Sorption of emerging trace organic compounds onto wastewater sludge solids

John Stevens-Garmon, Jörg E. Drewes, Stuart J. Khan, James A. McDonald, Eric R.V. Dickenson

Abstract

This work examined the sorption potential to wastewater primary- and activated-sludge solids for 34 emerging trace organic chemicals at environmentally relevant concentrations. These compounds represent a diverse range of physical and chemical properties, such as hydrophobicity and charge state, and a diverse range of classes, including steroidal hormones, pharmaceutically-active compounds, personal care products, and household chemicals. Solid-water partitioning coefficients ($K_d$) were measured where 19 chemicals did not have previously reported values. Sludge solids were inactivated by a nonchemical lyophilization and dry-heat technique, which provided similar sorption behavior for recalcitrant compounds as compared to fresh activated-sludge. Sorption behavior was similar between primary- and activated-sludge solids from the same plant and between activated-sludge solids from two nitrified processes from different wastewater treatment systems. Positively-charged pharmaceutically-active compounds, amitriptyline, clozapine, verapamil, risperidone, and hydroxyzine, had the highest sorption potential, log $K_d = 2.8$–3.8 as compared to the neutral and negatively-charged chemicals. Sorption potentials correlated with a compound’s hydrophobicity, however the higher sorption potentials observed for positively-charged compounds for a given log $D_{ow}$ indicate additional sorption mechanisms, such as electrostatic interactions, are important for these compounds. Previously published soil-based one-parameter models for predicting sorption from hydrophobicity (log $K_{ow} > 2$) can be used to predict sorption for emerging nonionic compounds to wastewater sludge solids.

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1. Introduction

A wide range of trace organic chemicals (TORCs) regularly enters municipal wastewater treatment systems, including steroidal hormones, pharmaceutically-active compounds, personal care products, and household chemicals. Some of these are of concern due to their persistence and toxicological effects in the environment (Snyder et al., 2003; Carucci et al., 2006; Kim et al., 2007). Treatment plant operators, regulatory agencies, and the public concerned about discharges of such TORCs are interested in the fate of these chemicals during wastewater treatment. TORC removal mechanisms during activated-sludge treatment include biological transformation and degradation, volatilization, and sorption. The low Henry’s constant for most pharmaceutically-active compounds and compounds targeted
in this study (H < 10^{-5}, H is the dimensionless Henry gas water partitioning coefficient (L_{wastewater}/L_{air})), indicates volatilization is negligible as a removal mechanism for these type of compounds (Schwarzenbach et al., 2003). Biotransformation is often the dominant removal process for some TOrCs, as described by Clara et al. (2005), Joss et al. (2006), Urase and Kikuta (2005), and Wick et al. (2009). Also, sorption onto solids can be a key process controlling the physical removal of many natural and xenobiotic organic chemicals in municipal wastewater treatment plants. Sorption mechanisms of organic compounds on wastewater solids consist of two processes: (1) adsorption of the organic compounds from the bulk liquid onto the surface of solids and (2) partitioning of the organic compounds between the aqueous phase and the organic matter within solids. The equilibrium partitioning of an organic chemical between the solid and aqueous phases is described by the solids-water distribution coefficient (K_d) (Schwarzenbach et al., 2003). K_d is the ratio of the equilibrium concentration of the chemical on the solids to the corresponding equilibrium aqueous concentration.

Previous studies have reported K_d values for the sorption of several pharmaceutically-active compounds, fragrances and steroidal hormones to various primary, activated and digested sludges (Golet et al., 2001, 2003; Simonich et al., 2002; Ternes et al., 2004; Artola-Garicano et al. 2003; Clara et al., 2004; Göbel et al., 2005; Urase and Kikuta, 2005; Andersen et al., 2005; Maurer et al., 2007; Yi and Harper, 2007; Carballa et al., 2008; Wick et al., 2009; Radjenovic et al., 2009). However, some of these studies have used TOrC concentrations in the µg/L to mg/L range to measure K_d (Ternes et al., 2004; Clara et al., 2004; Urase and Kikuta, 2005; Yi and Harper, 2007; Wick et al., 2009), which are orders of magnitude greater than concentrations observed in raw municipal wastewaters for many emerging contaminants. Some studies have relied on single point calculations rather than sorption isotherms for calculating K_d values (Ternes et al., 2004; Golet et al., 2003; Göbel et al., 2005; Urase and Kikuta, 2005; Maurer et al., 2007; Wick et al., 2009; Radjenovic et al., 2009), which may not be appropriate at other TOrC concentrations. Only a limited set of emerging TOrCs that typically enter wastewater treatment plants have been extensively studied in regards to their sorption onto wastewater solids; the sorption behavior of positively-charged compounds is especially limited (Siegrist et al., 2003; Golet et al., 2003). Also, some of these studies relied on chemical inactivation techniques (Clara et al., 2004; Maurer et al., 2007; Yi and Harper, 2007; Wick et al., 2009) as opposed to nonchemical techniques (Ternes et al. 2004; Andersen et al., 2005), such as the lyophilization and dry-heating technique (Kerr et al. 2000). Chemical inactivation techniques, such as sodium azide and mercury salts, have the potential to affect the sorption behavior of compounds via the chemicals altering the aqueous matrix or the solids surface characteristics. Large and diverse datasets of experimentally determined partitioning coefficients for environmentally relevant conditions are valuable, both directly as inputs into mass balance models and for developing predictive models for the estimation of partitioning coefficients for compounds for which no experimental data are available.

