Removal and attenuation of sewage effluent combined tracer signals of phosphorus, caffeine and saccharin in soil

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A B S T R A C T

Contaminants in septic tank effluent (STE) are expected to be removed by the soil system before discharging to the environment. However, potential contaminants such as phosphorus (P), caffeine and artificial sweeteners do find their way to watercourses impacting aquatic eco systems. In this study, the attenuation of STE P, caffeine and saccharin were investigated in untreated soil and in soil with reduced microbial activity, in aqueous solutions and in the complex matrix of STE. Time series sorption and desorption experiments using batch equilibrium and a column experiment of STE P attenuation were conducted. The results revealed that the soil distribution coefficients ($K_d$) were: P 81.57 $>$ caffeine 22.16 $>$ saccharin 5.98 cm$^3$/g, suggesting greater soil affinity to P adsorption. The data revealed that 80% of saccharin and 33% of caffeine attenuation was associated with microbial activities rather than adsorption processes. However, a complete removal of saccharin and caffeine did not occur during the equilibration period, suggesting their leaching potential. The dominant mechanism of P attenuation was adsorption (chemical and physical), yielding P retention of $>73\%$ and 35% for P in aqueous solution and in STE matrix, respectively, for batch equilibrium. The soil in the column acted as effluent P sink retaining 125 $\mu$g P/g soil of effluent P. The attenuation of P, caffeine and saccharin in the aqueous solution was greater than in STE, suggesting that the complex composition of STE reduced soil adsorption ability, and that other substances present in STE may be competing for soil binding sites. The data revealed that caffeine and P had similarities in the interaction with soils and thus caffeine may be considered as a STE tracer of anthropogenic source of P in receiving waters.

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1. Introduction

Small point sources such as septic tanks (STs) contribute to stream microbial and nutrient enrichment of receiving waters through the persistent direct discharge of effluents or diffusely through soil soakaway discharges (Dudley and May, 2007; Withers et al., 2014; Ockenden et al., 2014). The release of contaminants and their metabolites from septic tanks to surface waters poses potentially serious localised risks to human health and stream ecology. Streams are increasingly contaminated with pharmaceutical products, caffeine, artificial sweeteners, detergents and other man-made compounds (Haggard et al., 2006; Richards et al., 2015) most of which are not or only partially degradable by septic tank systems, nor by the more advanced wastewater treatment plants (WWTP) (Andreozzi et al., 2003; Ying et al., 2009). The transport and the reduction of these compounds may occur through dilution, hydrolysis, sorption and biodegradation which may reduce their toxicity to the environment (Gill et al., 2009a; Lin et al., 2006, 2010). For septic tank effluent (STE), these processes are expected to attenuate potentially harmful substances from the effluent within soil soakaway systems that constitute the final stage of household waste treatment. However, the ability of many soil systems to remove pollutants becomes increasingly exhausted with time (Jordan et al., 2005), or where soil conditions are not suitable (Withers et al., 2011; Gill et al., 2009a; 2009b). For many contaminants, the adsorption capacity diminishes as soil particles become saturated with contaminants causing them to spread further away

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from the soakaway and eventually reaching ground and surface waters (Guigard et al., 1996; Robertson et al., 1998, Robertson, 2008).

Little is known about the occurrence, extent, transport, and fate of many synthetic organic chemicals after their release. Only a few analytical methods have been developed that are capable of detecting these contaminants at the low concentrations that might be present in soil and aquatic environments (Barnes et al., 2004; Gros et al., 2006; Fatta et al., 2007). Their presence in the environment is of concern as their potential to cause harm to the environment is poorly understood. However, the presence of such contaminants in soil solutions and surface waters can also show the presence and migration of other potential key pollutants associated with wastewater discharge sources. Provided environmental behaviours of certain contaminants are known (e.g. degradation, sorption and desorption) they may be used as tracers for the presence of other chemicals that are more difficult to detect, or come from multiple environmental sources.

