Predicting the sorption of fatty alcohols and alcohol ethoxylates to effluent and receiving water solids ☆

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Abstract

Alcohol ethoxylates (AEs) are an important group of nonionic surfactants. Commercial AEs consist of a mixture of several homologues of varying carbon chain length (C_x) and degree of ethoxylation (EO_y). The major disposal route of AE is down the drain to municipal wastewater treatment plants that discharge into receiving surface waters. Sorption of AE homologues onto activated sludge and river water solids is an important factor in assessing exposure of AE in the environment. This study presents the experimental determination of sorption coefficients for a wide array of AE homologues including five alcohols under environmentally relevant conditions and combines these data with literature data to generate a predictive model for the sorption of AEs in the environment. These results demonstrate that sorption can be effectively modeled using a $\log K_d$ vs. C_x and EO_y predictive equation having the form $\log K_d = 0.331 C - 0.00897 EO - 1.126 (R^2 = 0.64)$.

1. Introduction

Alcohol ethoxylates (AEs) are an important group of nonionic surfactants. Commercial AEs generally consist of a mixture of several homologues of varying carbon chain length (C_x) and degree of ethoxylation (EO_y). These surfactants are widely used in domestic and commercial detergents, household cleaners, and personal care products. The major disposal route of AEs is down the drain through sewage systems and municipal wastewater treatment plants (WWTP) into receiving surface waters. This makes the fate and effects of residual AEs in treated sewage effluent of interest to industry and regulators alike. AEs have been the

subject of several environmental risk assessments including those of Little (1977), Goyer et al. (1981), Talmadge (1994), van de Plassche and de Bruijn (1997), van de Plassche et al. (1999), and Vandepitte and Feijtel (2000). These assessments have become increasingly sophisticated with numerous advancements in understanding analytical methods, exposure, fate, and effects in the environment.

The newly advanced pyridinium derivatization method has been used in Europe and North America (Dunphy et al., 2001; Eadsforth et al., 2005; Morrall et al., 2005) to monitor WWTP effluents containing AE. Concentrations of total AE in WWTP effluents ranged from 1.0 to 23 μg/L in Europe, Canada, and the United States (Matthijs et al., 1999; Eadsforth et al., 2005; Morrall et al., 2005). These data were gathered from well-operated activated sludge WWTP. Castillo et al. (2000), using a less specific and less sensitive analytical method and a different set of WWTPs, observed effluent total AE concentrations from <2 to 409 μg/L for three WWTPs on three occasions. The

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analytical method used by these authors is less specific in that it does not provide full homologue quantification (by carbon number and by ethoxylate number) but, rather, groups ethoxymers (EO_2–EO_{18}) into a single alkyl chain length. Additionally, the method does not detect any ethoxymers below EO_2. The reported detection limits in some cases are in the low-μg/L range, whereas the pyridinium method has a ng/L detection limit, an order of magnitude difference in sensitivity. Thus, the pyridinium method represents state of the art for AE quantification.

Another factor in effluent concentrations reported by Castillo (2000) is the operating conditions of the WWTP effluent plants. Poor operating conditions could account for the wide range of results. However, eight out of nine samples taken from three plants on three dates in the Castillo study showed total AE concentrations to be in the range of <2–40 μg/L, consistent with the other authors' results. One of the nine samples had a total AE of 409 μg/L. The WWTP used as a source of this effluent sample appears to have been operating under suboptimal conditions, as evidenced by total suspended solids (SS) removal of only 60–70% and low organic removal of 70% and this may explain the anomalous high value.

Total concentration does not reveal the relevant exposure of AE because the environmental fingerprint of the homologue distribution is of fundamental importance when assessing the risk of AE. With the advent of the pyridinium method, a full fingerprint of 114 AE homologues, including nonethoxylated alcohols, is achievable. These alcohols are present in sufficient amounts to be important in the risk assessment interpretation. In other studies, the presence of fatty alcohol in WWTP effluent is known to occur from natural microbial and metabolic processes (Leeming et al., 1994; Mudge and Norris, 1997; Mudge and Duce, 2005), use in consumer products (Modler et al., 2002), and degradation of alcohol-based surfactants (Wind et al., 2005).

Recently, investigators have gained further perspective on exposure of alcohols in WWTP effluents by determining their removal and metabolite formation in a benchtop continuous activated sludge test by Wind et al. (2005) and in batch radiotracer studies by Itrich and Federle (2005). Using AE as the sole surfactant source, these studies support an interpretation of extremely rapid biodegradation and address the fraction of alcohol present due to AE biodegradation (Wind et al., 2005). The application of this information to a risk assessment has also been demonstrated (Belanger et al., 2005).

Sorption onto activated sludge particles is an important process in removing surfactants from sewage (Brunner et al., 1998). Additionally, sorption onto receiving water and sediment solids plays an important role in bioavailability and should be taken into consideration when conducting ecological effects studies (Belanger et al., 2005; Kiewiet et al., 1996; Brownawell et al., 1997; Cano and Dorn, 1996a, b; McAvoy and Kerr, 2001). It is impractical to determine measured sorption constants for each of the 114

AE homologues. A quantitative correlation between carbon chain length and EO number and sorption coefficient is thus sought to account for the bioavailability, or free fraction, of each homologue in a risk assessment. Kiewiet et al. (1996) reported a sorption coefficient ($\log K_{s/w}$) predictive equation based on carbon and ethoxylate numbers using data from a set of 11 AE homologues:

$$\log K_{s/w} = 0.33C + 0.06EO - 1.7, \tag{1}$$

where C is the number of alkyl carbon atoms and EO is the number of ethoxy units.