Sorption of TOrCs to sludge solids can potentially depend on the fraction of organic carbon present on the solids. Sorption of nonionic solutes has been accurately expressed by the octanol-carbon distribution coefficient normalized to the organic-carbon content (Schwarzenbach et al., 2003)

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

where \( K_d \) is in L/kg_{solids}, \( K_{oc} \) is the organic-carbon distribution coefficient (L/kg_{orgc}), and \( f_{ac} \) is the fraction of organic carbon present on the solid (kg_{orgc}/kg_{solid}). Linear free energy relationships (LFERs) have been used for decades to estimate \( K_{oc} \) (Gawlik et al., 1997; Nguyen et al., 2005), where the octanol-water partitioning coefficient, \( K_{ow} \), has been widely used to estimate \( K_{oc} \) in one-parameter models (Gerstl, 1990; Sabljic et al., 1995; Huuskonen, 2003). These estimation techniques have the following form:

\[ \log K_{oc} = a \log K_{ow} + b \]

where \( a \) and \( b \) are constants estimated from empirical data. These models were developed using sorption datasets for soil/water systems and their applicability toward wastewater solids, where the fraction of organic carbon is much higher, requires verification.

The purpose of the current study was twofold: 1) to experimentally measure the partitioning coefficients of 34 emerging ionic and nonionic TOrCs onto sludge solids using a nonchemical lyophilization and air-heat inactivation technique, and 2) evaluate predictive models for partitioning based on \( \log K_{ow} \).

2. Methods

2.1. Sorption experiments

Sludge solids for sorption experiments came from three sources: primary clarifier sludge from Denver’s Wastewater Reclamation District facility (Denver Metro), mixed liquor from Denver Metro’s nitrified aeration basin, and mixed liquor from the nitrified aeration basin of the Colorado School of Mines’ (CSM’s) Mines Park laboratory-scale wastewater treatment system. Mixed liquor is defined as the mixture of raw or settled wastewater and activated-sludge in a bioreactor. Denver Metro’s treatment train consisted of primary clarification, a Modified Ludzack-Ettinger (MLE) process with nitrification, denitrification, and centrate side-stream treatment, secondary clarification and chlorination. The plant treated 344 MLD (344,000 m³/d) of municipal wastewater from the City of Denver, Colorado, which had an influent biochemical oxygen demand (BOD) of 300 mg/L. The plant was operated at a food to microbial (F/M) ratio of 0.3 and sludge retention time (SRT) of 5 days. The mixed liquor from Denver Metro had the following characteristics: pH 7, chemical oxygen demand (COD) = 11 mg/L, ammonia = 0.3 mg-N/L, nitrate = 0.3 mg-N/L, total suspended solids (TSS) = 2600 mg/L and total organic carbon (TOC) = 12 mg-C/L. Mines Park’s treatment train consisted of preliminary screening, secondary treatment with nitrification, and secondary clarification. The system treated 28 L/d (0.028 m³/d) from a student residential community at CSM, which had an influent COD of 900 mg/L. The plant was operated at a F/M ratio of 0.5, and SRT of 6 days. The mixed liquor from Mines Park had the following...
characteristics: pH 7, COD = 27 mg/L, ammonia = 0.5 mg-N/L, nitrate = 15 mg-N/L, TSS = 1500 mg/L and TOC = 8 mg-C/L.

Preliminary experiments were performed to determine the most appropriate method to biologically inactivate sludge solids, and these experiments and their results are described in Appendix B of the supplementary material. The lyophilization and dry-heat inactivation technique (Blackburn, 1985; USEPA, 1998; Kerr et al., 2000; Andersen et al., 2005) was chosen and used for isotherm sorption experiments since it is a nonchemical technique and it sufficiently inactivated sludge for the compounds examined. Using respirometry and measuring enzymatic activity Kerr et al. (2000) demonstrated this inactivation procedure selectively inhibited microbial activity for a period of approximately 24 h, and the type and degree of enzymatic activity was shown to be dramatically reduced in the sludge. Also the lyophilization and dry-heat method did not significantly alter the aqueous matrix as compared to the chemical inactivation technique, using 0.5% sodium azide and 5 mM Barium chloride and 5 mM nickel chloride (i.e., increase in ionic strength, trace divalent ions added). Preliminary inactivation comparison tests (shown in Appendix B) revealed the inactivation by chemical biocides affected the sorption of positively-charged compounds. Also, Kerr et al. (2000) demonstrated this lyophilization-dry-heat inactivation procedure did not significantly alter activated-sludge solids. Video-enhanced light microscopy revealed the structural integrity of the bacterial cell walls was maintained and zeta potential measurements confirmed this lyophilization-dry-heat inactivation procedure did not significantly alter activated-sludge solids. Video-enhanced light microscopy revealed the structural integrity of the bacterial cell walls was maintained and zeta potential measurements confirmed the negatively-charged surface was maintained on the solids.

