estrogens such as 17-β estradiol (E2) are endocrine-disrupting compounds and can affect the reproductive systems of aquatic organisms. Therefore, it is important to understand the mechanisms of their transport in the environment. E2 and its daughter product estrone (E1) are both strongly adsorbed by soil organic matter and have relatively short half-lives. Reduced contact time with soil make transport of E2 and E1 in soil more likely. In this study, intact soil cores from three soils representing a range of particle size distribution, structure, and organic matter content were used to compare the transport of E2 with and without the presence of colloidal material fractionated from soil or swine manure. In chemical transport experiments conducted with undisturbed soil columns, E2 and E1 were measured both in solution and attached to suspended solids in column effluent. During the transport experiments, colloids passed through, carrying E2, all soils with the exception of the sandy soil. The presence of colloids decreased the first detection time of E2 in the aqueous phase, was correlated with greater peak E2 concentrations in the effluent of both loamy and clayey soils, but not through the sandy soil, and increased mass fractions of the E2 that was transported.

Key indexing terms

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INTRODUCTION

There is growing awareness of the negative effects of estrogens and other endocrine disruptors on aquatic organisms (Oberdorster and Cheek 2000, Corcoran et al. 2010). This has led to concern about the environmental impacts of estrogenic hormones and other endocrine-disrupting chemicals (EDCs) and to an examination of the materials that contain them (e.g., animal manures and municipal biosolids). EDCs can have biological effects on aquatic organisms at very low concentrations. For example, E2 levels of 1 ng L^{-1} or less have been discovered to cause males of a certain fish species to produce vitellogenin, a protein associated with egg production (Purdom et al., 1994 and Hansen et al., 1998). Additionally, these chemicals have been shown to occur in waste water effluent and biosolids, apparently escaping degradation or removal during treatment (Aga, 2008). E2 is also present in livestock manure from concentrated animal feeding operations (CAFOs). Livestock manure is normally not given secondary treatment before land application (Aga, 2008; Lange et al., 2002). Thus, understanding the fate of estrogens is important for improving management of both biosolids and manure to maintain water quality and healthy aquatic ecosystems. A current area of inquiry is the co-transport of estrogens with colloids.

Colloids are often defined as having an effective diameter of < 1 - 2 µm and being larger than material that is truly dissolved. McCarthy and Zachara (1989) explored many of the possible factors in colloid-facilitated transport of contaminants in subsurface environments and identified many areas where research might be pursued. Sojitra et al. (1995) noted that the transport of hydrophobic organic contaminants can be linked to mobilized colloids. Some

examples of co-transport of organic contaminants with colloids include: Vinten and Yaron. (1983) who reported that dichlorodiphenyltrichloroethane (DDT) was transported through soil on suspended soil and organic particles, Seta and Karathanasis (1997) who reported that the herbicide atrazine could be transported by suspended soil colloids, and Villholth et al. (2000) who reported that the fungicide prochloraz could be transported by suspended particles. In most cases colloid-facilitated transport is considered possible if the compound of interest has a high K_d (partitioning coefficient) value, thus predicting limited aqueous-phase transport. Conditions that might make colloid-facilitated transport more likely include the possibility that the adsorbed phase is protected from degradation, sorption hysteresis (with slower desorption), and the presence of well-connected macropores in the soil. Prater (2012) reported that E2 degradation occurred primarily in the liquid phase and suggested that sorption may protect E2 from degradation. Desorption of E2 from soil was inferred to be slower than adsorption. Research in waste water treatment has indicated that E2, adsorbed to colloidal organic carbon, can be carried through the treatment process (Holbrook et al., 2003).

E2 and E1 exhibit a strong affinity to adsorb to soil organic matter (indexed by soil organic carbon, SOC); log K_{oc} (organic C normalized K_d) values are reported to be in the range of 2.3 to 4.2 for E2 and from 2.5 to 4.1 for E1 (Lee et al., 2003; Ying et al., 2003; Casey et al., 2005; Sangsupan et al., 2006; Sarma et al., 2008; Xie et al., 2008; Prater, 2012). Log K_{oc} values for E2 and E1 with suspended river colloids (3.95 for E2 and 4.18 for E1 (Liu et al., 2005)) are similar to log K_{oc} values measured with wastewater colloids (4.08 to 4.68 for E2 (Holbrook et al., 2003)) both of which are greater than those measured in soils.

The sorption of estrogens to soil and colloidal materials has been described as rapid (Lee et al., 2003; Casey et al., 2005; Prater, 2012), leading to the conclusion that transport of estrogens is only likely when macropores contribute to flow (leading to physical and chemical non-equilibrium conditions). The reason for this conclusion is two-fold. First, in the absence of colloids only rapidly moving soil solution with minimal soil contact would be capable of carrying the estrogens an appreciable distance before they were adsorbed and/or degraded. Second, it is likely that colloids can facilitate the transport of estrogens only in relatively large pores where the colloids themselves are less likely to be retained or filtered out by the soil material. These considerations make it unlikely that estrogens or similar compounds would be transported in significant quantities in unsaturated soils. Under varying conditions (column length, diameter, and flow rate), transport experiments with E2 in soil have produced different results. Relatively small soil columns used by Casey et al. (2005) (7-cm length) and Das et al. (2004) (10-cm length) resulted in significant transport of E2, while larger columns like those used by Casey et al. (2003) (15.2-cm length) and Fan et al. (2008) (30-cm length) resulted in little to no E2 transport.

Colloid transport has been reported to be more rapid than the transport of a conservative tracer such as Br^-. It is suggested by Poulsen et al. (2006) that this enhancement in transport velocity is a result of size exclusion, that is, the colloids are excluded from some of the smallest soil pores due to their size and thus do not travel in the slowest flowing water of small pores present in the soil. The presence of colloidal material offers a means for estrogen transport that allows for more rapid movement (via size exclusion) and protection from degradation (due to adsorption). Thus, the potential for colloid-facilitated transport of E2 poses a unique problem for

predicting arrival times and mass movement of chemicals like estrogens due to the as yet unpredictable interaction of E2 with colloids during transport.

Casey et al. (2005) reported that there was discrepancy between E2 sorption and degradation parameters measured with soils in static systems and those calculated from observations of E2 transport in repacked soil columns. Further, there was a large difference in arrival times of E2 in repacked soil columns and intact soil columns (Casey et al., 2005; Fan et al., 2008). The difference in E2 arrival times between repacked columns and intact soil columns has led to the inference that estrogen transport in soil could be enhanced by preferential flow or possibly colloid mediation. Both preferential flow (from soil aggregation and macropores) and the presence of suspended colloidal material could lead to enhanced E2 transport. Kjaer et al. (2007) noted a pronounced macropore flow effect on E2 and E1 transport to tile drains, suggesting that manure application to structured soils presented a risk to surface waters receiving tile drainage effluent. At least one field study has indicated that colloids may facilitate the transport of E2 through soil (Casey et al., 2008).