Phosphorus and trace organic molecules of human origin (caffeine and saccharin) found normally in STE discharges were selected to investigate their leaching verses attenuation behaviour in soil. Phosphorus was selected as it is a major pollutant constituent of STE discharges, which is present in high concentrations from 1 to 32 mg/l (Lowe et al., 2009; Withers et al., 2011; Richards et al., 2016a) and is of concern due to its role in surface water eutrophication. Saturation of adsorption sites of soakaway soils will also lead to plume migration, progressively toward ground and surface waters (Robertson et al., 1998, Robertson, 2008). In addition to P, the environmental behaviour in soil of two potential effluent tracer compounds was investigated. Caffeine was investigated due to the worldwide anthropogenic source, found in coffee, tea, soft drinks, medications and toothpastes. Caffeine is a moderately water soluble alkalioid (N-containing substance) of formula C8H10N4O2, extracted from plants (e.g. cacao, tea and coffee), and has the effects of temporarily preventing/reducing drowsiness and restoring alertness (Gürü and İçen, 2004). Caffeine is often excreted undegraded from the human body and is present in domestic STE at concentrations from 3 to 391 µg/l (Conn, 2008; Gill et al., 2009a; Richards et al., 2016b) due to its constant wide consumption in large quantities. The presence of caffeine in surface waters is directly indicative of human source and should indicate the source of pollutants (Buerg et al., 2003). Sotelo et al. (2012) studied the adsorption of caffeine solution to activated carbon and found its adsorption capacity was 270 mg/g, but its sorption by soil is not fully understood.

The globally abundant artificial sweetener saccharin was also investigated. Artificial sweeteners are often substitute sugars in processed food products to reduce calorie intake for dietary controls. Saccharin (C7H5NO3S) is 300 times as sweet as table sugar (Scheuer et al., 2009) and, as with all artificial sweeteners compounds, saccharin does not hydrolyse as do carbohydrates and is excreted without degradation by humans. Artificial sweeteners constitute an integral part of STE discharges with various concentrations from 15 to 51 µg/l (Richards et al., 2016b; Robertson et al., 2013) and have been detected in surface and ground waters (Buerge et al., 2009; Scheurer et al., 2009; Robertson et al., 2013).

Very few studies have been conducted on the attenuation of these compounds through soil using sewage effluent. Thus the factors controlling the migration of combined signals of tracer chemicals (e.g. caffeine, saccharin) alongside that of major environmental pollutants such as P, are not well understood. This knowledge is required to facilitate source tracing and apportionment from multiple sources in catchments. In this work the behaviour and the attenuation of P, caffeine and saccharin in soil was investigated through soil-solution batch equilibration comparing between simple aqueous solutions and the actual STE matrix. The STE was also used in a column experiment to further evaluate P attenuation in soil. The objectives were: 1) to determine the natural attenuation and the sorption of these compounds by a test soil; 2) to investigate biogeochemical processes of the attenuation (biotic or abiotic); 3) to determine real STE P behaviour in soil compared to aqueous solutions; 4) to investigate the potential of caffeine and saccharin to behave as tracers for STE discharges.

2. Materials and methods

2.1. Soil treatment and characterisation

Subsoil (10–30 cm depth) was collected from near Dunede, UK (NO307327) and used in sorption and column experiments. Soil was sieved (2 mm) then stored at 4 °C. A subsample of the soil was air-dried and characterised for pH (Hanna pH 210 m), moisture content, carbon and nitrogen content (Thermo-Finnigan, Flash EA 1112 CN analyser, Naples, Italy), particle size (Mastersizer 2000, Malvern, UK) and soil phosphorus (Olsen, Morgan, total and oxalate extractable phosphate tests). A fraction of the fresh soil was subjected to a constant stream of ozone flow for 4 h to reduce microorganism populations (Ravat et al., 2010; Ebihara et al., 2012) with minimum change to soil structure with the intention to compare abiotic and biotic attenuation in untreated soil to behaviour in a soil where microbial activity was reduced. We chose this method recognising that no soil sterilisation process is perfect for sorption and leaching studies, particularly for nutrients. Bacterial total viable counts (TVC) for ozone treated and untreated soil’s solutions were performed using a spread plating technique onto nutrient agar plates (Standard Methods for Examination of water and Wastewater, 1999). Plates were incubated at 37 °C for 24 h then bacterial colonies were detected and counted as colony forming units (CFU) in 100 ml.