Field sludge samples were processed immediately after collection. Sludge samples were allowed to settle and subsequently decanted in order to concentrate the solids. The remaining solids mixture was centrifuged (15 min., g-force ≈ 1050 g) in 250-mL polypropylene centrifuge bottles. The centrifuged supernatant was decanted and ultra pure water was added. The bottles were then shaken for 5 min and centrifuged again for 15 min. This process was repeated two more times for a total of three ultra pure water rinses. The supernatant was decanted and ultra pure water was added. The bottles were then shaken for 5 min and centrifuged again for 15 min. This process was repeated two more times for a total of three ultra pure water rinses. The supernatant was decanted and the remaining solids were placed into capped 50 mL clear glass jars. The solids were then lyophilized in a shelf-freeze dryer overnight (covered loosely with aluminum foil) using a LABCONCO FreeZone benchtop freeze drying system. For inactivation, the solids were lightly dried at ~80 °C for at least 24 h. The samples were then lyophilized in a shelf-freeze dryer overnight (covered loosely with aluminum foil) using a LABCONCO FreeZone benchtop freeze drying system. For inactivation, the solids were lightly ground and then placed in an oven at 103 °C overnight prior to being stored at 4 °C. The f<sub>oc</sub> of all dried sludge solids (Table S3) was measured by a UIC CMS014 coulometric solid-phase TOC analyzer. Prior to being used in a sorption experiment, freeze-dried solids were reheated at 103 °C overnight. Oven-dried solids were mixed with buffered synthetic wastewater (recipe listed in Appendix B of the supplementary material) using a shaker table followed by centrifugation and decantation. For primary-sludge solids a blender was required to initially homogenize the mixture. The rinsing procedure was repeated until the final aqueous TOC was <10 mg/L (Table 1). The inactivated-sludge solids were then used in sorption experiments immediately after washing.

Initial aqueous samples were collected (concentration data shown in Table S2 in supplementary material) before spiking TOrCs to determine the initial levels of the 34 TOrCs in the aqueous phase of the reconstituted freeze-dried sludge solution. Table 2 lists target TOrCs and Appendix A presents their structures and CAS numbers. Background concentrations in the buffered synthetic wastewater were below detection limits (data shown in Table S2 in supplementary material). Isotherm experiments were performed for freeze-dried TSS concentrations ranging between 500 and 10,000 mg/L (6 isotherm data points, shown in Table 1), and TOrCs were initially spiked at ~4 mM (exceptions being diazepam, omeprazole, and phenylphenol were spiked at lower concentrations; Table S1). All reactors were capped and mixed on a shaker table. Experiments were performed at ambient temperature (~ 19 °C) for 2 h. Based on preliminary kinetic tests (presented in Appendices B and C of the supplementary material), 2 h was determined to be sufficient for compounds to achieve partitioning equilibrium. The experimental procedure is presented in Appendix B and the following kinetic points were sampled: initial, 30 s, 1 h, 2 h, 4 h, and 24 h. Two hours was also used because concentrations of highly bio- amenable compounds, such as caffeine, were found to be reduced after 4 h during kinetic tests, suggesting the partial reactivation of sludge after this time. The initial conductivity was measured and pH was determined at the beginning and end of the experiments (Table 1). Isotherm tests were performed in duplicate.