Previous studies of estrogen-soil interaction have included batch sorption (Lee et al. 2003), disturbed and undisturbed soil column experiments (Das et al., 2004; Fan et al., 2008), and field-scale studies (Kjaer et al., 2007; Casey et al., 2008). These investigations, however, did not directly explore the effect of a mobile colloidal phase on the mobility and transport of E2 and E1. This mobile solid phase may have a considerable impact on assessing the environmental risks of E2 application with soil amendments of manures or biosolids.

The aqueous solubilities of E2 and E1 are affected by pH, ionic strength, and temperature. At typical environmental pHs, E2 and E1 are expected to be nonionized since their pK_as are greater than 10 (Table 1). High ionic strength has the effect of coagulating organic compounds by "salting out," thus decreasing their solubility (Shareef et al., 2006). Due to the potential effects of ionic strength on the solubility of E2 and E1 and stability of the colloidal suspension, a solution of low ionic strength that mimics the soil solution phase is suited for transport experiments.

The present study was designed to investigate how suspended colloidal material might enhance estrogen transport. Colloidal material, operationally defined as soil and manure particles smaller than 1-μm equivalent settling diameter, has the potential to enhance estrogen transport in two ways: by providing a mechanism for rapid transport and by protecting the estrogens from biodegradation during transport (Prater, 2012). Thus colloids may facilitate estrogen transport to locations where desorption could occur, leading to adverse biological and ecological effects. Hildebrand et al. (2006) demonstrated that desorption of E2 from the soil can occur in water if enough contact time is allowed. Besides the effects of adsorption, desorption, degradation, and preferential flow, anaerobic conditions and low temperatures may also affect the fate and transport of E2 and E1 (Prater et al., 2015; Raman et al., 2001). In the experiments performed for this paper, temperature was controlled and oxygen was at ambient conditions.

Due to the concern for enhanced E2 transport via colloid facilitation, the objectives of this study were to determine if suspended colloids might contribute to or enhance the transport of E2

(affecting arrival time, peak delivery, or mass fraction transported) and its primary metabolite E1 in intact soil cores representing a range of textures and organic carbon contents.

MATERIALS AND METHODS

Sample Collection

Three Iowa soils with a range of particle size distributions and organic matter contents were included in this study. Clarion soils are well-drained, upland soils formed in glacial till under native prairie vegetation; they are fine-loamy, mixed, superactive, mesic Typic Hapludolls. Hanlon soils are well drained, having formed in loamy alluvium under native prairie vegetation on natural levees along streams; they are coarse-loamy, mixed, superactive, mesic Cumulic Hapludolls. Zook soils are poorly drained soils formed in silty and clayey alluvium, usually in flood plains; they are fine smectitic, mesic Cumulic Vertic Endoaquolls. From three sites in Story County, Iowa, nine undisturbed cores (10 cm diameter, 20 cm length) were collected for each of these soils for transport experiments. These three soils provided a particle size distribution from fine sandy loam to clay loam along with a broad spectrum of saturated hydraulic conductivity.

Colloidal Materials

Water-dispersible colloids (WDCs) were collected from bulk soil samples by dispersing the soil samples to create a suspension, using gentle agitation with distilled water (1:8 soil to solution ratio) and a rotary shaker at 15 rpm for 12 hours (Kjaergaard et al., 1995). Particles < 1-μm equivalent settling diameter (assuming a particle density, $\rho_s = 2.65$ g cm^{-3}) were collected

from the suspension by sedimentation and siphoning. The resulting colloidal suspensions were concentrated using porous ceramic filters and then freeze dried.

Swine manure was collected from a farrowing house at an Iowa State University research farm. Manure colloids (particles < 1-μm equivalent settling diameter, assuming $\rho_s = 1.4$ g cm^{-3}) were collected by shaking and sedimentation. The manure colloids were concentrated on 0.45-μm nylon filters and then freeze dried for later use.

Characterization

After collection and fractionation, the soil and colloidal materials were analyzed for physical and chemical properties, including particle size distribution by using the pipette method (Gee and Or, 2002), soil organic carbon content by total combustion (Nelson and Sommers, 1996), pH (Thomas, 1996), and cation exchange capacity (CEC) by using sodium saturation and ammonium acetate displacement (Sumner and Miller, 1996). The characterization results are summarized in Tables 2 and 3.

Chemicals

Both E1 and E2 were obtained from Sigma Aldrich (98% purity). Estrogen stock solutions were prepared using methanol as a co-solvent (less than 1%) and then diluted in 1 mM $CaBr_2$. The effect on sorption of methanol as a co-solvent in limited quantities has been shown to be negligible (Bouchard, 2003).

Column Studies

The saturated hydraulic conductivity of each core was measured (Klute and Dirksen, 1986), and for each soil, three cores with similar saturated hydraulic conductivity were selected for chemical transport experiments. Average hydraulic conductivity of the Clarion cores was 6.7 * 10^{-5} m s^{-1}, and it was 1.5 * 10^{-4} m s^{-1} for the Zook soil cores. Hanlon soil cores had to be treated differently from others. Initial transport experiments with Hanlon soil cores yielded little or no E2 or E1 in the effluent after 15 pore volumes. For this reason, a subsampling of the larger cores was conducted to allow measurements to be made. These subsampled cores were 4.3 cm in diameter and 10 cm in length.

The column studies were conducted with bromide (Br$^-$) as a conservative tracer in tandem with a pulse of E2, with or without WDCs from soil or manure. Bromide was measured by using a flow-through ion-selective electrode (Microelectrodes Inc., Bedford, New Hampshire). Operation of the Br$^-$ electrode was well above its detection limit of 10^{-5} M ($\pm2\%$). Colloids in the effluent from each column were measured in line using a spectrophotometer with a flow-through cell and measuring light attenuation at $\lambda = 400$ nm, calibrated with prepared colloidal suspensions. A fraction collector collected the effluent for estrogen analysis. Thus Br$^-$ and colloid concentrations could be measured in the effluent without sacrificing any of the sample needed for estrogen analysis. A diagram of the experimental apparatus is in Fig. 1.

Columns were saturated over a period of 24 h from the bottom up using an electrolyte solution (0.25 mM CaBr$_2$ and 0.75 mM CaCl$_2$). Flow was then initiated in the upward direction under a hydraulic gradient of about three in order to facilitate the removal of entrapped air. When

bubbling ceased at the top of the core, the flow direction was reversed to the downward flow direction, and the column was flushed with the resident solution for at least 10 pore volumes. A steady flow rate of 4 -- 5 mL min^{-1} was then established. After achieving steady flow, the fraction collector collected effluent aliquots of no greater than 0.1 pore volumes each. For the smaller Hanlon cores, fractions of less than 0.5 pore volumes were used. A Br$^-$ and E2 pulse, with or without soil or manure colloids, was then applied for approximately 2 pore volumes. The initial concentrations of E2 were 2 mg L^{-1} for the condition of no colloids and 4 mg L^{-1} when colloids were present. These concentrations were chosen to correspond to previous batch experiments of equilibrium sorption and kinetic sorption and degradation (Prater, 2012). The 4 mg L^{-1} with WDCs was chosen as it would result in a solution concentration of ~2 mg L^{-1} after equilibration with the sterile colloids and thus be similar to the solution concentration of E2 under the experimental conditions without colloidal materials present.