2.2. Septic tank effluent and reagents for batch equilibrium experiments

Septic tank effluent was collected from an 11 year old concrete tank serving 3 people that discharged onto a soil bed. Effluent was collected at the tank exit before the soil soakaway. The effluent was filtered through a pre-washed GF/F (0.7 µm) filter stacked onto a 0.45 µm filter paper. The filtered effluent was used for batch equilibrium and column experiments. Phosphate (KH2PO4), caffeine and saccharin, (purity >98%) compounds were obtained from Sigma Aldrich (Dorset, UK). A stock solution was made for each compound by dissolving the appropriate amount in calcium chloride electrolyte solution (0.01 M) to give concentrations that equal mean concentrations found in STE discharges (Richards et al., 2016a) of approximately 10.0 mg/l for soluble reactive P (SRP) and 0.6 mg/l for caffeine and saccharin.

Sorption and desorption batch equilibrium experiments for effluent and aqueous solutions were conducted separately according to OECD guidelines for the testing of chemicals (2000), in triplicates at room temperature using sterilised glassware (450 °C for 18 h). For each compound, time series attenuation and sorption experiments were conducted in aqueous solution using untreated soil to investigate biotic plus abiotic processes (both sorption and biodegradation) and ozone treated soil to compare dominantly abiotic processes (principally sorption). An additional batch equilibrium experiment was conducted on untreated soil using the effluent matrix composition. Soil and effluent mixtures (1:30 dry matter to solution ratio) were shaken on an orbital shaker (120 rpm) at room temperature and equilibrated for multiple time
points up to 24 h in the dark. Soil leaching in CaCl₂ electrolyte (0.01 M, pH 5.5) and blanks (no soil) for controls were also included in the experiments. The aqueous solution samples were taken off the orbital shaker at 0.5, 1, 1.5, 3, 6, 10, 16, 20 and 24 h time points during the equilibration period and filtered using pre-heated (450 °C) GF/F filter papers. Effluent samples were taken off the orbital shaker at 3, 6, 16, 20 and 24 h time points before filtering.

Subsequently desorption experiments were conducted on the soils that had 24 h contact with either aqueous solution or effluents. Soil was recovered by centrifuging and removing effluent and aqueous phase as recommended by OECD, 2000. The volume of the removed effluent and aqueous phase from the vessels was replaced by adding an equivalent volume of CaCl₂ (0.01 M) without the test substances to the soil. Following equilibration at 120 rpm for 24 h, the aqueous solution was recovered and analysed for desorption of the test substances.

The effluent and solutions of the sorption and desorption tests were analysed for pH (Hanna pH 210 m) and SRP by automated colorimetry (San + analyser, Skalar, Breda, Netherlands). Caffeine and saccharin concentrations were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) after the addition of a stable labelled internal standard of each compound using a Phenomenex Luna 5 C18 column. The presence of saccharin was detected in the negative and caffeine in the positive electrospray mode (Agilent 1100 series LC system interfaced to a Waters Quattro Ultima Platinum triple quadrupole mass spectrometer, Agilent Technologies, UK). Detailed method is provided in the supplementary material.

2.3. Column sorption and desorption using effluent

The column experiment was conducted using STE to examine P attenuation and behaviour in the test soil. Approximately, 31.5 g of dry untreated soil was packed into a glass column (2.5 cm diameter and 5 cm length) fitted with PTFE filters (20 μm). The column was allowed to saturate with Millipore water with upwards flow using a peristaltic pump. The soil pore volume (PV) was calculated as the difference between saturated and dry soil in the column: (PV = mass saturated column and soil — mass column and soil). Three phases of flow were initiated: 1) Electrolyte (NaCl 1 mM) was pumped to the column at a flow rate of 0.3 ml/min to collect a volume of 6 mL every 20 min for 3.3 h; 2) this was immediately switched to STE pumped into the column for 24.3 h until approximately expected breakthrough; 3) the column was then leached with 1 mM NaCl electrolyte for a further 23 h. Collected column fractions were analysed for SRP and DOC colorimetry (San + analyser, Skalar, Netherlands); and pH (Hanna pH 210 m). Column hydraulic parameters were attained using a subsequent pulse breakthrough experiment with an inert tracer chloride (Cl—). The column was first flushed with Millipore water for 3.3 h then switching to a pulse of 4.91 cm³ of 500 mgCl/l for the duration of 15.5 min, before switching back to Millipore water. Chloride concentrations in the collected fractions were determined ( Dionex DX600, Dionex, California, USA).