A chemical abiotic control (with 0.5% sodium azide, 5 mM Barium chloride, and 5 mM nickel chloride) was performed in parallel which confirmed the freeze-dried sludge was sufficiently inactivated (recovery data shown in Table S5 in supplementary material). Abiotic controls were performed in duplicate. In addition, a sorption control was performed in
Table 2. List of measured $K_d$ and log $K_{oc}$ values for experimental TOrCs in each sludge, previously reported $K_d$ values for primary (p) secondary (s) sludge solids, charge state of the dominant species at pH 7, and log $D_{sw}$ at pH 7. Measured $K_d$ values in italics are based on single point calculations. Numbers in parenthesis for measured $K_d$ values are 95% confidence intervals with the exception of the these numbers in italics which are standard deviations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Denver Metro AS $K_d$ (L/kgSS)</th>
<th>Denver Metro Primary $K_d$ (L/kgSS)</th>
<th>Mines Park AS $K_d$ (L/kgSS)</th>
<th>Literature data $K_d$ (L/kgSS)</th>
<th>Charge at pH 7</th>
<th>log $D_{sw}$ at pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inactivated $K_{oc}$</td>
<td>Fresh $K_{oc}$</td>
<td>Inactivated $K_{oc}$</td>
<td>Fresh $K_{oc}$</td>
<td>Fresh $K_{oc}$</td>
<td>Fresh $K_{oc}$</td>
</tr>
<tr>
<td>Amitriptyline</td>
<td>4555 (±386) 4.01</td>
<td>386) 4.06</td>
<td>2343 (±292)</td>
<td>3.78</td>
<td>193 (±104)</td>
<td>3.63</td>
</tr>
<tr>
<td>Clozapine</td>
<td>1642 (±180) 3.56</td>
<td>1730 (±824)</td>
<td>1324 (±96)</td>
<td>3.41</td>
<td>193 (±104)</td>
<td>3.63</td>
</tr>
<tr>
<td>Verapamil</td>
<td>1501 (±77) 3.52</td>
<td>1644 (±348)</td>
<td>1232 (±149)</td>
<td>3.44</td>
<td>1017 (±76)</td>
<td>3.39</td>
</tr>
<tr>
<td>Risperidone</td>
<td>861 (±119) 3.28</td>
<td>964 (±99)</td>
<td>669 (±70)</td>
<td>3.17</td>
<td>808 (±171)</td>
<td>3.25</td>
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<tr>
<td>Hydroxyzine</td>
<td>819 (±125) 3.26</td>
<td>778 (±154)</td>
<td>920 (±190)</td>
<td>3.25</td>
<td>808 (±171)</td>
<td>3.25</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>119 (±49) 2.42</td>
<td>251 (±99)</td>
<td>193 (±104)</td>
<td>3.63</td>
<td>213 (±104)</td>
<td>3.63</td>
</tr>
<tr>
<td>Atenolol</td>
<td>&lt;30</td>
<td>46 (±6)</td>
<td>35</td>
<td>BD</td>
<td>35</td>
<td>BD</td>
</tr>
<tr>
<td>Ethynylestradiol (−17α)</td>
<td>1550 (±223) 3.54</td>
<td>1017 (±105)</td>
<td>607 (±148)</td>
<td>3.13</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Estrone</td>
<td>645 (±87) 3.16</td>
<td>636 (±104)</td>
<td>419 (±80)</td>
<td>2.97</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Estradiol (−17β)</td>
<td>771 (±108) 3.23</td>
<td>560 (±67)</td>
<td>136 (±17)</td>
<td>2.48</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Androsterone</td>
<td>579 (±108) 3.11</td>
<td>534 (±81)</td>
<td>136 (±17)</td>
<td>2.48</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Testosterone</td>
<td>157 (±36) 2.54</td>
<td>178 (±22)</td>
<td>134 (±13) BD</td>
<td>2.47</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Androstenedione</td>
<td>156 (±6) 2.54</td>
<td>174 (±22)</td>
<td>134 (±13) BD</td>
<td>2.47</td>
<td>1506 (±476)</td>
<td>3.74</td>
</tr>
<tr>
<td>Estril</td>
<td>63</td>
<td>58 (±22)</td>
<td>54</td>
<td>BD</td>
<td>54</td>
<td>BD</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>411 (±25) 2.98</td>
<td>314 (±66)</td>
<td>505 (±83)</td>
<td>3.05</td>
<td>505 (±83)</td>
<td>3.05</td>
</tr>
<tr>
<td>Phenylphenol</td>
<td>347 (±64) 2.89</td>
<td>652 (±161)</td>
<td>259 (±69) BD</td>
<td>2.76</td>
<td>217 (±27)</td>
<td>2.76</td>
</tr>
<tr>
<td>Diazepam</td>
<td>241 (±59) 2.73</td>
<td>291 (±50)</td>
<td>197 (±31)</td>
<td>2.64</td>
<td>197 (±31)</td>
<td>2.64</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>50 (±1) 2.05</td>
<td>65 (±5)</td>
<td>36 (±2)</td>
<td>1.90</td>
<td>36 (±2)</td>
<td>1.90</td>
</tr>
<tr>
<td>DEET</td>
<td>42</td>
<td>1.97</td>
<td>100 (±19)</td>
<td>2.30</td>
<td>100 (±19)</td>
<td>2.30</td>
</tr>
<tr>
<td>Omeprazole</td>
<td>107 (±25) 2.38</td>
<td>130 (±25)</td>
<td>169 (±40) 226</td>
<td>2.57</td>
<td>169 (±40) 226</td>
<td>2.57</td>
</tr>
<tr>
<td>Atrazine</td>
<td>60 (±2) 2.12</td>
<td>122 (±24)</td>
<td>193 (±89)</td>
<td>2.89</td>
<td>193 (±89)</td>
<td>2.89</td>
</tr>
<tr>
<td>TCEP</td>
<td>65 (±20) 2.16</td>
<td>162 (±72)</td>
<td>231</td>
<td>2.51</td>
<td>162 (±72)</td>
<td>2.51</td>
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<tr>
<td>Primidone</td>
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<td>45 (±10)</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
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</tr>
<tr>
<td>Neopropanamide</td>
<td>&lt;30</td>
<td>42 (±12)</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>BD</td>
<td>&lt;30</td>
<td>&lt;30</td>
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<tr>
<td>Caffeine</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>BD</td>
<td>&lt;30</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Atorvastatin</td>
<td>198 (±69) 2.64</td>
<td>216 (±82)</td>
<td>93</td>
<td>2.64</td>
<td>106 (±36)</td>
<td>2.32</td>
</tr>
<tr>
<td>Dilantin</td>
<td>81</td>
<td>2.26</td>
<td>45 (±22)</td>
<td>1.95</td>
<td>32</td>
<td>106 (±36)</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>45</td>
<td>2.00</td>
<td>45 (±9)</td>
<td>1.95</td>
<td>30</td>
<td>106 (±36)</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>BD</td>
<td>&lt;30</td>
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<tr>
<td>Diclofenac</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
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<tr>
<td>Naproxen</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>BD</td>
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<tr>
<td>Sulfamethoxazole</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;150</td>
<td>&lt;30</td>
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<tr>
<td>Enalapril</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>BD</td>
<td>&lt;30</td>
<td>&lt;30</td>
</tr>
</tbody>
</table>