Thus, both the alkyl chain length (carbon number) and the number of ethoxy units (EO) affect sorption. Previous studies have consistently shown a direct relationship between increasing carbon number and sorption. However, these studies disagree on the effect of EO units. Kiewiet et al. (1996) and Cano and Dorn (1996a, b) reported a direct relationship between increasing EO number and sorption. McAvoy and Kerr (2001), however, reported an inverse relationship between sorption and EO number. In all cases, it is clear that the alkyl chain length dominates as a sorption determinate and EO number plays a secondary minor role in sorption.

Sorption data are reported in some cases (Kiewiet et al., 1993, 1996, 1997; McAvoy and Kerr, 2001) as a linear sorption isotherm with a constant distribution ratio while others (Brownawell et al., 1997; Cano and Dorn, 1996a, b) found the sorption to be nonlinear and represented by a Freundlich isotherm:

$$C_s = K_f C_w^n, \tag{2}$$

where K_f is the Freundlich sorption coefficient that expresses the affinity of a surfactant for a given solid sorbent, while the exponent, n, is a measure of isotherm nonlinearity.

The nonlinearity of these results is attributable to some combination of the starting concentration (dominating) and the effect of increasing ethoxy groups on the sorption to the surface of the substrate, whereas linear isotherms are observed for lower concentrations and/or increasing carbon numbers.

Normalization of the sorption coefficient, K_d, to the sediment organic carbon fraction, f_{oc}, has been done in some studies such as Kiewiet et al. (1997) and McAvoy and Kerr (2001), and the sorption coefficient has been reported as K_{oc}. However, Brownawell et al. (1997), Kiewiet et al. (1996), and Cano and Dorn (1996a, b) reported sorption coefficients without carbon normalization. These authors reported the f_{oc} of these sediments, however. Sediment organic carbon fraction is not the only factor affecting sorption. Cation exchange capacity, clay fraction, and surface area also play roles in sorption and can interact with both the alkyl chain and the EO units. Cano and Dorn (1996a) speculated that clay and EO number have a direct relationship, for example. All authors state that the length of the alkyl side chain (hydrophobe) plays the dominant role in sorption, which supports a strong role for f_{oc} as a sediment characteristic.

To increase the ability of ecological risk assessments to account for environmental factors, it is desirable to produce a predictive equation for AE sorption and bioavailability building on the equation by Kiewiet et al. (1996) by the inclusion of additional literature data and new data from this study. This paper presents the results of an experimental determination of sorption coefficients of five AE homologues and a series of five alcohols under environmentally relevant conditions. Alcohols are included to account for their specific bioavailability and to determine whether their sorption behavior is consistent with that of the ethoxylated homologues in the distribution. These experimental results are combined with the literature sorption data for a wide range of AE homologues to generate a general predictive model for the sorption of AEs in the environment based on 69 sorption coefficients and representing 33 individual AE homologues.

2. Materials and methods

Two sorption studies, conducted in separate laboratories, are described below. The first study evaluated the sorption of five AE homologues with activated sludge and river water and is an extension of a previously reported study (McAvoy and Kerr, 2001). The second study evaluated the sorption of five alcohols onto a mixture of activated sludge and river water SS. Each study utilized activated sludge and river water samples in close proximity to the respective laboratory. The unique characteristics of the sampling and sorption procedures are described in the following sections.

2.1. AE sorption to activated sludge and river water solids

2.1.1. Test substances

Five ^{14}C-radiolabeled AE homologues ($C_{12}EO_3$, $C_{14}EO_3$, $C_{16}EO_3$, $C_{14}EO_1$, and $C_{14}EO_6$) were synthesized by Procter & Gamble and then used to determine AE sorption onto river water and activated sludge solids. Radiolabeled homologues were synthesized in the Procter & Gamble Laboratory (Cincinnati, OH) as described by McAvoy and Kerr (2001). The radiolabeled AE materials were characterized by thin-layer chromatography (TLC) with radiochemical imaging detection. A 1–2-µL aliquot of each AE was spotted on a 20×20-cm^2 silica gel plate (Whatman No. 485820). The following solvent systems were used to cover the range of test substance polarities: (1) 2% methanolchloroform for $C_{12}EO_3$, $C_{14}EO_3$, and $C_{16}EO_3$; (2) 95:5:1 methylene chloridemethanolformic acid for $C_{14}EO_6$; and (3) 3:1 hexaneethyl acetate for $C_{14}EO_1$. The plates were allowed to develop in the appropriate solvent system and then analyzed using a Bioscan Imaging Scanner. Radiochemical purities and specific activities were determined and are reported in Table 1.

2.1.2. River water

A river water grab sample was collected for the AE sorption experiments from the Ohio River in Covington, Kentucky near the mouth of the Licking River. The sample was taken following a period of high rainfall to maximize SS concentration. SS concentration was determined to be 150 mg/L using Standard Methods (APHA, 1995).

2.1.3. Activated sludge

An activated sludge grab sample was collected from the Polk Run Sewage Treatment Plant (STP) (Loveland, OH) (>90% domestic sewage) and immediately preserved with 4% formalin (v/v). The activated sludge mixed liquor suspended solids (MLSS) concentration was determined to be 3000 mg/L and the total organic carbon (TOC) concentration was measured at 1020 mg C/L using Standard Methods (APHA, 1995). These two values result in a fraction organic carbon (f_{oc}) content of 0.34.