2.3.1. Calculations for batch equilibrations

Sorption data were collected and the difference between the initial and final P, caffeine and saccharin concentrations were considered to be due to degradation and sorption to soil. Concentration means and standard errors were calculated and the absorbed amount of P, caffeine and saccharin along with the percentage of Removal (R %) for biotic and abiotic uptake were calculated from the decrease in their concentration after equilibrating time using equation (1):

\[ R\% = \left(\frac{C_0 - C_f}{C_0}\right) \times 100 \]  

(1)

where: R is the adsorbed percentage of P, caffeine and saccharin and C₀ is their initial concentration (mg/l) and Cₖ is equilibrium final concentrations (mg/l). The adsorption capacity of the soil was calculated by concentration difference, and the uptake (mg/g) was calculated as per equation (2):

\[ R = \left(\frac{C_0 - C_t}{C_0}\right) \times \left(\frac{V}{M_{soil}}\right) \]  

(2)

where: R is the mass of P, caffeine or saccharin removed (mg/g soil); V is volume of equilibrium solution (l) and M is dry soil mass (g). The distribution coefficient K_d is the most common measure used to describe the extent to which contaminants are adsorbed to soils. The distribution coefficient, K_d, is also defined as the ratio of the quantity of the adsorbate (P, caffeine and saccharin) adsorbed, to the amount of the adsorbate remaining in solution at equilibrium, and was obtained from theoretical calculation as per equation (3) (OECD, 2000):

\[ K_d = \left(\frac{m_p}{m_{aq}}\right) \times \left(\frac{V}{M_{soil}}\right) \]  

(3)

where: K_d is the partition coefficient of the substance of interest (cm³/g), m_p = mass of adsorbed substance on the soil at adsorption equilibrium (μg), m_{aq} = mass of substance remaining in the solution at equilibrium (μg), M_{soil} = mass of dry soil (g) and V = initial aqueous volume in contact with the soil (ml or cm³). The organic carbon normalised adsorption coefficient (K_{oc}) connects the distribution coefficient K_d to organic carbon content in the soil and allows comparison between the present study and others reporting K_d and K_{oc} values across soils varying in C contents. Therefore, K_{oc} values depended on the characteristics of the soil's humic substances and were calculated as per equation (4):

\[ K_{oc} = \left(\frac{K_d}{\% OC}\right) \times 100 \]  

(4)

where: K_{oc} is the organic carbon normalised adsorption coefficient (ml/g) and % OC is the percentage of organic carbon in the soil (g/g).

During the desorption phase, the mass of test substance desorbed was calculated using equation (5):

\[ m_{des} = \frac{(C_0(V/1000)) - (C_{des}(V/1000))}{M_{soil}} \times 1000 \]  

(5)

where: m_{des} is the mass of test substance desorbed (μg), C₀ is the initial desorption concentration (mg/l), V is solution volume (ml), C_{des} is desorption concentration (mg/l) and M_{soil} is dry soil mass (g).

2.3.2. Calculations for the column experiments

The convective-dispersive transport characteristic of the solution by the soil was determined using equation (6) (Stutter et al., 2007):

\[ C_L(t) = \left(\frac{M_R}{2\sqrt{\pi Dt^3}}\right) L \exp\left(-\frac{(L - vt)^2}{4Dt}\right) \]  

(6)

where: C_L(t) is average Cl concentration (mg/l); Q is column flow rate (ml/min), L is the length of the column (cm), t is the time of the
3. Results

Soil characteristics are summarised in supplementary material (Table S1). The soil can be described as a well-drained silty-loam (7% clay particle size, 55% silt and 38% sand), with organic matter content of 5% of which carbon content was 3% and soil pH in water and CaCl₂ was 5.98 and 5.56, respectively. The silty loam soil covers >58% of Scottish soils in the N. E. of Scotland. Treating soil with ozone exposure reduced microbial abundance by 65% compared to untreated soil (Figs. 1c and 2c). Attenuation curves of saccharin exhibited great separation between untreated and treated soils (Fig. 2c), suggesting that saccharin attenuation by soil included microbial degradation.

