Sorption and biodegradation characteristics of the selected pharmaceuticals and personal care products onto tropical soil
Mahsa Foolad, Jiangyong Hu, Ngoc Han Tran and Say Leong Ong

ABSTRACT
In the present study, the sorption and biodegradation characteristics of five pharmaceutical and personal care products (PPCPs), including acetaminophen (ACT), carbamazepine (CBZ), crotamiton (CTMT), diethyltoluamide (DEET) and salicylic acid (SA), were studied in laboratory-batch experiments. Sorption kinetics experimental data showed that sorption systems under this study were more appropriately described by the pseudo second-order kinetics with a correlation coefficient ($R^2 > 0.98$). Sorption equilibrium data of almost all target compounds onto soil could be better described by the Freundlich sorption isotherm model. The adsorption results showed higher soil affinity for SA, following by ACT. Results also indicated a slight effect of pH on PPCP adsorption with lower pH causing lower adsorption of compounds onto the soil except for SA at pH 12. Moreover, adsorption of PPCPs onto the soil was influenced by natural organic matter (NOM) since the higher amount of NOM caused lower adsorption to the soil. Biodegradation studies of selected PPCPs by indigenous microbial community present in soil appeared that the removal rates of ACT, SA and DEET increased with time while no effect had been observed for the rest. This study suggests that the CBZ and CTMT can be considered as suitable chemical sewage indicators based on their low sorption affinity and high resistance to biodegradation.

Key words | biodegradation, chemical markers of wastewater, groundwater, pharmaceutical and personal care products, sorption, tropical soil

INTRODUCTION
The impacts of wastewater contamination on urban groundwater have been increasingly gaining attention due to the presence of many chemical pollutants as well as pathogenic microbes in wastewater sources. Particularly this concern has increased with regards to the direct discharge of raw wastewater from hospital, industrial, and municipal effluents into the receiving water bodies in developing countries where most hospitals and residences are not equipped with wastewater treatment plants (Dizer & Hagentorf 1991; Emmanuel et al. 2009; Tran et al. 2014b). The groundwater contamination is attributed to the infiltration from artificial aquifer recharge sites, bank filtration sites, irrigated farms, and sewage disposal sites where a large amount of treated or raw wastewater, river water containing sewage effluent, septic tank effluents, and sewer leaks have infiltrated into the ground (Held et al. 2006; Nakada et al. 2008; Leschik et al. 2009; Kuroda et al. 2012; Wolf et al. 2012). Numerous efforts have been made to detect and evaluate impacts of wastewater contamination on groundwater using microbial and/or chemical markers (Osenbrück et al. 2007; Gasser et al. 2010, 2011; Scheurer et al. 2011; Kuroda et al. 2012; Tran et al. 2014a, b). For example, it has been widely proposed that several pharmaceuticals and personal care products (PPCPs), such as carbamazepine, crotamiton, diethyltoluamide and acetaminophen are appropriate to be used as chemical markers of wastewater contamination in urban groundwater (Gasser et al. 2011; Kuroda et al. 2012; Tran et al. 2014a). To date, most studies on the detection and evaluation of wastewater contamination impacts on urban groundwater have been based on the occurrence data of the markers in groundwater only. However, it is noted that the concentration of the PPCPs in groundwater is a function of several factors, such as dilution by rainfall, sorption, and biodegradation onto the...
soil (Teržić et al. 2008; Tran et al. 2014a). Therefore, it is inaccurate to evaluate the extent of wastewater contamination based on the information on the concentration level of the target markers only. For this reason, it is critical to evaluate the impacts of wastewater contamination on the receiving water bodies and to study the environmental fate and transport of the target chemical markers in the subsurface environment. So far, most studies have focused on addressing the fate of PPCPs in engineered systems like wastewater treatment plants (WWTPs), while studies on natural systems are still limited. Particularly, there is little information on the biodegradation and sorption behaviors of particular PPCPs (e.g. acetaminophen, carbamazepine, crotamiton, diethyltoluamide, and salicylic acid) that have been widely used as suitable chemical markers of wastewater contamination in surface water and groundwater.