Before the transport experiments, both manure and soil colloids were autoclaved (60 min at 134°C), sonicated to re-suspend, and allowed to equilibrate with the E2 solution on a stir plate (24 h at 20°C). Initial colloid concentrations in the leaching suspensions were 3 g L^{-1} for soil-derived colloids (representing a "run-on" erosion condition in the range of suspended solids in run-off reported by Ginting and Mamo, 2006) and 0.3 g L^{-1} for manure-derived colloids (a smaller concentration of manure colloids was used because the amount of material that could be isolated was limited). The colloidal pulse was followed with at least 10 pore volumes of the resident solution (up to 50 pore volumes for the Hanlon cores).

Collected effluent fractions containing colloids were centrifuged (800 x g for 16 min) as soon as possible to separate solid and solution. E2 and E1 were measured in an aliquot of the solution using a pre-concentration and clean-up solid-phase extraction (SPE) step (C-18 LiChrolut EN) resulting with the analytes in a methanol and acetone solution (Xie et al., 2008). A gentle N_2 gas stream at 40°C was then used to evaporate the solvent before the analytes were dissolved in methanol for analysis.

The solid-phase portion of the centrifuged fraction was freeze dried and subsequently extracted with methanol (24 h on a shaker at 20°C) with a solid-to-solution ratio of 85 mL of methanol to each gram of solid to ensure reproducible recovery. In preliminary studies using this extraction method, we found that recovery of E2 and E1 adsorbed by the colloidal phases was 64% ± 3% (n = 5). To concentrate the sample for analysis, an aliquot of the methanol extract was evaporated under N_2 gas at 40°C to approximately 1 mL.

Concentrations of E2 and E1 in methanol were then determined by using high-performance liquid chromatography (HPLC) (Beckman System Gold). The HPLC instrumental parameters were: sample loop, 50 μL, flow rate, 1.5 mL min^{-1}; mobile phase, 45:55 acetonitrile:H_2O (pH ~4); column, C-18 reverse phase (Alltima); UV detector, $\lambda = 202$ nm. These parameters were similar to those used by Lee et al. (2003). The method detection limit was 2.5 μg L^{-1} in a 30 mL sample (defined as 3 times the background signal) and the limit of quantitation was 6 μg L^{-1} in a 30 mL sample (defined as the lowest standard used). HPLC analysis was deemed more efficient for our goals of measuring transport properties compared to slower, costlier methods with lower detection limits.

RESULTS AND DISCUSSION

The impact of preferential flow cannot be overstated when dealing with suspended colloids and rapidly adsorbing chemicals. In this study, a preliminary experiment using a packed sand column with no continuous cracks or channels showed that very few colloids were transported; most of the colloids added to the top of the column were retained in the top few centimeters of sand (data not shown). Further evidence of the role of preferential flow and soil structure in the transport of colloids and E2 came from the undisturbed Hanlon soil cores which exhibited very little pedogenic structure. The first 10-cm diameter Hanlon core investigated yielded almost no detectable E2 or E1 in the column effluent. In this coarse-textured, weakly structured soil with relatively high organic matter content, there was little transport of E2 or E1, whether colloids were present or not. We elaborate on this observation subsequently.

Clarion Loam

With only bromide and E2 added to the leaching solution, the Clarion soil core exhibited a significant delay in E2 and E1 breakthrough compared to the bromide (Br^-) tracer (Fig. 2). Effluent concentrations of both E2 and E1 peaked at approximately 1.5% of the added E2 concentration (0.015 relative concentration), and then displayed significant tailing, with E1 exhibiting a longer tail than E2. The presence of E1 indicated that some E2 had been transformed into E1 in the soil column. The delay in arrival and small peaks of both compounds indicated that sorption and degradation were occurring in the soil column. This observation is consistent with rapid sorption and degradation of E2 that were observed in batch studies with this same soil material (Prater, 2012).

In contrast, when either soil colloids or manure colloids were added to the leaching solution, the Clarion soil cores exhibited a much earlier arrival of E2 in the liquid phase relative to the Br$^-$ tracer (Table 4 and Figs. 3 and 4). The breakthrough of E2 associated with colloidal material was coincident with or earlier than the Br$^-$ tracer. Moreover, the peak liquid-phase E2 concentration in the Clarion core with soil colloids added approached 90% of the added E2 concentration (Fig. 3). With swine manure colloids, the peak liquid-phase E2 concentration approached 50% of the added E2 concentration (Fig. 4). In conjunction with this large solution-phase peak of E2, there were also colloid-associated (adsorbed) E2 peaks, showing that colloids can carry E2 with them through a soil column (Figs. 3 and 4). Colloids that were transported through the soil columns had adsorbed concentrations of E2 that were similar to those of the added adsorbed concentration (an indication that little desorption of E2 occurred). Some colloids, however, were retained by the soil column. We hypothesize that E2 originally associated with these retained colloids made some contribution to the prolonged tailing of both E2 and E1 (through desorption).

We calculated the mass fractions of E2 that were transported through the columns over ~12 pore volumes (Table 5; see also Supplemental Information for graphical displays). The mass fractions of E2 transported in solution form were higher in the Clarion columns with added colloids than in the column without colloids added (Table 5). However, in the Clarion column with only Br$^-$ and E2 added there was a greater mass fraction of E1 (as a fraction of the added E2) transported than E2. It is likely that this trend toward more E2 being transported in solution, both as expressed in peak concentration eluted and mass fraction eluted, is due to desorption of E2 from the added colloidal material. E2 contributed into the solution phase from colloids was likely from colloids retained by the soil column as suggested by the negligible difference

between E2 concentrations adsorbed on *eluted* colloids and E2 concentrations adsorbed on *added* colloids.

Hanlon Sandy Loam

As noted above, the large (10-cm diameter) Hanlon cores had little pedogenic structure or macroporosity, leading to strong retention of both E2 and colloids during the transport experiments. To make comparisons with transport phenomena in the Clarion and Zook soil columns, we reduced the size of the Hanlon cores for the transport experiments. With only Br^- and E2 added to the leaching solution in a Hanlon soil core, a modest peak of E2 was eluted with a maximum concentration of 7% of the initial E2 concentration (Fig. 5). This experimental condition also yielded a delayed and very broad E1 peak of an amplitude similar to that of the E2 peak. The first detection times of E2 and E1 were significantly delayed behind the Br^- tracer by approximately three pore volumes.

In the Hanlon soil core with soil colloids added to the leaching solution (Fig. 6), E2 appeared in the effluent earlier than in the previous case with no colloids (Fig. 5). With soil colloids present, E2 was first detected at 0.8 pore volumes, the peak E2 concentration was less than two pore volumes out of phase with the peak Br^- concentration, and the peak E2 concentration approached 20% of the initial concentration (Fig. 6). Similar to the Hanlon core with only Br^- and E2 added, the Hanlon core with soil colloids added to the leaching solution exhibited a very broad E1 peak, but with much more extensive tailing. Only a small amount of colloidal material was transported through this column, and so a very small amount of E2 was transported in the adsorbed phase. Compared to the no-colloids case there was some

enhancement in transport of E2 in the presence of soil colloids. The time of first detection was earlier (Table 4) and the mass fraction transported as E2 in solution was greater (Table 5 and Supplemental Information).