3.2. The attenuation of test substances present in STE by untreated soil (batch equilibrium)

Sorption behaviours of P, caffeine and saccharin with the untreated soil in the effluent matrix are presented in Figs. 1 and 2 and Fig. S1. Effluent pH did not vary greatly (5.6—5.9) during the 24 h equilibration period. The soil had a strong affinity to sorb effluent P and a lesser affinity for caffeine and very weak affinity for saccharin. The K_d value in the effluent matrices were 20% and 50% of that in aqueous solution for P and caffeine, respectively, while the saccharin K_d remained more similar in both matrices (Table 1). Phosphorus mass reduced (batch equilibrium) from the effluent was 91 µg P/g, which was much less compared to 212 µg P/g in aqueous solution despite similar pH ranges (5.6—5.9 and 5.8—6.0) in effluent and aqueous solution, respectively; (Fig. 2a). Caffeine mass reduced from the effluent by the soil was 6.3 compared to 7.2 µg/g in the aqueous solution and saccharin mass reduced was 2.8 and 3.2 µg/g in the effluent and the aqueous solution, respectively. While attenuation of P was greatest in aqueous solution compared to STE, caffeine and saccharin attenuation was more similar in both media.

3.3. Desorption of test substances (untreated soil)

The desorption tests aimed to investigate whether a substance was reversibly or irreversibly adsorbed by the untreated test soil and thus inform on the leaching potential. Desorption tests showed that the mass of P and caffeine desorbed from STE was greater than the mass desorbed from the aqueous solution matrix (Table 1). Approximately 20% of the adsorbed P was desorbed from the effluent compared to 7% from aqueous solution, while for caffeine 74% and 49% were desorbed from the effluent and the aqueous solution, respectively. Saccharin desorption from the effluent and aqueous solution matrices were comparable 20% and 18%, respectively (Table 1). Saccharin had the lowest desorption value (0.58 µg/g soil), consistent to both effluent and aqueous solution.

3.4. Septic tank effluent P sorption to soil (column experiment)

Fig. 3 shows the sorption and desorption of P in STE and the break-through curve for SRP at initial concentration of 19.2 mg/l, soil mass 31.5 g, flow rate of 0.3 ml/min and pH for the leachate leaving the column (7.06—8.20). The cumulative P removed from the column was 3.96 mgP = 125.58 µg/g soil at 31 PVs (28.7 h) from the effluent. Fig. 3 showed that after the switch from effluent to background electrolyte (zero P concentration) at 31 PVs (29 h), the eluent P concentration continued to increase to its maximum of 10.1 mg/l at 35 PVs (32 h) after which, P concentration declined to reach its minimum of 3.5 mg/l at 55 PVs (51.7 h). Approximately 25% of the adsorbed P mass was desorbed from the column 0.97 mgP, equivalent to 30.7 µg/g was leached. The subsequent Cl pulse breakthrough experiment gave a calculated Péclet number of 538 suggesting that solution transport inside the column was of a convective nature.

4. Discussion

This study aimed to evaluate the solid: solution partitioning of three solutes often found in wastewaters using batch and column sorption and desorption methods comparing interactions of aqueous and real STE matrices with one test soil.