Thus, the main objective of this study was to investigate the biodegradation and sorption behavior of the selected PPCPs in the tropical soil. To the best of our knowledge, this study provides the first biodegradation and sorption data of the two PPCPs (crotamiton and diethyltoluamide) in the soil.

**MATERIALS AND METHODS**

**Target PPCPs**

The target chemical markers used in this study were five PPCPs, which have been widely used as molecular markers of wastewater contamination in surface water and groundwater (Nakada et al. 2008; Buerge et al. 2009, 2011; Scheurer et al. 2011; Van Stempvoort et al. 2011; Tran et al. 2014a). These compounds were acetaminophen (ACT), carbamazepine (CBZ), crotamiton (CTMT), diethyltoluamide (DEET), and salicylic acid (SA). The chemical structure and physicochemical properties of these compounds are shown in Table A1 (Supplementary information, available in the online version of this paper).

**Tested soil**

The soil used in this study was obtained from a local area in Singapore. Particle size analysis was determined by the soil sieving method, and the soil was categorized in the sandy soil group. The soil samples were air-dried and sieved through 2 mm openings for the experiment. The main characteristics of soil, such as the contents of sand, silt, clay, and organic matter are shown in Table A2 (Supplementary information, available online).

**Design of experiments**

To evaluate the sorption behavior of the target PPCPs, a series of batch experiments were conducted in sterilized 300 mL amber glass bottles containing 100 mL artificial groundwater with the composition of mineral salts as shown in Table A3 (Supplementary information, available online). The target PPCPs in water were then added to the bottles to achieve an initial concentration of 100 – 1,000 μg/L depending on the experimental purposes. For example, for kinetic studies the initial concentrations of the target PPCPs were set at 100 μg/L, while for sorption isotherm experiments, the concentrations of the target PPCPs were set at 100, 200, 400, 600, and 1,000 μg/L. It should be noted that the concentration levels of target PPCPs are similar to those found in wastewater samples. The amount of sterilized soil in the bottle was adjusted to have a 4 g soil for each bottle. The pH of sorption systems was kept at approximately 6.5 for kinetic and sorption isotherm studies. For the experiments to evaluate the effects of solution pH on sorption, different pH values in the range of 2 – 12 were examined. Furthermore, to determine the effect of natural organic matter (NOM) on adsorption of selected PPCPs onto the soil, different concentrations of humic acid (0, 20, 50, 100 ppm) were tested. The stock solutions were prepared with 0.2 g of humic acid dissolved in water and pH was adjusted by NaOH and HCl. Then, it was diluted to the required final concentration.

To assess biodegradation of the target PPCPs, a series of batch experiments were carried out using non-sterilized soil with the same amount of 4 g. The initial concentrations of the target PPCPs were set at 100 μg/L, and the pH of the solution was 6.5. In addition to biodegradation and sorption tests by soil, the elimination of the target PPCPs may be attributed to hydrolysis, photolysis and sorption onto glass bottle walls. Thus, to assess the impact of hydrolysis, photolysis and sorption onto glass bottle walls, a series of tests were conducted in parallel in the artificial groundwater with the absence of soil, while other parameters, such as pH, temperature, and the initial concentrations of the PPCPs, were kept the same as implemented in biodegradation tests. During the experiments, concentrations of the target PPCPs in water phase were measured. All batch experiments were implemented in triplicate and conducted at a temperature of 25 °C through an aerobic condition by shaking at 150 rpm.

**Quantification of the target PPCPs in aqueous phase**

The concentration of target PPCPs were measured using high performance liquid chromatography–tandem mass spectrometry (LCMS-8030, Shimadzu, Japan) coupled with
isotope dilution as fully described in our recent study (Tran et al. 2015) with a slight modification. Briefly, water samples from the experiments were filtered using 0.45 μm nylon filters (Whatman®GD/X syringe filters). The quantification of target PPCPs in the filtered water samples was carried out by direct injection of 10 μL into LC–MS/MS.