In the Hanlon core with swine manure colloids in the leaching solution, there was no measurable E2 in the effluent and only a small peak for E1 that was significantly delayed behind the Br^- tracer (Fig. 7). We attribute the lack of E2 transport, colloid transport, and colloid facilitated transport of E2 to the core's weakly expressed soil structure and few if any macropores. It is likely that the lack of rapid flow paths would allow more soil contact time and lead to more sorption and degradation of both E2 and E1 (no chromatography peak for E1 degradation product, estriol, was observed). If there were no continuous macropores present, then it is likely that the swine manure colloids would be retained in the pores of the upper portion of this soil, similar to the results of the preliminary study using a sand column (noted earlier).

Zook Clay

In the Zook soil core with only Br^- and E2 added to the leaching solution, the first breakthrough of E2 was similar to that of Br^- (Fig. 8). Similarly in the columns with colloids in the suspension, E2 was first eluted at nearly the same time as Br^- (Fig. 9 and 10, Table 4). In the columns with colloids added, there was a greater peak E2 concentration and mass fraction of E2 in solution transported (Table 5 and Figs. 8, 9, and 10).

The three Zook columns represented the most physically similar set of soil columns in this study (similar Br^- first detection pore volumes and similar pore volumes of Br^- at $C_r = 0.5$), so some additional specific observations can be made (Table 4). The Zook column with only Br^-

and E2 added to the solution differed from the column with Br⁻, E2, and soil WDCs added, indicating that there was some enhancement of transport by soil WDCs (Figs. 8 and 9). This enhancement was in the form of a three-fold increase in the peak E2 solution concentration. There was not a large difference in the eluted E1 concentrations among the columns. In addition to enhanced transport in the liquid phase, the colloids themselves carried E2 through the column. Moreover, the mass fraction of E2 transported in the solution phase in the column with soil colloids added was nearly four times larger than it was in the column carrying E2 without added colloids (Table 5). There was also an indication of enhanced E2 transport in the Zook column with added swine manure colloids in the leaching solution. In that column, the peak concentration of effluent E2 was twice that of the column with only Br⁻ and E2 added (Figs. 8 and 10). Also in that column, the mass fraction of E2 transported in solution was almost three times greater than in the column without added colloids (Table 5). Taken together, the three observations of earlier times of first detection, the larger mass fraction of solution E2 transported, and the fact that colloids were transported with adsorbed E2, suggested that suspended colloidal material had a profound impact on E2 transport in the Zook soil columns.

Comparisons Across Soils

Comparisons across all soils showed some consistent trends. In soil cores with only Br⁻ and E2 added, there was a significant delay in E2 and E1 compared to the Br⁻ tracer (Figs. 2, 5, and 8; Table 4). In all soils, both E2 and E1 also exhibited smaller peak concentrations when added in the absence of added colloids than when added with colloids. Additionally, in all of the soils there was a larger mass fraction of E2 transported in the solution phase when colloids were

added and transported (Table 4-5). The exception to this observation was the Hanlon soil column with swine manure colloids added to the solution, which resulted in no E2 or measurable colloids in the eluent.

In the mass fraction assessment, soil colloids generally promoted greater transport of E2 than did swine manure colloids. This is a direct result of a greater mass fraction of the added soil colloids being transported than manure colloids, as the E2 adsorbed-phase concentrations on the eluted colloids were very similar to the initial E2 adsorbed-phase concentrations on respective colloids (an indication that very little desorption of E2 from transported colloidal materials occurred under these experimental conditions, data not shown). Additionally no E1 was detected on transported colloids. The difference in the mass fraction of E2 transported while adsorbed on soil colloids versus swine manure colloids may be due to several factors, e.g., the size of the suspended particles, the density of the colloidal materials, and the mineralogy and charge concentration of the soil WDCs.

The presence of suspended colloids enhanced overall transport of E2, but it also increased soluble E2 transport. We hypothesize that colloids deposited on pore walls became a source of E2. This phenomenon of colloid transport wherein deposited colloids become a source of a chemical being transported was also invoked by Albarran et al. (2011) in a study of strontium transport on bentonite colloids in a constructed granite fracture. However, in contrast to the results of Albarran et al. (2011), the presence of colloids in soils in this case decreased the time of first detection and increased the relative concentration of the applied chemical emerging from the column at its peak by a factor of 20 to 50. The possibility that adsorbed colloids were a

source of E2 transported in the solution is further corroborated by a photograph showing deposited colloids lining a macropore in a Clarion soil column (presented in the Supplemental Material).

The coating of soil macropores by transported colloidal materials is a well-known pedological process. Once deposited, E2-containing colloids may release (desorb) E2 as the soil solution concentration of E2 declines by sorption, degradation, and transport processes. Hildebrand et al. (2006) also noted that estrogens such as E2 and E1 could be desorbed from soil and sediment materials. Thus, deposited E2-containing colloids may buffer the solution concentration in macropores by desorbing E2 and promoting soluble E2 transport in the faster portion of the soil flow regime.

The enhancement of E2 transport due to the presence of colloidal material is illustrated in the data in Table 4. In the soil columns with only Br^- and E2 added to the leaching solution, there was a distinct delay in the time of first detection of E2 versus Br^-. The delay in first detection of E2 was least in the Zook soil cores. Across all soil columns, the first detection of Br^- was similar (with the exception of Hanlon columns due to their high flow rate to pore volume ratio; see Table 4). In contrast to the soil columns without colloids added to the solution, all of the soil columns where colloids were added and eluted, Br^- and E2 were detected at nearly the same time. A further indication of the role of suspended colloid material in the early arrival of E2 is suggested by the similar times of first detection of the colloidal materials relative to the first detection of E2 and Br^- in the Clarion and Zook cores. Moreover, if the pore volume at one-half relative concentration (C_r) is used as a proxy for preferential flow (values < 1 indicate

preferential flow), E2 transport was enhanced by the presence of swine manure colloids in a Clarion core even without an indication of preferential flow (Table 4).

Colloid transport in soil has long been recognized as an important soil process, but only in recent decades has it been considered as a process for contaminant movement and co-transport. The presence of colloids in soils is not an environmental problem *per se*, despite their capability to facilitate contaminant transport. Colloids and their movement in a soil profile can contribute to more uniform distributions of nutrients and organic matter with depth. In the present study, the presence of colloids with adsorbed E2 under saturated flow conditions did lead to greater transport of estrogen molecules in columns of structured soil but not in columns of sandy, poorly structured soil. Within-soil transport of colloids might be reduced by effective pH management and stabilization of near-surface soil aggregates. But to limit contaminant transport from soil either by overland transport or by leaching, it is also important to reduce erosion and to manage manure application to reduce colloid-facilitated transport of E2 or other contaminants found in manure.