2.1.4. Sorption procedures for AE
2.1.4.1. Test for linear isotherm AE.
To determine accurate sorption coefficients (K_d), it is essential that the concentration of the substance being tested fall within the linear portion of the sorption isotherm. This was accomplished in this study by determining the linear portion of the isotherm for both the river water and the activated sludge samples using $C_{14}EO_6$, which is the largest of the homologues being tested. The dose concentrations for the isotherm experiment were 25, 50, 100, and 200 µg/L, and the isotherm was determined with a single replicate test. The procedure followed for determining the aqueous and sorbed phases concentration is described in Section 2.1.4.2. These isotherms were used to determine the AE working concentration range for the subsequent river water and activated sludge sorption experiments.

2.1.4.2. River water sorption procedure.
Sorption coefficients for the five AE homologues with the Ohio River water solids were determined by a batch equilibrium method. Triplicate samples were prepared by placing 100 mL of river water into 250-mL polycarbonate centrifuge bottles; 4 mL of formalin was added to each sample as a preservative to avoid any biological activity. Initial experiments determined that formalin had no effect on the sorption behavior of these compounds. TLC was also used to verify that the test substance did not degrade during the experiment.

Each AE homologue was added to the appropriate centrifuge bottle at the range of concentrations given in Table 3, and the samples were equilibrated for 2 h on an orbital shaker (Lab-Line Instruments Model 3520) at 2000 rpm. Initial screening experiments determined that a 2-h equilibration time was sufficient to achieve equilibrium. Samples were then centrifuged (Beckman Model J2-21 centrifuge with rotor JA-14) at 10,000g for 20 min. Two 1-mL aliquots of the supernatants were removed and analyzed by liquid scintillation counting (LSC). The remaining supernatant was discarded. Several Milli-Q water washes were used to transfer the solids to a filtration device that contained a preweighed Whatman GF/C glass fiber filter. The solids were collected on the filter and then dried at 103 °C. The dried filter was weighed and the weight of the solids was determined by difference. The filters containing the solids were then combusted using a Packard Sample Oxidizer (Model 307), and the resulting radiolabeled CO_2 was trapped in scintillation cocktail and analyzed by LSC. A sorption coefficient (K_d) was determined by the ratio of the solid-phase concentration to the aqueous-phase concentration:

$$K_d = \frac{C_s}{C_w}, \tag{3}$$

where C_s is the concentration of AE homologues in the solid phase (mg/kg) and C_w is the concentration of AE homologues in the aqueous phase (mg/L).

2.1.4.3. Activated sludge sorption procedure.
Only the $C_{16}EO_3$ is reported as a new result for activated sludge. The other four AEs shown in Table 1 were previously reported (McAvoy and Kerr, 2001). A serious of 10-mL volumes of 4% (v/v) formalin-preserved activated sludge was placed into 15-mL glass centrifuge tubes. Each homologue was then spiked into the tubes at the concentrations shown in Table 3. Triplicate samples were equilibrated for 2 h on a LabQuake Shaker (Catalog No. T400-110) at a rate of 21 turnovers/min. The samples were then centrifuged (fixed-rotor Fisher Model 228) at 2000g for 5 min and two 1-mL aliquots of the supernatant were analyzed by LSC. The remaining supernatant was decanted and solids were analyzed by the same procedure as described above for the river water samples. Once the aqueous- and solid-phase concentrations were determined, the sorption coefficients (K_d) were calculated from the ratio of the solid-phase concentration (mg/kg) to the aqueous-phase concentration (mg/L) using Eq. (1).

2.1.4.4. Activated sludge plus river water sorption procedure.
The Ohio River water was spiked with the Polk Run activated sludge to simulate the river water matrix found below an STP outfall. A 2-L volume of Ohio River water was spiked with 2 mL of the Polk Run activated sludge. The mixture was stirred and then 100-mL volumes were transferred into 250-mL polycarbonate centrifuge bottles. With an initial activated sludge

Table 1
Test substances used in the activated sludge and river water sorption experiments

Test substance	CAS no.	Common name	Radio purity (%)	Specific activity (mCi/g)
[2-^{14}C]3,6,9-Trioxa-1-heneicosanol	3055-94-5	AE, $C_{12}EO_3$	92.3	17.0
[2-^{14}C]3,6,9-Trioxa-1-tricosanol	26826-30-2	AE, $C_{14}EO_3$	95.8	13.7
[2-^{14}C]3,6,9-Trioxa-1-pentacosanol	4484-59-7	AE, $C_{16}EO_3$	99.1	14.0
[1-^{14}C]3-Oxaheptadecanol	2136-70-1	AE, $C_{14}EO_1$	96.9	23.2
[16-^{14}C]3,6,9,12,15,18-Hexaoxadotricontanol	5157-04-0	AE, $C_{14}EO_6$	98.1	10.3

Table 2
Test alcohols used in activated sludge–river water sorption study

Test substance (lot number)	CAS no.	Common name	Radio purity (%)	Specific activity (mCi/g)
Dodecanol (030626)	112-53-8	$C_{12}EO_0$	99	295
Tetradecanol (030627)	112-72-1	$C_{14}EO_0$	99	257
Pentadecanol (030626)	629-76-5	$C_{15}EO_0$	99	232
Hexadecanol (030513)	36653-82-4	$C_{16}EO_0$	99	227
Octadecanol (030627)	112-92-5	$C_{18}EO_0$	99	203

solids concentration of 3000 mg/L and a river water SS concentration of 150 mg/L, the resulting final diluted activated sludge concentration was 3 mg/L. The sorption coefficients for all five AEs in Table 1 were determined using the river water procedure as described above and at AE test concentrations given in Table 3.