**Data analysis**

Adsorption kinetics of target PPCPs were investigated by fitting the data to the first-order Equation (1) and second-order Equation (2) adsorption kinetic equations.

\[
\log \left( C_s^e - C_s^t \right) = \log \left( C_s^e \right) - \frac{k_1 t}{2.303}
\]

\[
t \cdot \frac{C_s^e}{C_s^t} = \frac{1}{k_2 C_s^e} + t \frac{C_s^e}{C_s^t}
\]

where \( C_s^e \) and \( C_s^t \) are the amounts of adsorbed PPCPs onto the soil (μg kg\(^{-1}\)) at equilibrium and at \( t \) time, respectively. \( k_1 \) and \( k_2 \) are the first-order and second-order rate constants for the model, respectively.

Isotherm behavior for five selected PPCPs was analyzed using Langmuir and Freundlich isotherm models. The Langmuir and Freundlich isotherm are represented by the Equations (3) and (4), respectively.

\[
\frac{1}{C_s^e} = \frac{1}{K_L C_{\text{Smax}}} \times \frac{1}{C_e^s} + \frac{1}{C_{\text{Smax}}}
\]

\[
\log C_s^e = \log K_F + n \log C_e
\]

where \( C_{\text{Smax}} \) is the monolayer capacity of the absorbent (μg kg\(^{-1}\)), \( K_L \) is the Langmuir constant that is related to the free energy of adsorption, \( K_F \) is the Freundlich constant that reflects the sorption affinity of the contaminants into the soil and \( n \) is a constant measuring adsorption intensity (Vasudevan et al. 2011; Yadav & Tyagi 2011; Song et al. 2015).

Moreover, experimental distribution coefficient \( K_d \) (L kg\(^{-1}\)) values of selected compounds is calculated by Equation (5) (Xu et al. 2009).

\[
K_d = \frac{C_s}{C_w}
\]

where \( C_s \) is the concentration of compounds (i.e., PPCPs) in the soil (μg kg\(^{-1}\)) and \( C_w \) is their concentration in water (μg L\(^{-1}\)).

Organic carbon partition coefficient \( K_{oc} \) values were calculated from the experimental \( K_d \) values and amount of organic carbon present in the soil \( f_{oc} \) by Equation (6) (EPA 2001).

\[
K_{oc} = \frac{K_d}{f_{oc}}
\]

Acidic and basic compounds can be ionized in subsurface area. Therefore, sorption coefficient can be divided into sorption coefficient of ionic \( K_d^i \) and neutral \( K_d^N \) forms at different pH values. These values help to understand the proportion of ionized and neutral species under subsurface condition, Equation (7) (Amiri 2005).

\[
K_d = K_d^N + K_d^d
\]

where \( K_d^N \) can be calculated using Equation (8).

\[
K_d^N = \left( 1 - \alpha \right) \cdot K_{oc}^N \cdot f_{oc} + \alpha \cdot K_{oc}^d \cdot f_{oc}
\]

where \( K_{oc}^i \) can be estimated to be 0.015 × \( K_{oc}^N \) and degree of protonation \( \alpha \) can be calculated based on Equations (9) and (10) for acidic and basic compounds, respectively (EPA 2001).

\[
\alpha = \frac{1}{1 + 10^{pH - pK_a}}
\]

\[
\alpha = \frac{1}{1 + 10^{pK_a - p\alpha}}
\]

**RESULTS AND DISCUSSION**

**Sorption studies**

**Sorption kinetics of target PPCPs on soil**

Adsorption experiments were carried out to identify the adsorption rate and to find out the effects of time and concentration on the adsorption process. Control experiments were conducted at the same condition without soil (adsorbent), and no concentration change was observed. This finding indicates that selected PPCPs were not eliminated by hydrolysis and photodegradation at room conditions or by sorption onto the walls of the bottle.
The effect of adsorption \((C_s)\) of all five selected PPCPs onto tropical soil versus time is shown in Figure 1. It can be seen that the adsorbed amount of PPCPs increased with the contact time and then remained nearly constant after 24 h.