BD — compound degraded, so $K_d$ could not be determined.
α — percentage distribution of the acid species.
1Radjenovic et al., 2009; 2Göbel et al., 2005; 3Ternes et al., 2004; 4Urase and Kikuta, 2005; 5Wick et al., 2009; 6Andersen et al., 2005; 7ChemAxon, 2010; 8Dickenson et al., 2010.
torc fraction of compound in the aqueous phase (\( \text{aq} \)) was taken as the measured concentration at 2 h minus the initial aqueous concentration as measured from aqueous blanks. Assuming equilibrium partitioning of initially present TOrCs had occurred before TOrCs were dosed, \( M_{\text{aq}} \) is the amount of dosed TOrC that remained in the aqueous phase. As utilized in other studies (Andersen et al., 2005), the amount of any given TOrC in the solid phase (\( M_{\text{s}} \)) was calculated from the mass balance equation: \( M_{\text{s}} = M_{\text{aq}} + M_{\text{d}} \), where the amount of TOrC dosed (\( M_{\text{d}} \)) was measured from the dosing controls. This assumes the TOrCs will only be present either in the aqueous or solid phases. Data was omitted where the 95% confidence interval for some compounds. For low sorbing compounds, the data did not fit a linear isotherm and single point \( K_d \) values were determined.

2.2. Analytical methods

TOrCs were measured by an isotope-dilution LC-MS/MS method using an Applied Biosystems API 4000 Q-Trap. This method was based on the methods developed by Vanderford et al. (2003) and Vanderford and Snyder (2006). Vanderford and Snyder (2006) observed that without employing isotope dilution, TOrC levels can be greatly underestimated due to matrix suppression of ion formation. Accordingly, isotope dilution was used to correct for matrix suppression, solid-phase extraction losses, and reconstitution and instrument variability. Details of the LC-MS/MS method and the monitored mass spectral transitions are provided in Appendix E in the supplementary material. New isotopic dilution methods were developed for the following compounds: omeprazole, clozapine, amitriptyline, verapamil, and hydroxyzine. External calibration results for phenylphenol were uncorrected as the transitions for its isotope surrogate failed QA/QC criteria, and results for TCEP were also uncorrected because an isotopic standard was not available.

250 mL of sludge samples for TOrC analysis were initially centrifuged (15 min., g-force = 1050 g) with 250 mL polypropylene centrifuge bottles and then the supernatant was filtered with a 1.2 \( \mu \)m filter (Whatman® GF/C glass fiber filter) prior to solid-phase extraction. Centrifuge and filtered controls were performed to assess losses during centrifugation followed by filtration. For this test target compounds were spiked between 369 and 5260 ng/L in buffered synthetic wastewater (pH 7). Samples were collected prior to centrifugation and after centrifugation/filtration. Results are shown in Table S4. For most compounds, recoveries were near 100% indicating very little loss of compounds during centrifugation and filtration.

After centrifugation/filtration a solution containing 100 ng of each of the isotopically labeled standards was added to samples at pH 6–7 prior to solid-phase extraction with plastic Waters Oasis® HLB cartridges (6 cc/500 mg, 60 \( \mu \)m; Part# 186000115). Cartridges were sequentially preconditioned using 5 mL of MTBE, 5 mL of methanol, and 5 mL of ultra pure water. Then cartridges were loaded with sample at approximately 5 mL/min. After loading, the cartridges were rinsed with 5 mL of ultra pure water. Cartridges were then dried under nitrogen until they were visibly dry. Dried cartridges were stored and cooled at 4 °C in sealed plastic bags pending analysis.