This work shows that the expectations one has for solutes do not necessarily hold in the context of colloid transport. For the included sandy soil, Hanlon, the first detection of E2, the first detection of Br^-, the first detection of WDC, and the peak of WDC-E2 were all delayed compared with the other soils. These observations were likely related to a lack of macropore pore continuity in the poorly structured Hanlon cores as compared to the Clarion and Zook soil cores. With macropores present in the other two soil types used, colloids appeared to enhance miscible chemical transport. Colloid-facilitated transport may also be expressed as increased, but delayed,

miscible transport when contaminant molecules are desorbed from colloids that have been retained by the soil.

The results of this study point to a possible link between colloids and enhanced transport as suggested by Arnon et al. (2008) upon their finding that E2 moved beyond what might be expected for miscible transport. Thompson et al. 2009 also pointed to colloids as an explanation for anomalous E2 transport. Additionally the results of this work showed similar behaviors of E2 without colloids to previous similar experiments indicating the importance of macropores as exhibited in the Clarion and Zook cores in this study contrasted with the Hanlon cores (Casey et al., 2005; Fan et al., 2008). Kjaer et al. (2007) also noted a macropore effect on E2 transport.

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Table 1. Chemical structure and properties of 17 β-estradiol and estrone. The pK_a is the pH at which 50% of the molecules in solution are ionized. Log K_{ow} is the log of the octanol-water partition coefficient.

	17β-Estradiol	Estrone
Acronym	E2	E1
Structure	##	##
Molecular mass (g mol^{-1})	272.4	270.4
Water solubility (mg L^{-1})	13 - 21.6	2.1 - 13
pK_a	10.2	10.4
Log K_{ow}	3.1 - 4.0	3.1 - 3.4

Table 2. Soil physical and chemical characteristics.

	Hanlon	Clarion	Zook
	sandy loam	loam	clay
pH	6.9	4.7	6.0
Sand (g kg^{-1})	724	445	219
Silt (g kg^{-1})	204	379	382
Clay (g kg^{-1})	72	176	400
Coarse silt (g kg^{-1})	137	212	132
Fine silt (g kg^{-1})	67	167	250
Coarse clay (g kg^{-1} of clay)	795	755	591
Fine clay (g kg^{-1} of clay)	205	245	409
CEC (cmol kg^{-1})	12.3	20.1	58.9
Total carbon (g kg^{-1})	7.2	18.4	30.1
Total nitrogen (g kg^{-1})	1.0	1.8	2.7
C:N (ratio)	7.3	10.0	11.0

Table 3. Organic C and N concentrations of water-dispersible colloidal materials (WDCs).

	Hanlon WDC	Clarion WDC	Zook WDC	Manure WDC
Total C (g kg^{-1})	38.9	55.9	38.1	346.0
Total N (g kg^{-1})	5.3	6.4	4.3	63.2
C:N	7.4	8.7	9.0	5.5

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Table 4. Chemical transport experiment pore volumes (PV) of arrival, peak (maximum), and relative concentration equal to 50% ($C_r = 0.5$). Data for bromide (Br-), 17 β-estradiol (E2), water-dispersible swine manure (SM) colloids (WDC), and soil WDC.

	Conditions	First Detection E2	First Detection Br^-	Br^- C_r = 0.5	First Detection WDC	Peak E2 WDC
		---------------------------- PV ----------------------------				
Clarion	Br^- & E2	2.23	0.06	0.74	-	-
	Br^-, E2, & soil WDC	0.07	0.09	0.45	0.01	1.59
	Br^-, E2, & SM WDC	0.06	0.04	1.05	0.04	1.76
Hanlon	Br^-, & E2	2.8	0.28[*]	0.96	-	-
	Br^-, E2, & soil WDC	0.79	0.25[*]	0.85	0.37	4.7
	Br^-, E2, & SM WDC	-	0.31[*]	0.69	-	-
Zook	Br- & E2	0.15	0.06	0.43	-	-
	Br-, E2, & soil WDC	0.07	0.09	0.49	0.07	2.05
	Br-, E2, & SM WDC	0.06	0.08	0.52	0.06	1.42

Values with an asterisk ([*]) differ from others due to the higher ratio of flux to pore volume as a result of the smaller core size used for Hanlon soil columns.

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Table 5. Mass fraction of 17 β-estradiol (E2) eluted at 12 pore volumes as E2 and estrone (E1) in solution and adsorbed by water-dispersible colloids (WDC).

	Conditions	⎯	⎯	⎯⎯	⎯
		------------------12 Pore Volumes-------------------			
Clarion	Br⁻, and E2	0.01	0.03	-	0.95
	Br-, E2, and soil WDC	0.78	0.15	0.12	0.95
	Br⁻, E2 and swine manure WDC	0.40	0.16	0.08	0.97
Hanlon	Br⁻ and E2	0.11	0.90	-	0.99
	Br⁻, E2, and soil WDC	0.30	0.14	*	1.03
	Br⁻, E2 and swine manure WDC	-	0.01	-	1.01
Zook	Br⁻ and E2	0.08	0.13	-	1.01
	Br⁻, E2, and soil WDC	0.23	0.12	0.11	1.02
	Br⁻, E2 and swine manure WDC	0.21	0.16	0.09	1.00