The adsorption kinetic equation parameters were calculated from the slope and intercept of the first-order and second-order plots (Table 1) (figures not shown). As the data show, kinetics of selected PPCPs on tropical soil were described well by second-order kinetics equation with a coefficient of determination of \(R^2 > 0.98\).

Table 1 presents that SA with highest adsorption affinity (2,500 \(\mu\)g kg\(^{-1}\)) followed by ACT (828.4 \(\mu\)g kg\(^{-1}\)) were the least mobile and CTMT with lowest adsorption affinity (288.4 \(\mu\)g kg\(^{-1}\)) was the most mobile in the soil. The adsorption capacity of the five PPCPs on soil was in the following order: SA > ACT > CBZ > DEET > CTMT. The lower sorption affinity of CBZ, CTMT, and DEET in comparison to SA and ACT may be related to their chemical structure and molecular weight (Table A1, available in the online version of this paper). SA as carboxylic emerging organic contaminants (EOCs) has two ionizable hydrogen ions in \(-\text{COOH}\) and \(-\text{OH}\) groups that may help adsorb to the negatively charged site of soil particles (i.e., organic matter and clay) suggesting its lowest tendency to move through subsurface area (Dubus et al. 2001; Hanna et al. 2012). Following SA, ACT as phenolic EOCs showed higher removal efficiency in comparison to the others (around 20%). The phenols group may form hydrogen bonding with soil surface sites by acting as a proton acceptor (Delle Site 2001). The sorption tendency of ACT onto the soil was observed in previous studies (Lin et al. 2010; Li et al. 2014). Conversely,

![Figure 1](https://iwaponline.com/wst/article-pdf/73/1/51/464323/wst073010051.pdf)
CBZ, CTMT, and DEET as amid EOCs had the lower adsorption affinity onto the soil. This finding is in agreement with Shinohara’s findings that showed poor adsorption of amid EOCs onto the soil (Shinohara et al. 2006). Beside the difference between the chemical structure of selected chemical compounds, CBZ, CTMT and DEET have a higher molecular weight in comparison with ACT and SA. This may suggest that chemicals with lower molecular weight can attenuate onto the soil more than those with higher molecular weight. The other possible reasons may be due to their high resistance to hydrolysis and their neutral charge that cause little interaction with soil mineral compounds (Lapworth et al. 2012).

Sorption isotherms of target PPCPs on soil

Table 2 shows theoretical sorption capacity (C*) obtained from the Langmuir and Freundlich isotherm models.

According to the experimental results, it is seen that the $R^2$ value of Freundlich model was higher than that of Langmuir model, indicating that the adsorption of all tested compounds could be better described with the Freundlich isotherm. A non-linear sorption was observed for all compounds with $n$ values ranging from 0.33 to 0.74. The low $R^2$ for CBZ, CTMT and DEET may be due to the very low adsorption rates of these compounds onto the soil. The results are agreeable with previous studies which indicated that the adsorption isotherms of most of the PPCPs onto the soil were best fitted to the Freundlich adsorption isotherm (Xu et al. 2009; Jodeh 2012; Yu et al. 2013).

To understand and predict the fate and transport of chemical compounds, the partition coefficient of chemicals between water and soil was determined. The soil–water partition coefficient ($K_d$) was measured by laboratory batch experiment. Sorption coefficient results are shown in Table 3. Based on the experimental results, CTMT had the lowest ($0.8 \pm 0.4$ L kg$^{-1}$) and SA had the highest ($395.3 \pm 38.8$ L kg$^{-1}$) $K_d$ values. The higher $K_d$ value of SA determines the higher reduction in the dissolved concentration of SA due to the adsorption and, therefore, the lower tendency in movement with a water solution. On the other hand, the lower $K_d$ value of CTMT indicates lower adsorption to the soil and thus higher tendency to move with a water solution.