3. Results and discussion

3.1. Sorption isotherm experiments

Isotherm plots for 2 compounds, estrone and verapamil, on activated-sludge solids from Denver Metro and primary sludges from Denver Metro are illustrated in Fig. 1. Isotherm plots for other compounds are presented in Appendix D in the supplementary material. Table 2 lists \( K_d \) values for each compound in each sludge, as well as the compound’s charge state and octanol-water partitioning coefficient at pH 7, and, if available, previously reported partitioning coefficients for primary and secondary sludges. Single point \( K_d \) values should be considered rough estimates, though they are low, indicating these compounds sorb relatively poorly. Compounds with \( K_d < 30 \text{ L/kg} \) for inactivated sludge are compounds with low sorption potential, since \( f_w > 0.8 \) for these compounds. Likewise, \( K_d \) values for atenolol, carbamazepine, diclofenac, gemfibrozil, ibuprofen, naproxen, primidone, and sulfamethoxazole have been previously reported to be low (<100 L/kg) (Ternes et al., 2004; Andersen et al., 2005; Urase and Kikuta, 2005; Maurer et al., 2007; Wick et al., 2009; Radjenovic et al., 2009).

Nineteen compounds in Table 2 do not have previously reported partitioning sorption coefficients for secondary and primary-sludge solids. Interestingly, positively-charged aromatic compounds, such as amitriptyline, clozapine, verapamil, risperidone, and hydroxyzine, have the highest \( K_d \) values. Like-wise, \( K_d \) values for atenolol, carbamazepine, diclofenac, gemfibrozil, ibuprofen, naproxen, primidone, and sulfamethoxazole have been previously reported to be low (<100 L/kg) (Ternes et al., 2004; Andersen et al., 2005; Urase and Kikuta, 2005; Maurer et al., 2007; Wick et al., 2009; Radjenovic et al., 2009).

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also have high log $K_d$ values of $\sim 4$ (Golet et al., 2003). However, positively-charged compounds, trimethoprim and atenolol, had a noticeably lower potential to sorb to sludge solids. Similar $K_d$ magnitudes for trimethoprim were observed by others (Göbel et al., 2005; Radjenovic et al., 2009). One chemical characteristic difference between atenolol and the other positively-charged compounds (i.e., amitriptyline, clozapine, verapamil, risperidone, hydroxyzine) is that the latter compounds are distinctly more hydrophobic at pH 7 (log $D_{ow}$ 1–3) as compared to atenolol (log $D_{ow}$ –2.14). This suggests the hydrophobic sorption interactions are still important for positively-charged compounds. However, trimethoprim and risperidone have similar log $D_{ow}$ values at pH 7, 0.92 and 0.86, respectively, though risperidone has a much higher sorption potential. The reason for this is unknown. It is important to point out the pH varied from 6.7 to 7.9 between the different sludge concentrations (Table 1), which likely affected the results for the partly charged compounds near neutral pH, like clozapine ($pK_a$ 7.35), hydroxyzine ($pK_a$ 7.92), and trimethoprim ($pK_a$ 7.16).

The neutral hormones, 17α-ethinylestradiol, 17β-estradiol, androsterone, and estrone have high $K_d$ values ranging from 419 to 1550 L/kgSS, though these are lower, except for 17α-ethinylestradiol, than the highly-sorbing positively-charged compounds. For these compounds the high $K_d$ values corresponded to high log $K_{ow}$ values (3.7–4.3). Interestingly, these log $K_{ow}$ values are 1 log unit higher than the log $D_{ow}$ values for the positively-charged compounds that had a higher sorption potential. Assuming hydrophobic interaction is a sorption driver for steroidal hormones it is unknown why androstenedione with a log $K_{ow}$ of 3.93 and similar in structure, did not have a higher sorption potential, $K_d$ is only 134–174 L/kgSS.

A set of other neutral compounds, testosterone, bisphenol A, phenylphenol and diazepam generally has lower $K_d$ values, 136–652 L/kgSS, than the before mentioned high-sorbing steroidal compounds. These lower $K_d$ values corresponded with lower log $K_{ow}$ values of 3.1–4.0. Interestingly, omeprazole has comparable $K_d$ values of 107–169 L/kgSS, eventhough it has a lower log $K_{ow}$ value of 2.43. Though the neutral species for omeprazole dominates at pH 7 (99.2%) the protonated form is 0.59% present, which could be responsible for the increased sorption due to electrostatic interactions. Neutral compounds, estriol, carbamazepine, DEET, atrazine, TCEP, primidone, meprobamate, acetaminophen, and caffeine, have lower $K_d$ values <30–162 L/kgSS, which corresponded with lower log $K_{ow}$ values of −0.5 to 2.8. In general, increasing log $K_{ow}$ is indicative of increasing sorption potential for neutral compounds.