*E2 is the total E2 eluted in the aqueous phase, E1 is the total E1 eluted in the aqueous phase, E2-WDC is the total E2 eluted attached to colloids, $E2_i$ is the total aqueous E2 added, and E2-WDC$_i$ is the total E2 attached to colloids added. Br^- is the total bromide eluted, and Br^-_i is the total bromide added. The * indicates that E2 was detected with the colloids, but the mass fraction was < 0.01. The -- indicates none detected.
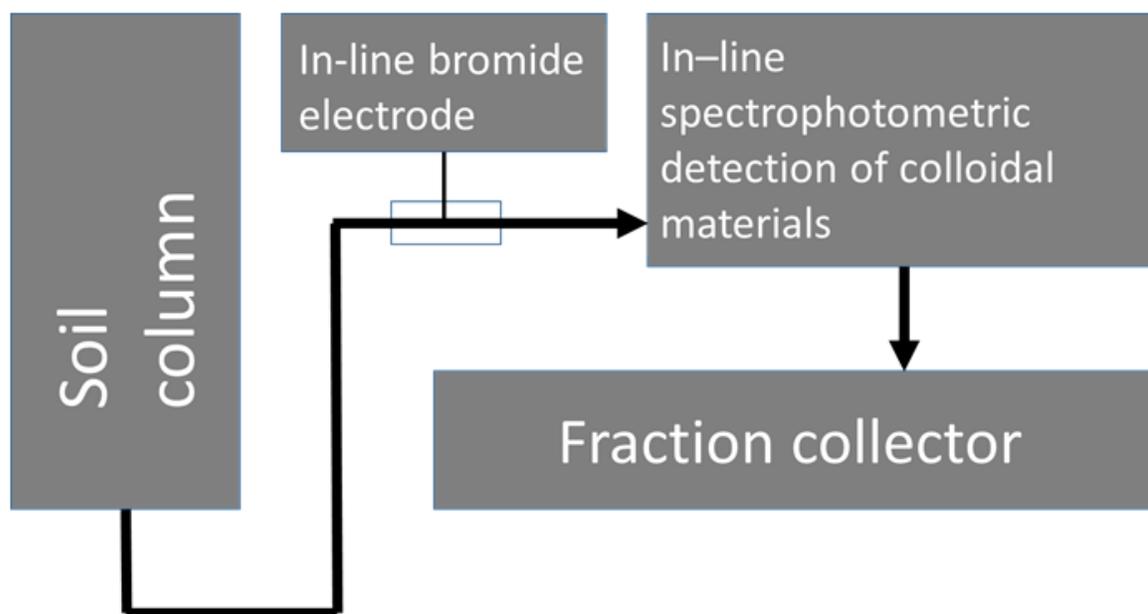
Figure 1. Column transport experimental set-up.
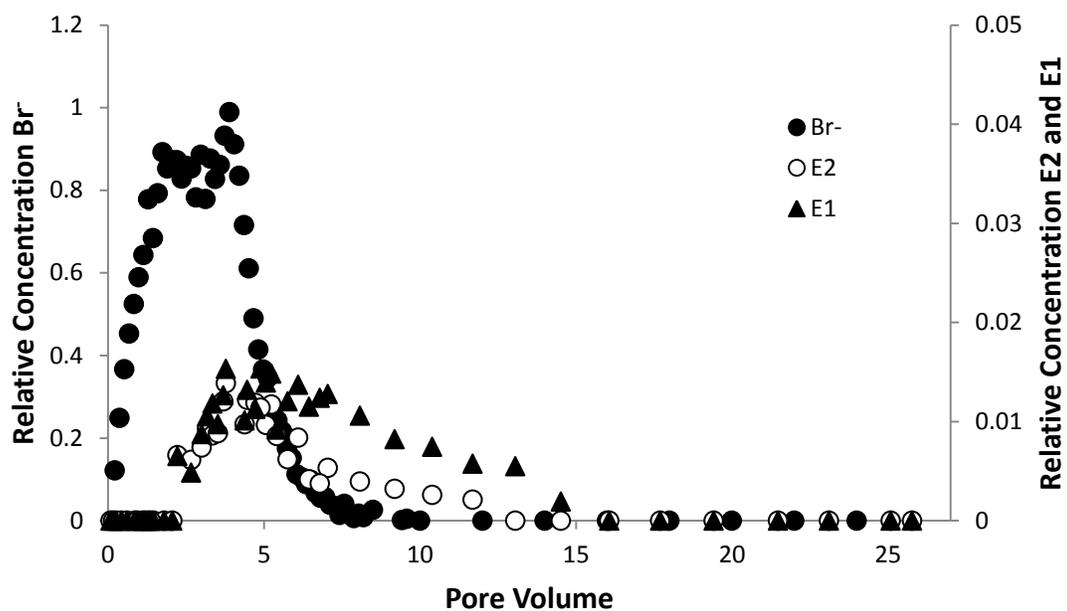
Figure 2. Clarion soil column breakthrough curves for bromide (Br⁻), 17 β-estradiol (E2), and estrone (E1) in the effluent.