Table 3 also provides the calculated data for $K_{d}^{N}$ and $K_{d}^{I}$. Since all tested PPCPs in this study except SA, are neutral compounds, their entire sorption coefficients are related to the non-ionized organic compounds ($K_{d}^{I} = 0$).

These findings suggest that for compounds with their pKa values greater than the experimental pH value (6.5), the total sorption was solely dominated by the sorption of neutral compounds. Whereas, for SA as an acidic organic compound with pKa values less than the experimental pH value (6.5), some portion of partition coefficient was related to charged species. Therefore, the pH condition has an effect on the sorption of charged and neutral species (EPA 2013). The results regarding the effect of pH on selected PPCPs are shown in the later section.

Effects of environmental factors on PPCP sorption

Effect of environmental pH values on PPCP sorption

Several previous studies noted that pH was an important factor that could affect adsorption behavior of PPCPs onto the soil (Hari et al. 2005; Zhang et al. 2009). The pH effect on adsorption depends on physicochemical characteristics of compound and soil composition. The correlation between adsorption of five selected PPCPs and pH of the solution was examined.

The data shown in Table 4 demonstrate the adsorption behavior of all selected chemicals at different pH values. For all compounds, adsorption was slightly increased by increasing the pH except SA at pH 12. From the table, it can be seen that there was a large decrease in adsorption capacity of SA at pH 12. SA is a weak acid so with the

<table>
<thead>
<tr>
<th>Target PPCPs</th>
<th>$K_d$ (L kg$^{-1}$)</th>
<th>$K_{d}^{N}$ (L kg$^{-1}$)</th>
<th>$K_{d}^{I}$ (L kg$^{-1}$)</th>
<th>$K_f$ (L kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>3.7 ± 0.7</td>
<td>90.2 ± 1.2</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td>CBZ</td>
<td>1.5 ± 0.5</td>
<td>27.0 ± 1.6</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>CTMT</td>
<td>0.8 ± 0.4</td>
<td>17.4 ± 2.1</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>DEET</td>
<td>1.5 ± 0.3</td>
<td>25.5 ± 1.9</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>SA</td>
<td>395.3 ± 38.8</td>
<td>9,847.8 ± 1.1</td>
<td>4.7</td>
<td>390.6</td>
</tr>
</tbody>
</table>

Table 2 | Freundlich and Langmuir adsorption isotherm parameters

<table>
<thead>
<tr>
<th>Target PPCPs</th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (L g$^{-1}$)</td>
<td>$C_{\text{max}}$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>ACT</td>
<td>3.8 ± 10$^{-3}$</td>
<td>2,500.0</td>
</tr>
<tr>
<td>CBZ</td>
<td>3.0 ± 10$^{-3}$</td>
<td>833.3</td>
</tr>
<tr>
<td>CTMT</td>
<td>2.0 ± 10$^{-2}$</td>
<td>400.0</td>
</tr>
<tr>
<td>DEET</td>
<td>1.5 ± 10$^{-2}$</td>
<td>500.0</td>
</tr>
<tr>
<td>SA</td>
<td>7.0 ± 10$^{-2}$</td>
<td>20,000.0</td>
</tr>
</tbody>
</table>
increase of the pH the ionization of carboxylic groups of SA occurs and consequently negatively charged sites will increase and, therefore, the adsorption of SA decreases. Previous literature have reported similar adsorption behavior of SA with change in different pH solutions (Dubus et al. 2001; Dyson et al. 2002; Gondar et al. 2013). Another reason is the presence of positively charged adsorption surface like aluminum and iron oxides in the soil, especially in tropical soil due to the weathering process. At higher pH their net charges become more negative and consequently decrease the adsorption rate (Baskaran et al. 2002; Dubus et al. 2001). Other tested PPCPs including ACT, CBZ, CTMT and DEET were slightly affected by changing pH condition. As can be seen in Table A1 (available online), these compounds have high pKa values and consequently their adsorption was slightly affected (Hari et al. 2005; EPA 2013).