2.2. Alcohol sorption to activated sludge and river water solids

2.2.1. Alcohol test substances

Five linear primary alcohols C_xEO_0 uniformly radiolabeled with ^{14}C (250 µCi of each) were obtained from American Radiolabeled Chemicals Inc. of St. Louis, MO. Radiochemical purities and specific activities determined by the manufacturer of these alcohols are given in Table 2. The manufacturer indicated that radiolabeled impurities were nondetectable (pers. comm.).

Each alcohol was transferred from its supply vial to a 10-mL volumetric flask with methanol. The octadecanol vial was also finally rinsed with ca. 1 mL of ethyl acetate. These solutions were counted by LSC and the actual amount of each alcohol in solution was calculated. These values were compared to concentrations obtained by analysis of the solutions against unlabeled alcohols (Fluka, 97–99% purity) of the same carbon lengths by gas chromatography (GC). The ratios of the GC concentration to the LSC concentration are 0.95, 0.87, 0.83, 0.96, and 0.86 for C_{12}, C_{14}, C_{15}, C_{16}, and C_{18}, respectively.

2.2.2. River water

River water for the alcohol sorption study was collected from the River Gowy, Ellesmere Port, UK on August 5 and 6, 2003. Water from the two samplings was blended together to give a composite sample containing 12 mg/L SS. To prevent biological growth in the water prior to mixing with settled activated sludge, 0.01% (m/v) mercuric chloride was added.

2.2.3. Activated sludge

In the alcohol study, activated sludge was obtained from Chester, UK (United Utilities, Sealand Road) sewage treatment works, a plant that receives mainly (>90%) domestic-derived wastewater. Activated sludge (37 L) was collected from aeration tanks on July 31, 2003. The activated sludge was stirred at 150 rpm and aerated until August 5, 2003 when the MLSS and mixed liquor volatile SS were determined according to Standard Methods (APHA, 1995) to be 2940 and 2210 mg/L, respectively. The TOC content of the activated sludge was 880 mg/L. The activated

sludge was then deactivated by the addition of 37 g mercuric chloride to the 37 L of activated sludge (equivalent to 0.1% m/v).

2.2.4. Sorption procedures for alcohols

2.2.4.1. Preliminary settling studies on activated sludge.
Simulated STP effluent was prepared by settling activated sludge in batches according to the following procedure. Simulated STP effluent is defined here as the supernatant liquid that contains 30 mg/L SS after the activated sludge has been allowed to settle. Therefore, the settling time required to achieve 30 mg/L SS in the supernatant had to be determined. To do this, six 500-mL graduated glass bottles were filled with activated sludge. After the bottles were gently and consistently agitated to ensure that the contents were as well mixed as possible, a 100-mL aliquot of the supernatant liquid was withdrawn from one of the bottles by syringe at times ranging from 10 to 225 min. Each sample was collected from the supernatant at a consistent (from bottle to bottle) level below the liquid surface. The graduated marks on the bottles were used to locate the sample point. The first set of samples was collected at a level below the surface corresponding to the 400-mL graduation mark on the bottle. The SS in each 100-mL volume were measured. Settling time to 30 mg/L was determined from a graph of SS concentration vs. time, as shown in Fig. 1. The two final points did not fit a smooth curve, so a limited second study was conducted using the same procedure except that samples were collected at a level corresponding to the 300-mL graduation mark on the bottles. On the basis of the two sets of data, a settling time of 100 min to achieve a supernatant of 30 mg SS/L was determined.

2.2.4.2. Activated sludge spiking with alcohols.
The following procedures are illustrated by the flow scheme in Fig. 2. A 4-L aliquot of the activated sludge (2940 mg/L MLSS), which was inactivated with mercuric chloride (0.1% m/v), was dispensed into each of five 10-L aspirators. These were set to stir gently at 80 rpm, a speed sufficient to keep the solids in suspension but not too great to cause physical breakdown of the particles. Each vessel was then spiked with a stock solution of one of the radiolabeled alcohols to give a concentration of 100 ± 2 µg/L. The concentrations of the stock solutions were 93, 95, 125, 104, and 121 mg/L for C_{12}, C_{14}, C_{15}, C_{16}, and C_{18} alcohols, respectively. The volumes used were 4.3, 4.2, 3.2, 3.85, and 3.3 mL for C_{12}, C_{14}, C_{15}, C_{16}, and C_{18} alcohols, respectively. The sample was stirred for 24 h, which was found in preliminary testing to be adequate to achieve equilibrium.

2.2.4.3. Mixing settled activated sludge with river water. The spiked activated sludge sample for each alcohol was dispensed into 5500-mL bottles (Fig. 2). The aspirators containing the alcohols were gently agitated during and between subsampling to ensure as much homogeneity of activated sludge suspension as possible. The 25 bottles (five replicates of five different alcohols) were gently shaken, and allowed to settle for 100 min and 100-mL subsamples were taken from close to the 300-mL graduation of each bottle as described under preliminary settling studies on activated sludge and added to new flasks. This resulted in five synthetic STP effluent bottles having 30 mg/L SS for each of

the five alcohols being tested. Based on the preliminary settling rate test, each subsample of settled activated sludge was assumed to contain 30 mg/L SS.