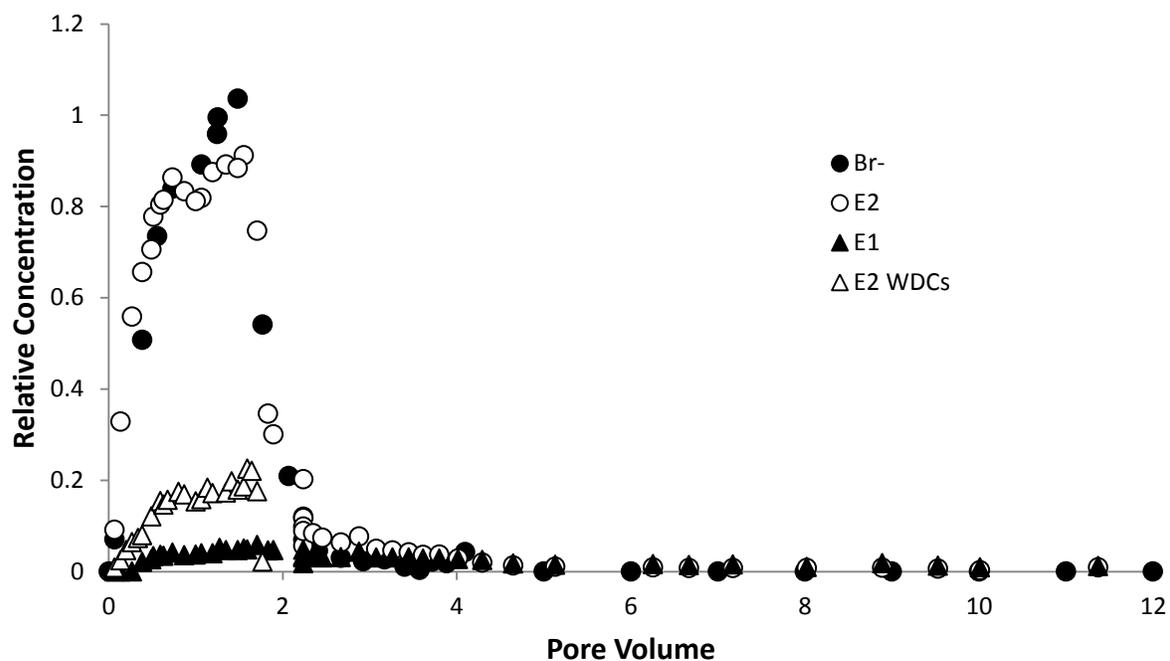
Figure 3. Clarion soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible soil colloids (WDCs).
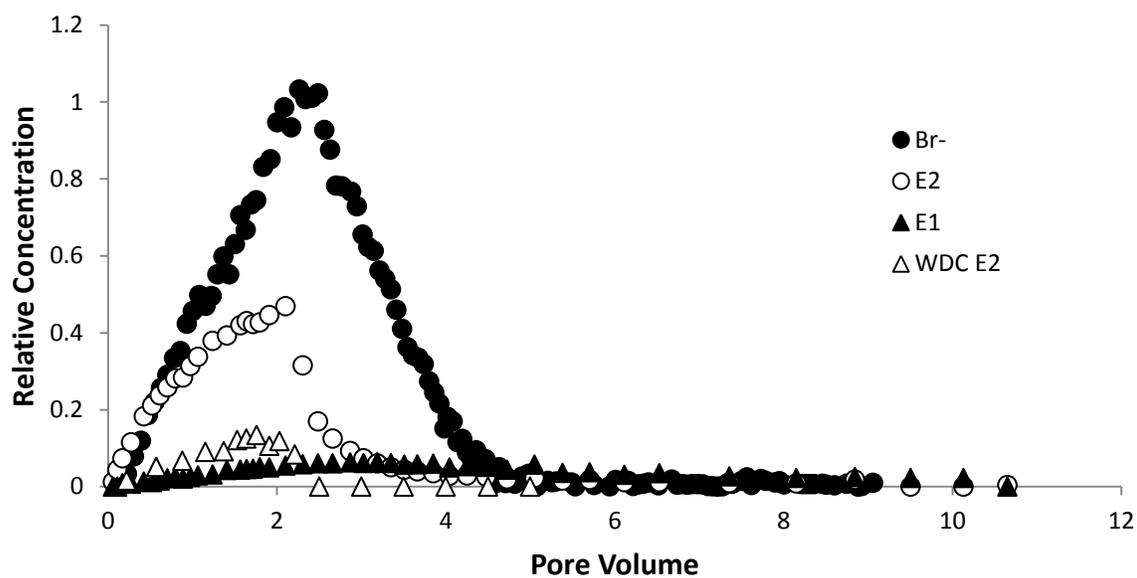
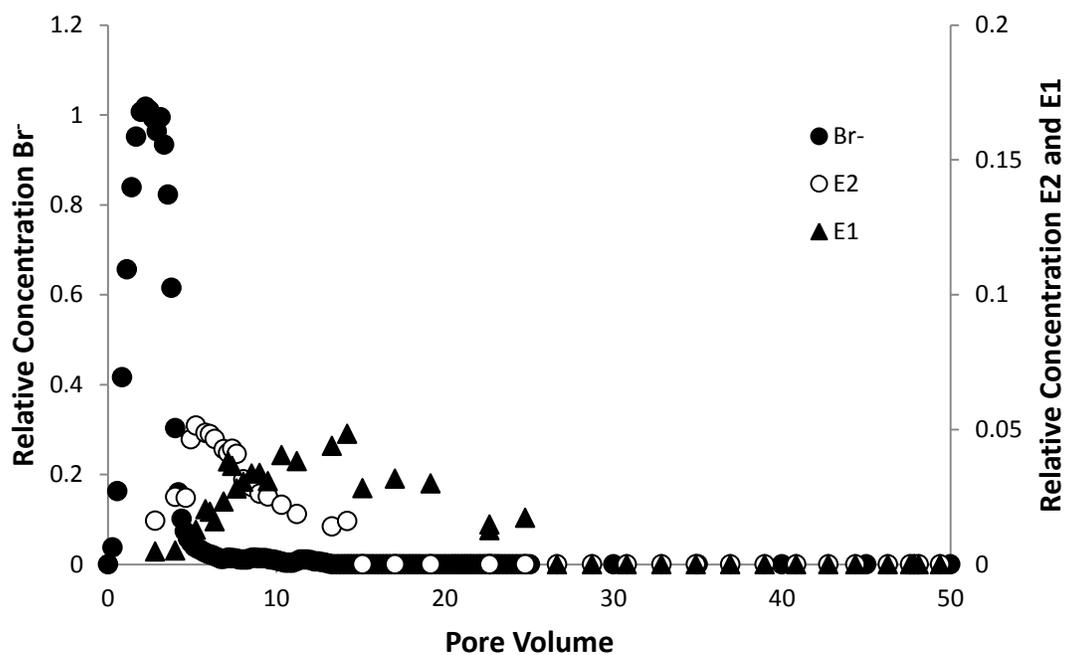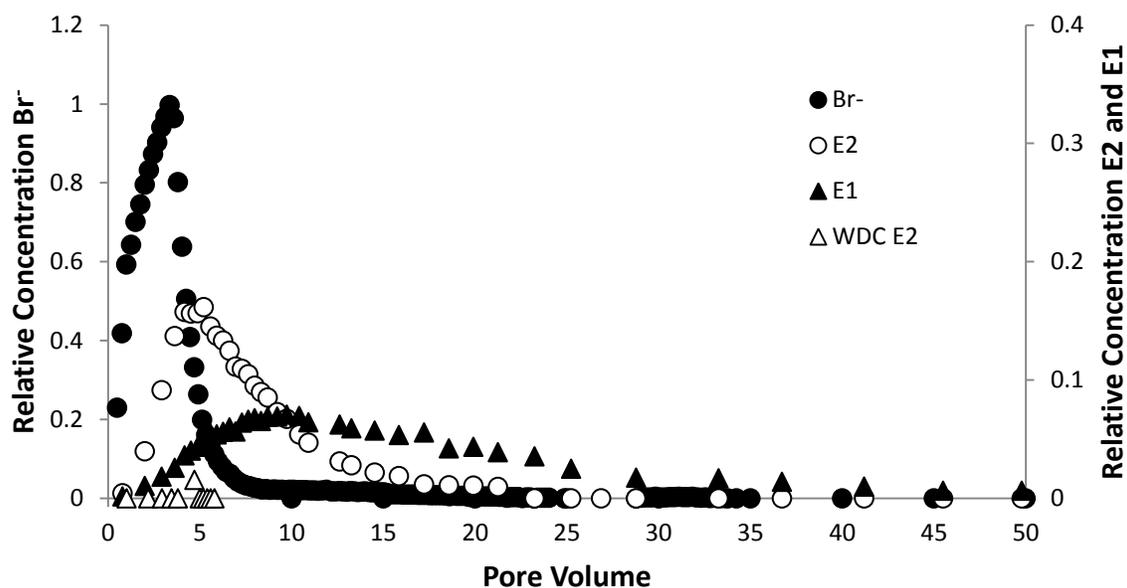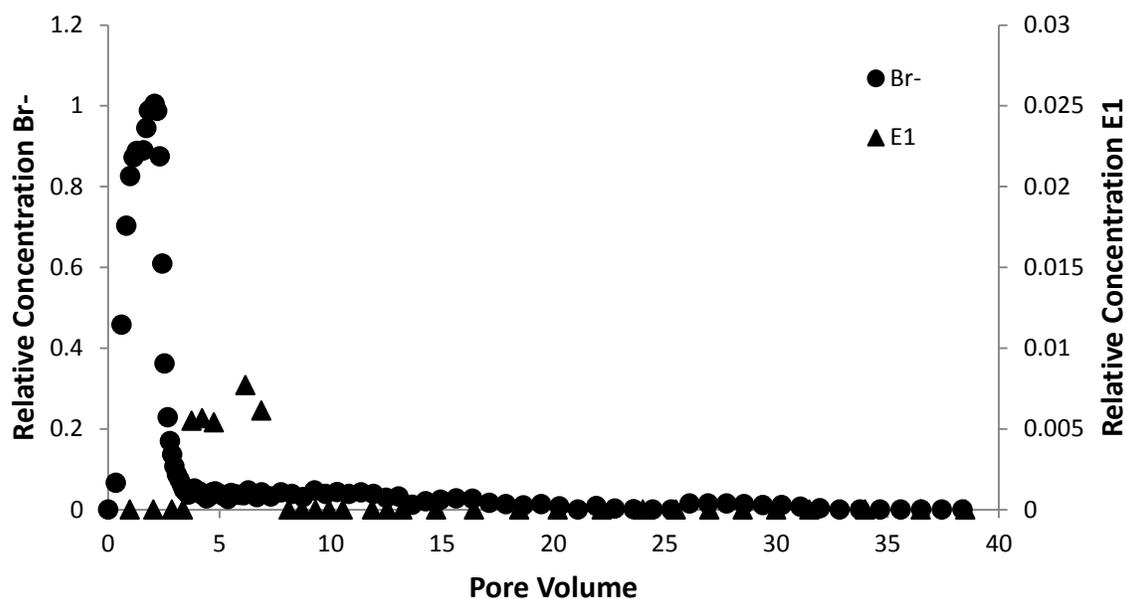**Figure 4. Clarion soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible swine manure colloids (WDCs).**
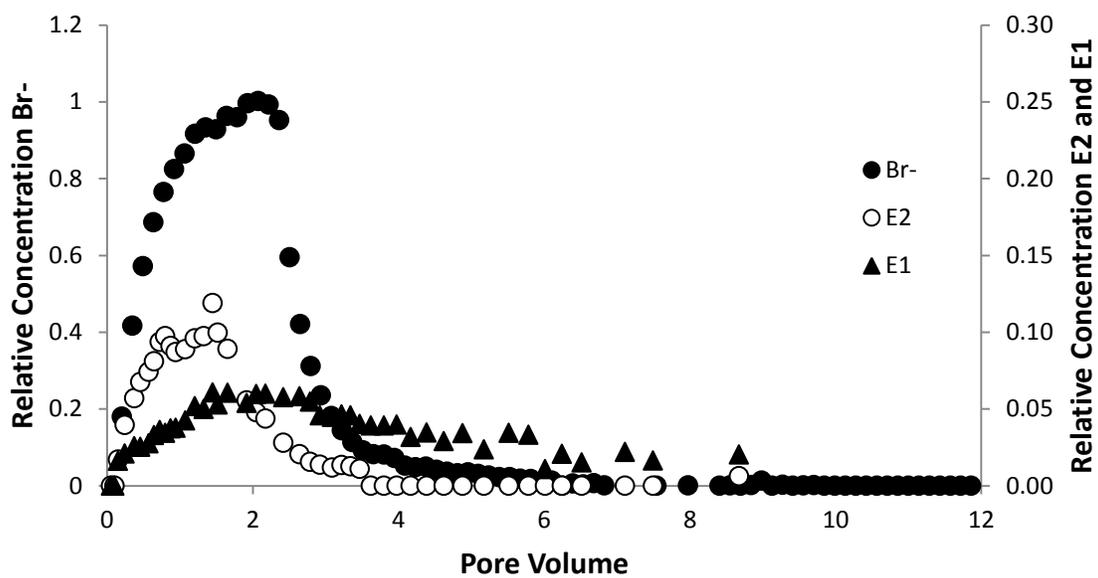
Figure 5. Hanlon soil column breakthrough curves for bromide (Br⁻), 17 β-estradiol (E2), and estrone (E1) in the effluent.