Effect of NOM values on PPCP sorption

NOM is a humic or non-humic fraction that remains from dead organisms such as animals and plants and plays an important role in mobility, solubility and bioavailability of both inorganic and organic compounds in the environment (Waksman 1936; Wang & Mulligan 2006). Previous studies have shown different results for the effect of NOM on sorption of PPCPs. In one way, NOM may act as a promoter in the mobility of PPCPs with water and thereby increase the possibility of groundwater pollution. The main mechanism can be due to the negative charged of NOM that enables them to adsorb to the positively charged surface of clay and thus interfere with sorption of other compounds (Kan & Tomson 1990; Kim et al. 2003). In another way, NOM may act as an antagonist in mobility of chemical compounds by creating binding sites (Chefetz et al. 2008; Sun et al. 2008; Arye et al. 2014; Borgman & Chefetz 2013). Table 5 shows the adsorption of five selected PPCPs at different concentrations of NOM.

As can be seen, NOM decreased the retardation of selected PPCPs by soil when the concentration of NOM changed from 0 to 20 mg L$^{-1}$. Therefore, this study is in agreement with those studies that suggested that organic matter enhanced the transport of organic compounds in subsurface area. The reason is that NOM competes with PPCPs for adsorption in the soil which may increase the possibility of groundwater pollution. However, no difference was found in adsorption of selected PPCPs by changing NOM concentration from 20 to 50 mg L$^{-1}$. This could be due to the higher amount of NOM in comparison to the amount of soil (Navon et al. 2011).

<table>
<thead>
<tr>
<th>NOM (mg L$^{-1}$)</th>
<th>CBZ</th>
<th>ACT</th>
<th>CTMT</th>
<th>DEET</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.30 ± 0.49</td>
<td>3.65 ± 0.68</td>
<td>0.75 ± 0.36</td>
<td>0.80 ± 0.30</td>
<td>395.00 ± 38.80</td>
</tr>
<tr>
<td>20</td>
<td>0.84 ± 0.22</td>
<td>1.61 ± 0.26</td>
<td>0.57 ± 0.15</td>
<td>0.67 ± 0.17</td>
<td>312.86 ± 55.87</td>
</tr>
<tr>
<td>35</td>
<td>0.84 ± 0.23</td>
<td>1.63 ± 0.34</td>
<td>0.53 ± 0.17</td>
<td>0.67 ± 0.25</td>
<td>312.86 ± 55.87</td>
</tr>
<tr>
<td>50</td>
<td>0.82 ± 0.20</td>
<td>1.60 ± 0.50</td>
<td>0.55 ± 0.20</td>
<td>0.60 ± 0.06</td>
<td>315.26 ± 23.10</td>
</tr>
</tbody>
</table>

Biodegradation studies

Biodegradability of contaminants is dependent on the presence of microorganisms, physicochemical properties of

Table 4 | Sorption coefficient ($K_d$) of the target PPCPs onto the tropical soil under different environmental pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>CBZ</th>
<th>ACT</th>
<th>CTMT</th>
<th>DEET</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.83 ± 0.04</td>
<td>1.30 ± 0.58</td>
<td>0.28 ± 0.06</td>
<td>0.53 ± 0.23</td>
<td>238.63 ± 82.20</td>
</tr>
<tr>
<td>4</td>
<td>0.99 ± 0.20</td>
<td>2.60 ± 0.30</td>
<td>0.75 ± 0.26</td>
<td>0.82 ± 0.11</td>
<td>304.30 ± 17.00</td>
</tr>
<tr>
<td>6.5</td>
<td>1.30 ± 0.49</td>
<td>3.65 ± 0.68</td>
<td>0.75 ± 0.36</td>
<td>0.80 ± 0.30</td>
<td>395.30 ± 38.80</td>
</tr>
<tr>
<td>9</td>
<td>1.33 ± 0.20</td>
<td>3.60 ± 0.22</td>
<td>1.30 ± 0.75</td>
<td>0.86 ± 0.02</td>
<td>346.10 ± 15.86</td>
</tr>
<tr>
<td>12</td>
<td>3.38 ± 0.10</td>
<td>3.64 ± 0.27</td>
<td>1.30 ± 0.73</td>
<td>0.80 ± 0.15</td>
<td>26.24 ± 11.30</td>
</tr>
</tbody>
</table>