Four 20-mL volumes of synthetic STP effluent from each of the 100-mL subsamples were pipetted into separate 300-mL bottles for dilution with river water. The remaining 20 mL from the synthetic STP effluent was used to determine the relative amounts of radioactivity in the aqueous and solid phases. This was done by LSC measurement of the whole sample followed by centrifugation for 20 min at 600g and subsequent counting of the supernatant.

Each of the other four 20-mL subsamples of synthetic STP effluent was diluted with 180-mL river water and agitated for 1, 5, 16, 30, or 72 h. It was anticipated that 72 h would be sufficient to achieve equilibrium in the samples. After the specified time the four replicates were filtered simultaneously through a 47-mm GF/C glass fiber filter under vacuum. The filter was retained for combustion and subsequent scintillation counting. The filtrate was subsampled in duplicate for scintillation counting. The emptied filtration flask, glass filtration funnel, and acrylic filter support were rinsed with methanol back into the sample bottle for estimation of amount of activity adsorbed onto these surfaces. This methanol was transferred to a scintillation vial, the methanol was evaporated, and the aqueous residue was counted by LSC.

2.2.4.4. Sorption of alcohols onto filters. Five sets of duplicate 200-mL volumes of filtered river water were spiked with each alcohol (at a level of activity equal to about twice the amount found in the settled activated sludges) and filtered through a GF/C filter to determine the amount of alcohol sorbed on to the filter when no solids were present. The filter was combusted as described above.
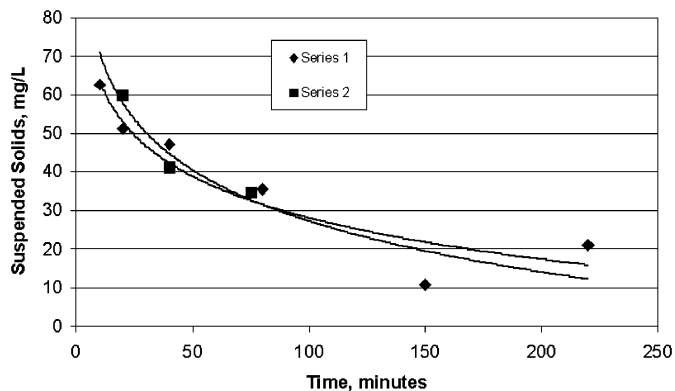

Fig. 1. Solids settling curve to determine time to achieve 30 mg/L suspended solids for alcohol sorption test.
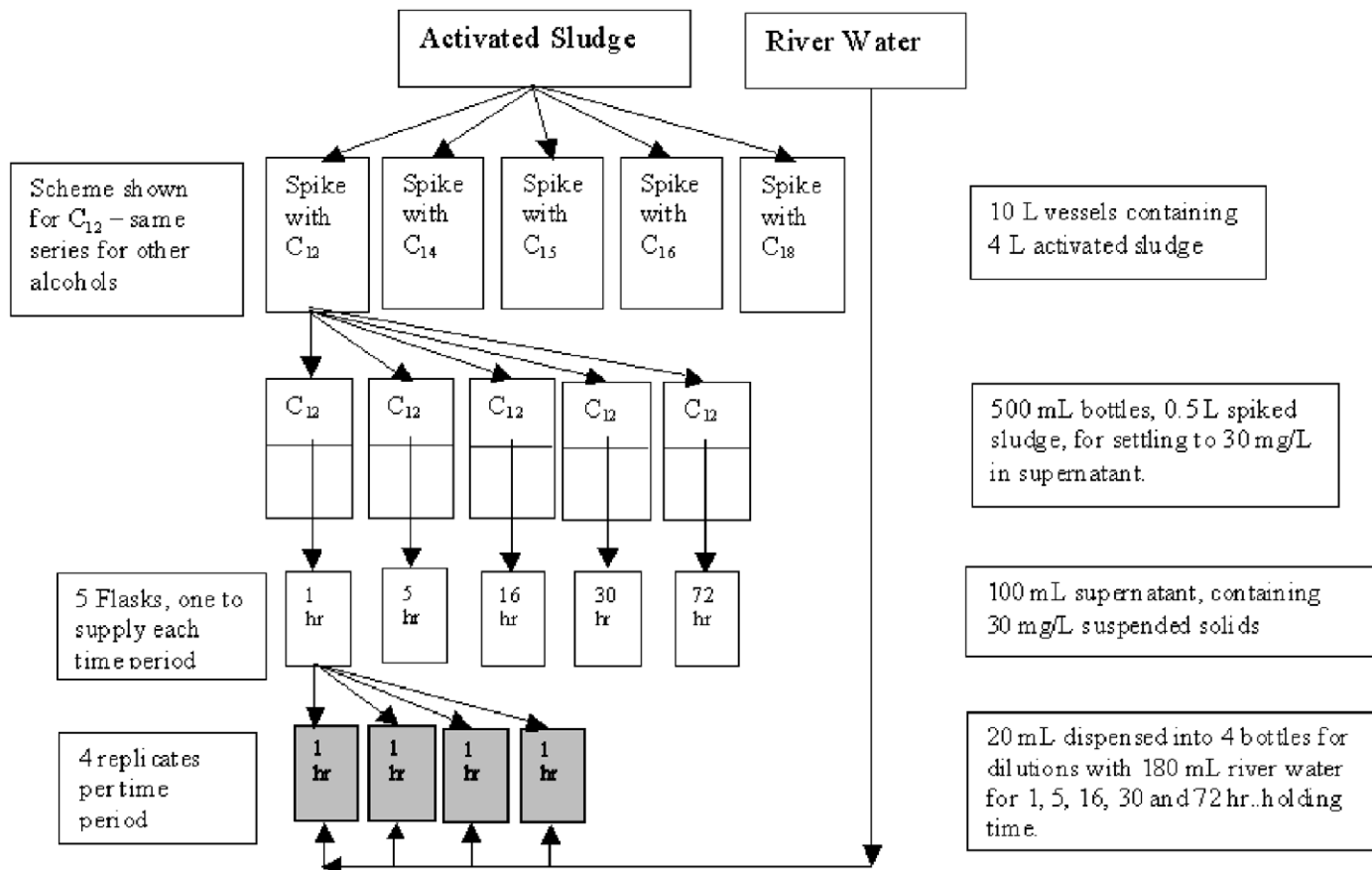