Negatively-charged compounds, atorvastatin, dilantin, and gemfibrozil, have $K_d$ values of 93–216, 32–81, and 30–45 L/kgSS, respectively, which correlates in descending order with their respective log $D_{ow}$ values of 2.8, 2.1 and 1.9. The other negatively-charged compounds, ibuprofen, diclofenac, naproxen, sulfamethoxazole and enalapril, have $K_d$ values <30 L/kgSS, where log $D_{ow}$ is <1.7 for these compounds. Similar to the neutral compounds, increasing log $D_{ow}$ is indicative of increasing sorption potential for negatively-charged compounds.

Mines Park $K_d$ values determined using the lyophilized and dry-heated inactivation technique were comparable with those generated with fresh activated-sludge for positively-charged compounds, amitriptyline, clozapine, verapamil, risperidone, hydroxyzine, and trimethoprim, neutral compounds, omeprazole and diazepam, and the negatively-charged compound, atorvastatin (Table 2). These compounds were observed to be recalcitrant in complementary biodegradability studies using mixed liquor sample from the same Mines Park aerobic/nitrified treatment process (Dickenson et al., 2010). Kerr et al. (2000) further confirmed good agreement between $K_d$ values determined by the lyophilized and dry-heated inactivation technique with those derived from fresh activated-sludge for four surfactant, quaternary ammonium and chelator compounds. These results indicate the sorption behavior on lyophilized and dry-heated inactivation technique with those derived from fresh activated-sludge for positively-charged compounds.

An abiotic control was performed, which consisted of the addition of chemical biocides, 0.5% sodium azide, 5 mM...
barium chloride, and 5 mM nickel chloride, to reconstituted lyophilized and dry-heated sludge solids. For most compounds and sludges the compound concentrations after 2 h in the sorption tests were comparable to the levels observed after 2 h in the abiotic controls (recoveries are reported in Table S5), indicating the compounds were not attenuated by biological mechanisms during sorption tests. The abiotic tests also allowed for assessment of the impact of the applied chemical biocide in the abiotic control on sorption behavior. For example, sorption potential for lyophilized and dry-heated sludge solids was significantly higher for highly-sorbing positively-charged compounds, amitriptyline, clozapine, hydroxyzine, risperidone and verapamil, (indicative of recoveries >170% in Table S5). It is believed the increased removal was not due to biological attenuation mechanisms, since these compounds were observed to be recalcitrant in complementary biodegradability studies. Furthermore, since the sorption behavior of these compounds on lyophilized and dry-heated sludge solids and fresh solids are comparable, this suggests these chemical biocides are leading to an underestimation of the sorption potential and should not be used for assessing sorption for highly-sorbing positively-charged compounds.

The sorption behavior of estrone, 17β-estradiol and 17α-ethynylestradiol to activated-sludge has been previously studied (Ternes et al., 2004; Urase and Kikuta, 2005; Andersen et al., 2005; Yi and Harper, 2007). For these nonionic compounds it is assumed that sorption is governed by partitioning to the organic phase \((f_{oc})\) in the activated-sludge, and therefore a comparison of \(\log K_{oc}\) values was assessed. \(K_{oc}\) was calculated using reported \(K_d\) values and measured or assumed \(f_{oc}\) values. The \(f_{oc}\) of 34 and 27.7% was measured by Ternes et al. (2004) and Urase and Kikuta (2005), respectively, and 40% was assumed for the Urase and Kikuta (2005) and Yi and Harper (2007) studies. \(\log K_{oc}\) values obtained for estrone, 2.8–3.2 (Urase and Kikuta, 2005; Andersen et al., 2005), 17β-estradiol, 3.1–3.2 (Urase and Kikuta, 2005; Andersen et al., 2005), and 17α-ethynylestradiol, 2.9–3.3 (Ternes et al., 2004; Urase and Kikuta, 2005; Andersen et al., 2005; Yi and Harper, 2007) are similar to those measured for Denver Metro and Mines Park activated-sludge solids, 3.1–3.5, as reported in Table 2.

\(K_d\) values are comparable between the three sludges (Fig. 2). The high correlation of coefficients between activated- and primary-sludge solids \((r = 0.96, n = 23)\) indicates that sorptive behavior is relatively similar during these two stages of wastewater treatment at Denver Metro. \(K_d\) values obtained from the two activated-sludge sources are also highly correlated \((r = 0.97, n = 21)\), indicating that these results are replicable across two aerated and nitrified sludges, even though the sludge solids derive from two systems operated at extremely different scales, 344,000 m²/d versus 0.028 m³/d, and treating different types of wastewater, municipal versus one from a university student population. Interestingly, Carballa et al. (2008) also found that sorption potential for digested sludges are similar to primary and secondary sludges for pharmaceutically-active compounds, such as carbamazepine, ibuprofen naproxen, diclofenac, and sulfamethoxazole, and estrogens, such as estrone, 17β-estradiol and 17α-ethynylestradiol.