Table 5 | Effect of NOM concentrations on the sorption coefficient ($K_d$) of target PPCPs in tropical soil

<table>
<thead>
<tr>
<th>NOM (mg L$^{-1}$)</th>
<th>CBZ</th>
<th>ACT</th>
<th>CTMT</th>
<th>DEET</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>3.65 ± 0.68</td>
<td>0.75 ± 0.36</td>
<td>0.80 ± 0.30</td>
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<td>20</td>
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<td>0.60 ± 0.06</td>
<td>315.26 ± 23.10</td>
</tr>
</tbody>
</table>
compounds and the amount of primary substrate in the soil. For biodegradation experiments, the disappearance curves of each PPCP are shown in Figure 2.

Figure 2 shows that all five selected PPCPs displayed a stable concentration in the control study which indicates that other reactions such as hydrolysis, photolysis and sorption to the walls of the bottle had no effect on the degradation. In Figure 2, there is a clear trend of decreasing the concentration of ACT and SA due to the adsorption and biodegradation processes. However, the rates of decreasing due to the adsorption and biodegradation together were much higher than adsorption only. As it can be seen, the concentrations of ACT and SA decreased to zero within seven days by adsorption and biodegradation together with the rate constant equal to 0.4 d^{-1} and 0.9 d^{-1}, respectively, while by adsorption only, it happened after 28 days and 21 days with the rate constant equal to 0.01 d^{-1} and 0.03 d^{-1}, respectively. These findings can support previous existing studies which indicate biodegradability of SA and ACT as a carbon source in soil and consequently, lead to fast removal in the soil (Kagle et al. 2009; Vasiliadou et al. 2015). For example, Lin et al. studied the biodegradation and sorption of four PPCPs (i.e., ACT) into aqueous environment and determined that biodegradation was the primary mechanism for degradation of ACT in soil (Lin et al. 2010; Li et al. 2014). Similar to ACT and SA, DEET is also biodegradable, and the concentration reached zero after 21 days with the rate constant equal to 0.04 d^{-1} by biodegradation process only. Thus, this study has shown that the movement of SA and ACT was not only limited by adsorption, but also limited by the biodegradation process while DEET was only limited by the biodegradation process.

It is apparent from Figure 2 that both CBZ and CTMT were neither adsorbed nor biodegraded during the experiment. CBZ has a stable heterocyclic structure and, therefore, is known as a persistent PPCP in aquatic environments (Nakada et al. 2008; Gasser et al. 2011; Nödler et al. 2013; Jurado et al. 2014). CTMT also showed the high persistence during secondary treatment (Nakada et al. 2010; Fukahori et al. 2012) and thus has a high possibility of reaching the water bodies.

CONCLUSION

This study has gone some way towards enhancing our understanding of transport behavior, in particular, biodegradation and adsorption of the five PPCPs into the tropical soil. Adsorption studies showed that all five selected PPCPs reached the equilibrium within 24 h and they preferably followed second-order kinetics and their adsorption was fit well to Freundlich adsorption isotherm. It was shown that all five selected PPCPs except SA and ACT had high persistence and partitioning in water solution. Another major finding was that indigenous soil microorganism could biodegrade SA, ACT, and DEET and, therefore, increased the rates of their removal through time. Furthermore, findings related to the effect of environmental

Figure 2 | Changes in the normalized concentration (C_t/C_0) of the target PPCPs in water phase during control, sorption and biodegradation experiments.
factors showed adsorption of all selected PPCPs (except SA), lower pH and higher amounts of NOM could decrease the sorption affinity of selected PPCPs into the soil. Taken together, the evidence from this study suggests that CTMT and CBZ can be considered as sewage chemical indicators in aquatic environment because of their high persistency in water solution and no biodegradation by soil microorganisms. Moreover, environmental factors (i.e., NOM) had a slight effect on their adsorption onto the soil.

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