4.1. Substance behaviour in aqueous solution (batch equilibrium)

Sorption results indicate that P, caffeine and saccharin had a
Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Matrix</th>
<th>Unit</th>
<th>SRP</th>
<th>Caffeine</th>
<th>Saccharin</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Kd for Untreated soil</td>
<td>Aq.</td>
<td>cm$^3$/g</td>
<td>81.57</td>
<td>22.16</td>
<td>5.98</td>
</tr>
<tr>
<td>Kd for Treated soil</td>
<td>Aq.</td>
<td>cm$^3$/g</td>
<td>90.98</td>
<td>19.72</td>
<td>2.58</td>
</tr>
<tr>
<td>Kd for Untreated soil</td>
<td>STE</td>
<td>cm$^3$/g</td>
<td>16.34</td>
<td>12.86</td>
<td>5.02</td>
</tr>
<tr>
<td>Log Kd for Untreated soil</td>
<td>Aq.</td>
<td></td>
<td>3.49</td>
<td>2.96</td>
<td>2.36</td>
</tr>
<tr>
<td>Log Kd for Treated soil</td>
<td>Aq.</td>
<td></td>
<td>3.54</td>
<td>2.88</td>
<td>1.99</td>
</tr>
<tr>
<td>Log Kd for Untreated soil</td>
<td>STE</td>
<td></td>
<td>2.80</td>
<td>2.75</td>
<td>2.35</td>
</tr>
<tr>
<td>Mass reduced Aq.</td>
<td></td>
<td>µg/g</td>
<td>212.29 ± 1.67 (73%)</td>
<td>7.20 ± 0.28 (42%)</td>
<td>3.21 ± 0.25 (17%)</td>
</tr>
<tr>
<td>Mass reduced STE</td>
<td></td>
<td>µg/g</td>
<td>15.75 + 0.05 (7%)</td>
<td>3.59 ± 0.16 (49%)</td>
<td>0.58 ± 0.03 (18%)</td>
</tr>
<tr>
<td>Mass desorption Aq.</td>
<td></td>
<td>µg/g</td>
<td>15.67 ± 0.15 (7%)</td>
<td>3.59 ± 0.16 (49%)</td>
<td>0.58 ± 0.03 (18%)</td>
</tr>
<tr>
<td>Mass desorption STE</td>
<td></td>
<td>µg/g</td>
<td>18.27 ± 0.45 (20%)</td>
<td>4.72 ± 0.09 (74%)</td>
<td>0.58 ± 0.03 (20%)</td>
</tr>
<tr>
<td>Mass reduced (column) STE</td>
<td></td>
<td>µg/g</td>
<td>125.58 (14%)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mass desorbed (column) STE</td>
<td></td>
<td>µg/g</td>
<td>30.71 (25%)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 1. Mass concentration and pH against time in artificial aqueous solutions (untreated and treated soil) and in septic tank effluent (untreated soil), including 2xS.E. for (a) Soluble reactive phosphorus (SRP), (b) Caffeine and (c) Saccharin (note different axis scale).
strong, moderate and low tendency to partition from the aqueous to the solid phase, respectively. In the aqueous matrix, there were similarities in caffeine and saccharin’s sorption behaviours as both reached their maximum adsorption within 3 and 1.5 h of equilibration, respectively (Fig. 2). There was also a distinct difference in their attenuation behaviour between different soil treatments (as defined by mass removed from solution). Caffeine’s attenuation curves over time for untreated and treated soils were very close (Fig. 2b) suggesting that only a very small proportion of caffeine attenuation was associated with microbial degradation during the 24 h equilibration, and hence was dominated by abiotic sorption. Conversely, large separation between the attenuation curves for saccharin with untreated and treated soils suggested that a substantial proportion of the saccharin was degraded by soil microorganisms, which is in agreement with Buerge et al. (2011).

Schleheck and Cook (2003) suggested that saccharin was a source of carbon and energy for microorganisms which was readily converted to cell material, sulphate, ammonium and CO₂. Conversely, caffeine degradation by microorganisms involved a slow rate enzymatic process of the demethylation of caffeine compound (Middelhoven and Bakker, 1982).

The mobilization/migration property of a chemical in soil is related to the chemical’s hydrophobic characteristics and its distribution in a media (Swann et al., 1983), and is expressed by the chemical’s $K_d$ and log $K_{oc}$ values, in which low values show high mobility in soil solution phases. Caffeine $K_d$ and Log $K_{oc}$ values produced in this current work for untreated soil (Table 1) are in agreement with that produced by Karnjanapiboonwong et al. (2010) of 18.5 cm$^3$/g and 3.89, respectively, for similar sandy loam soil. Our results also showed that caffeine had greater values of $K_d$ and $K_{oc}$ than saccharin (Table 1), suggesting caffeine’s stronger affinity for soil surfaces relative to weaker for saccharin and that saccharin would readily leach from soil. The low adsorption potential of saccharin can be explained by its small molecular weight of 183.18 g/mol, small surface area, therefore hydrophobic interaction with soil is not likely to occur (Hofman-Caris et al., 2015).
Moreover, a saccharin molecule contains 3 oxygen atoms, an amide and sulphide group, all of which may be involved in the formation of hydrogen bonds with soil particles. Therefore, hydrogen bonding would be the more likely process to occur for saccharin adsorption to soil, and thus, saccharine would be in competition with water molecules over hydrogen bond binding sites on soil particles.

The results of treated and untreated soil also suggested that saccharin attenuation may be dominantly due to microbial degradation rather than chemical or physical adsorption, which is in agreement with Robertson et al. (2013). However, a complete degradation did not occur during the experimental period suggesting that saccharin may leach to surface or groundwater. Saccharin leaching was shown by Robertson et al. (2013), who reported saccharin concentrations in ground waters similar to that found in STE. Saccharin retention curve on soil surfaces (Fig. 2c) suggests that saccharin is the least retained compound of the tested substances and that the soil under our experimental conditions was not effective in saccharin removal. Thus, the presence of saccharin in surface and groundwaters not only can indicate anthropogenic activity but also may be used as a tracer for sewage effluent.