Based on observed effects of charge and hydrophobicity on sorption behavior, compounds were subdivided into three classes of compounds: 1) nonionic, 2) negatively-charged, and 3) positively-charged compounds at pH 7. Fig. 3 plots measured \(\log K_{oc}\) in Denver Metro activated-sludge against calculated \(\log D_{ow}\) as estimated by Marvin Calculator Plugins version 5.1.5 (ChemAxon, 2010) for the three classes of compounds. A similar Figure (Appendix F of the supplementary material) combines all the measured \(\log K_{oc}\) values for the three sludge-solids studies. The Denver Metro activated-sludge experimental results showed some correlation between \(\log K_{oc}\) and \(\log D_{ow}\) for nonionic compounds \((r = 0.82, n = 14)\). Considering nonionic and negatively-charged compounds together, the correlation is slightly higher \((r = 0.83, n = 17)\). For the positively-charged compounds alone a correlation is also observed \((r = 0.61, n = 6)\), suggesting sorption of positively-charged compounds is related to hydrophobic interactions, but since their \(\log K_{oc}\) values are consistently higher than nonionic or negatively-charged compounds with similar \(\log D_{ow}\) values, this also suggests other types of sorption mechanisms (e.g., electrostatic interactions) are involved and, in some cases, may be dominating.

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Fig. 2 – Comparison of \(K_d\) values obtained from Denver Metro primary sludge (left) and Mines Park activated-sludge (right) to \(K_d\) values obtained from Denver Metro activated-sludge.
3.2. Evaluation of log $K_{oc}$ based models

Previous studies have developed simple LFER models for predicting log $K_{oc}$ from log $K_{ow}$ using soil-based systems. Three such models are listed below.

$$\log K_{oc} = 0.52 \times \log K_{ow} + 1.02 \quad \text{(Sabljic et al., 1995)}$$

$(n = 390, R^2 = 0.63)$

$$\log K_{oc} = 0.679 \times \log K_{ow} + 0.663 \quad \text{(Gerstl, 1990)}$$

$(n = 419, R^2 = 0.83)$

$$\log K_{oc} = 0.6 \times \log K_{ow} + 0.84 \quad \text{(Huuskonen, 2003)}$$

$(n = 403, R^2 = 0.79)$

These models were developed using large, diverse sets of organic compounds. Fig. 4 plots log $K_{oc}$ observed in Denver Metro activated-sludge against log $K_{ow}$ for nonionic compounds. The three models above are represented by lines that overlay the data. Sabljic et al. (1995) provides the best-fit model, having the lowest root mean square error (RMSE) of 0.296. The RMSE incorporates both bias as a measure of accuracy and error variance as a measure of precision, giving a measure of overall fit. Even though these models are based on soils systems, they can be applied to sludge solids and are able to predict the log $K_{oc}$ within 1 log unit for log $K_{ow} > 2$. Carballa et al. (2008) found similar results, where they compared measured $K_{oc}$ values for sorption of nonionic compounds to digested sludge with estimated $K_{oc}$ using the following linear equation: log $K_{oc} = 0.74 \times \log D_{ow} + 0.15$. They found for the neutral compounds (log $K_{ow} > 2.5$) the model consistently under predicted the measured $K_{oc}$, but the predictions were still within 1 log unit. In comparison, the best-fit linear model possible for our dataset is log $K_{oc} = 0.602 \times \log K_{ow} + 0.695$, which has a RMSE of 0.285. Similar simplified relationships are lacking and needed for positively-charged compounds, since these compounds with log $D_{ow} > 1$ have a strong sorbing tendency.

4. Conclusions

Experimental sorption partitioning coefficients, $K_d$, were quantified for a diverse suite of TOCs for three different wastewater sludge solids, where 19 of these chemicals did not have previously reported values. Five positively-charged compounds had the highest sorption potential. Sludge solids were inactivated by a nonchemical lyophilization and dry-heat technique, which provided similar sorption behavior as compared to fresh sludge. The sorption behavior was comparable between primary- and activated-sludge solids and activated-sludge solids from two nitrifying basins from different wastewater treatment systems. Simple LFERs based on log $K_{ow}$ can be used to predict the solids-water partitioning of emerging TOCs in primary or activated-sludge. However simplified empirical models to predict the sorption behavior for positively-charged compounds are lacking. These are critical fate estimating techniques, since many TOCs, such as pharmaceuticals, are charged at wastewater pH conditions. For the development of robust prediction techniques additional high-quality sorption data for structurally diverse compounds, specifically ionic compounds, is needed.
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Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.watres.2011.03.056.

REFERENCES


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