Fig. 2. Experimental schematic for determination of fatty alcohols sorption with activated sludge plus river water solids.

2.3. Mathematical fitting of sorption data

Experimental and literature data were plotted and mathematically fitted using the linear regression feature in Microsoft Excel:

$$\log K = xC + yEO + b, \tag{4}$$

where K is the sorption coefficient in L/kg, C is the carbon number of the alkyl side chain, and EO is the number of ethoxy units in the surfactant. The parameters x, y, and b are fitted by the regression routine that minimizes the least-squares residual (R^2).

3. Results

3.1. AE sorption isotherms on activated sludge and river water solids

Sorption coefficients were determined for the selected AE homologues in river water, 14 activated sludge, and in river water spiked with activated sludge. The linear portion of the isotherm for both the river water and the activated sludge samples was determined for the $C_{14}EO_6$ homologue (Fig. 3). The linear range of sorption for this homologue in river water was from 0 to 100 µg/L, while the linear range for activated sludge was from 0 to 200 µg/L. Based on these isotherm results, a concentration of 0.209 µM ($C_{14}EO_6$ at 100 µg/L) was chosen for subsequent determinations of the sorption coefficients for each of the homologues. Keeping the molar concentration the same for each homologue tested ensured that the sorption coefficients would be in the linear range. This concentration (0.209 µM) provides for the greatest analytical sensitivity within the linear range of the isotherm.

The sorption data for the AE homologues tested are shown in Table 3. These results demonstrate that the alkyl chain length is an important factor in the sorption of AE to activated sludge and river water solids. For river water the sorption coefficient increased more than an order of magnitude when the alkyl chain length increased from C_{12} to C_{16} (770–8970 L/kg). There was a similar trend for the activated sludge diluted into river water (1742–19,400 L/kg).
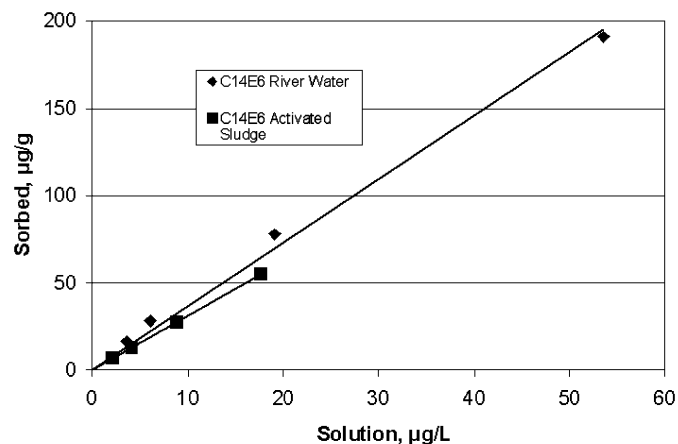

Fig. 3. Test for linear sorption range for AE with activated sludge and river water solids.

For sorption with activated sludge, there was an increase from C_{12} to C_{14} (1450–4140 L/kg) but not from C_{14} to C_{16} (4140–3900 L/kg). The ethoxylate group number exhibited an increase in sorption with an increase in the number of ethoxylate units for river water, although to a lesser extent than carbon number as shown for $C_{14}EO_1$ vs. $C_{14}EO_3$ (2330–5170 L/kg). The effect of EO units diminishes as shown by the sorption coefficients for $C_{14}EO_3$ vs. $C_{14}EO_6$ (5170–6410 L/kg). For activated sludge diluted in river water, the effect was similar for $C_{14}EO_1$ vs. $C_{14}EO_3$, but an increase in EO units beyond three suggests a slight negative effect on the sorption. This phenomenon was also observed with the activated sludge samples. The activated sludge diluted in the river water increased the sorption coefficient for all of the AE homologues tested, further supporting the importance of the hydrophobic interaction of the alkyl chain with an organic surface.

3.2. Alcohol sorption isotherms on activated sludge and river water solids

Sorption onto the glass fiber filter resulted in 1%, 9%, 11%, 25%, and 21% for the C_{12}, C_{14}, C_{15}, C_{16}, and C_{18} alcohols, respectively. These values were used to correct the sorption coefficient calculations for alcohols. The total recovery of radioactivity from the filtrate and filters was 100%, 75%, 81%, 85%, and 89% for C_{12}, C_{14}, C_{15}, C_{16}, and C_{18}, respectively. The remainder of the radioactivity was assumed to be lost to adsorption of alcohols onto glass surfaces during the experiments.