Conversely, the stronger adsorption of caffeine (moderate values of \( K_d \) and log \( K_{oc} \); Table 1) can be explained by caffeine being a hydrophilic organic base: \( pK_a \) 14 at 25°C (Clarke, 1986), moderately soluble in water: 2 g/100 ml (Pavia et al., 2005). The log \( K_{oc} \) values (2.75–3.59) for caffeine obtained in this study are in agreement with those reported by Karnjanapiboonwong et al. (2010) of 3.89 and 2.87 for sandy loam and silt loam soils, respectively. Caffeine is a small organic molecule and contains 2 oxygen atoms, so its hydrophilic nature (2 g/100 ml) suggests that caffeine may have the potential for great mobility through soil particles (Roy and De Datta, 1985; Sakadevan and Bavor, 1998; Gichangi et al., 2008; Gill et al., 2009b).

4.2. Substance behaviour in septic tank effluent

Saccharin had similar \( K_d \) values and similar mass adsorbed for effluent and aqueous solution alike in untreated soil (Table 1 and Fig. 2) suggesting that the limited sorption that occurred was not greatly affected by the matrix. Conversely, caffeine sorption behaviour differed between effluent (\( K_d = 12.86 \)) and aqueous solution (\( K_d = 22.16 \); Table 1 and Fig. 2) The low soil affinity for caffeine in the effluent resulted in 12.5% less caffeine mass removed from the effluent compared to aqueous solution (Fig. 2b). Phosphorus in the effluent also had lower \( K_d \) value than in aqueous solution (Table 1) resulted in a 56%, less effluent P was adsorbed, suggesting that components of the complex matrix composition of the effluent such as metals, bacteria and DOC were in competition with P and caffeine for soil adsorption sites, which is in agreement with Grohmann et al. (1995).

4.3. Substances desorption behaviour

In aqueous solution, the adsorption and desorption of caffeine of 7.20 and 3.59 \( \mu g/g \), respectively, suggests that caffeine may have the potential for great mobility through soil particles. However, phosphorus sorption seemed to be a dominantly irreversible processes as 73% of P was adsorbed (aqueous matrix) and only 7% of that P sorbed was subsequently desorbed over 24 h. Desorption in the aqueous matrix followed the order: caffeine 49% > saccharin 18% > P 7%, suggesting that caffeine and saccharin were more weakly and reversibly sorbed than P. However, the high P accumulation on the soil resulted in a proportionally higher concentration of P to desorb than caffeine and saccharin, which was confirmed by the mass desorbed from effluent (\( \mu g/g \) soil): P (18.3)> caffeine (4.7) > saccharin (0.6) \( \mu g/g \) soil, which may be attributed to their different initial concentrations and mass loading. Thus, soil condition may favour P desorption implying the likelihood of P to leave the soil and contaminate groundwaters in higher concentrations.

![Fig. 3. Adsorption/desorption kinetics of septic tank effluent phosphorus (P) in column reactor and the corresponding pH.](image-url)
attenuation did not occur during a 24 h equilibrium period, suggesting that saccharin and caffeine leaching potential to surface and groundwaters. The experimental data also suggested that the adsorption of saccharin on soil particles was particularly weak, and the soil under the experimental conditions was not effective in the removal of saccharin from both STE and aqueous solution. Conversely, phosphorus attenuation was dominated by adsorption processes and its $K_d$ value was the greatest of all 3 substances. The fraction removed of all 3 substances in the aqueous matrices was greater than in STE, suggesting that the complex composition of STE reduced the adsorption of these substances and that other substances present in STE may be competing over soil binding sites. Thus, soakaway soil may not provide a complete removal of pollutants during STE secondary treatment in the soil, increasing the risk of a proportion of effluent contaminants and pollutants reaching ground water untreated. This was confirmed by the desorption data, which revealed that for STE P had the greatest leaching potential followed by caffeine. Thus, soil condition may favour P and caffeine desorption suggesting the likelihood that P and caffeine would reach surface and groundwaters. Moreover, the presence of saccharin and caffeine in surface and groundwaters can indicate anthropogenic source and may be considered as tracers for sewage effluent in water courses.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.01.024.

References