Figure 6. Hanlon soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible soil colloids (WDCs).

Figure 7. Hanlon soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible swine manure colloids (WDCs).

Figure 8. Zook soil column breakthrough curves for bromide (Br⁻), 17 β-estradiol (E2), and estrone (E1) in the effluent.
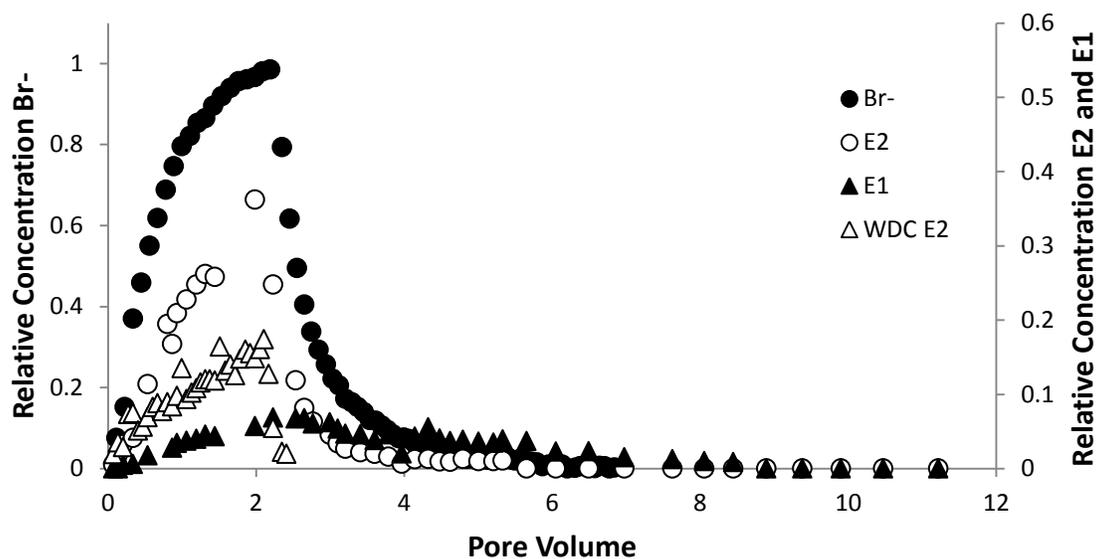
Figure 9. Zook soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible soil colloids (WDCs).
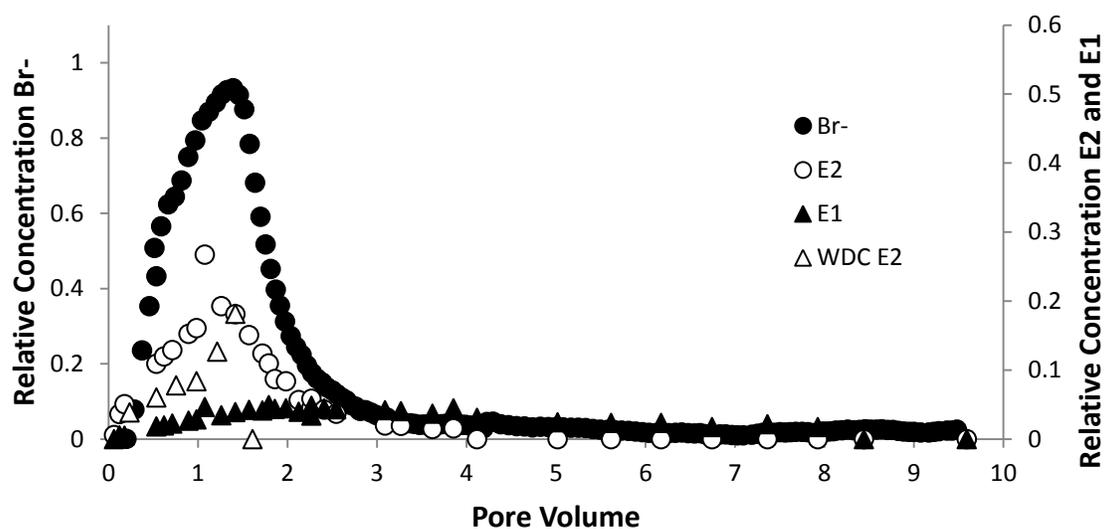
Figure 10. Zook soil column breakthrough curves for bromide (Br⁻), solution-phase 17 β-estradiol (E2) and estrone (E1), and E2 associated with water-dispersible swine manure colloids (WDCs).