Alcohol sorption coefficients ($n = 4$) vs. time and carbon number, corrected for sorption onto the glass fiber filter, are shown in Table 4. The 72-h results are used for the development of the predictive model. It is assumed for the calculation of K_d that there are 2.76 mg of total solids in the test, composed of 0.6 mg of the settled activated sludge from 20 mL of 30 mg/L supernatant and 2.16 mg from 180 mL of river water (200-mL final volume of each dilution). Thus, the ratio of the concentration of alcohol measured on the solids (µg/g) to the concentration of alcohol measured in solution (µg/mL) can be calculated according to Eq. (3).

A steady decrease in the partitioning of each alcohol between solid and aqueous phases is observed over time and approaches a steady state at approximately 72 h (Fig. 4) for C_{12} and C_{18} alcohols (30-h vs. 72-h values having overlapping error bars). The C_{14} and C_{16} alcohol 72-h mean values ($n = 4$) are lower than the 30-h mean values. The C_{16} 30- and 72-h error bars overlap somewhat, which could indicate experimental variability. Given the trend of the C_{14} and C_{16} alcohol K_d values to flatten out between 30 and 72 h, it is possible that experimental error played a greater role in the C_{14} and C_{16} results. Since longer times were not measured, the 72-h measurement was taken for development of the K_d predictive equation. Given the overlapping standard deviation ranges for the majority of the alcohols, the use of the 72-h data should introduce

Table 3
Sorption coefficients for selected AE homologues with Ohio River water (OWR) and Polk Run activated sludge

AE	Test concentration (µg/L)	Ohio River water K_d (L/kg)	ORW/activated sludge K_d (L/kg)	Polk Run activated sludge K_d (L/kg)
$C_{12}EO_3$	67	770 ± 28	1740 ± 240	1450 ± 42[a]
$C_{14}EO_3$[b]	72	5170 ± 1370	8560 ± 440	4140 ± 191[a]
$C_{16}EO_3$	78	8970 ± 1720	$19{,}400 \pm 2280$	3900 ± 194
$C_{14}EO_1$	54	2330 ± 230	4600 ± 800	1690 ± 79[a]
$C_{14}EO_3$[b]	72	5170 ± 1370	8560 ± 440	4140 ± 191[a]
$C_{14}EO_6$	100	6410 ± 1140	7320 ± 910	2740 ± 53[a]

The dose concentration was 0.209 µM for each homologue tested (note the corresponding mass concentrations). All samples were run in triplicate ($n = 3$). Results are presented as mean $\pm$ standard deviation.

[a]Reported in McAvoy and Kerr (2001) and tabulated here to illustrate trend, counted only once in equation fitting.
[b]Repeated in this table to show trend in EO unit increase vs. C number increase; counted only once in equation fitting.

Table 4
Change in measured partition coefficient (K_d) with time, corrected for sorption onto filter

Time (h)	K_d of each alcohol $n = 4$				
	C_{12}	C_{14}	C_{15}[a]	C_{16}	C_{18}
1	4100 ± 267	$14{,}700 \pm 645$	4070 ± 387	$34{,}100 \pm 1700$	$107{,}000 \pm 6330$
5	3410 ± 119	$12{,}700 \pm 675$	3820 ± 183	$33{,}300 \pm 1600$	$90{,}300 \pm 3070$
16	3320 ± 276	$10{,}500 \pm 167$	3590 ± 104	$28{,}600 \pm 1720$	$89{,}900 \pm 1980$
30	3100 ± 143	$10{,}200 \pm 670$	3480 ± 77	$27{,}600 \pm 1930$	$82{,}400 \pm 2970$
72	3000 ± 78	8490 ± 916	3080 ± 271	$23{,}800 \pm 3160$	$78{,}700 \pm 5350$

[a]Outlier data; not used in the development of the predictive equation.
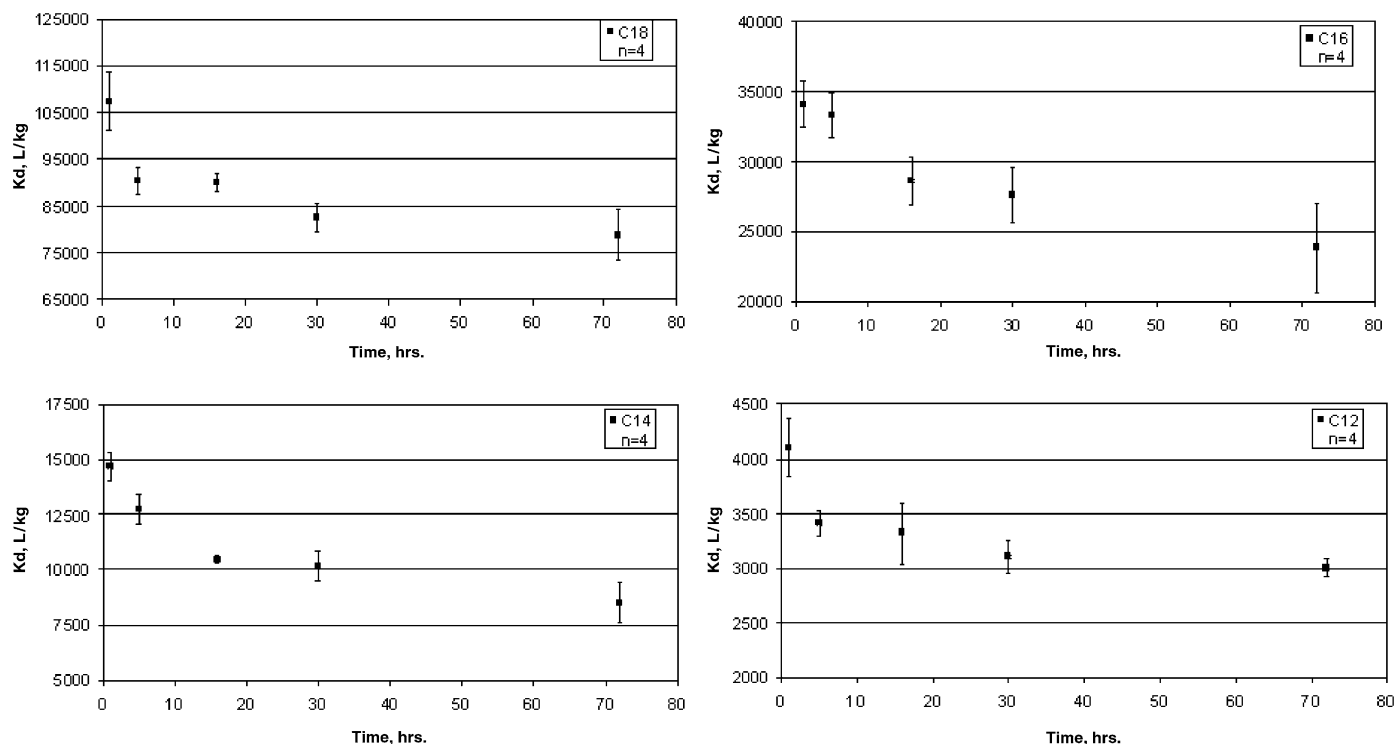

Fig. 4. Sorption K_d vs. time for fatty alcohols with activated sludge plus river water solids. Test for time to equilibrium.

negligible additional error into the predictive equation when taken in the context of the other data used.

The relative values of the alcohol sorption coefficients should be proportional to the changes in the alkyl chain length. However, the K_d for the C_{15} alcohol (Table 4) clearly represents an exception, as it is significantly outside the range between the K_d values for the C_{14} and the C_{16} alcohols. The radioactivity measured in the homogenized and centrifuged settled sludge is significantly higher in the C_{15} alcohol experiment than for the other alcohols, although no obvious reason for this difference is apparent. Every effort has been made to ensure that all stages of the procedure were as consistent as possible and no clear explanation for the difference in the C_{15} values could be identified. Thus, the C_{15} data were taken as outliers and not used in the development of the predictive model.

3.3. Evaluation of literature sorption data for use in the predictive model

The several AE sorption studies reported in the literature and compiled herein express sorption results in a variety of ways. It was necessary to put these results into a standard format for the predictive model. Data are reported by some authors as linear sorptions isotherms with constant distribution ratios while other authors found the sorption to be nonlinear and represented by a Freundlich isotherm (Eq. (2)). Additionally, data are reported both as a K_d based on the total mass of the substrate and as normalized

by the substrate fraction of organic carbon, K_{oc}. This was done to determine which form (K_d or K_{oc}) would give the best fit in the predictive equation. Since the literature-reported values include a characterization of the solid substrate with an organic carbon fraction, K_d values can be converted to K_{oc} values and vice versa (see below). This allows for a consistent comparison of the two K values for determining the best fit when regressed against alkyl chain length and ethoxylate numbers.

The following sections discuss the development of a standard format by estimating a linear sorption constant from data reported in nonlinear fashion (Freundlich isotherm) and by subsequently calculating both a K_d and a K_{oc} for each value.

3.3.1. Transformation of Freundlich isotherm constants into a linear K_d value

To generate a predictive equation from the cited results, values reported as nonlinear Freundlich isotherms were transformed into linear relationships. Brownawell et al. (1997) and Cano and Dorn (1996a) reported Freundlich isotherm values for their sorption data. The data had varying degrees of linearity, with Freundlich isotherm exponent, n, values from 0.61 to 0.92.

Cano and Dorn (1996b) also fit their data to a Freundlich isotherm with varying degrees of nonlinearity ($n = 0.45$–0.97). The nonlinearity increases (decreasing value of n) with increasing EO number. Sorption was correlated to both the organic carbon and the clay contents

Table 5
Results of linearized Freundlich sorption data

AE	Reported Freundlich K_f	Reported Freundlich n	Estimated K_d in linear range (L/kg)[a]	R^2	Substrate	Reference
$C_{13}EO_3$	73	0.92	258	0.998	EPA-12 Sediment	Brownawell et al. (1997)
$C_{13}EO_6$	11	0.77	451	0.981	EPA-12 Sediment	
$C_{13}EO_9$	2	0.61	1146	0.915	EPA-12 Sediment	
$C_{13}EO_6$	59	0.74	3924	0.974	EPA-13 Sediment	
$C_{13}EO_6$	40	0.75	2257	0.977	EPA-25 Sediment	
$C_{13}EO_6$	60	0.78	2103	0.983	EPA-16 Sediment	
$C_{13}EO_6$	62	0.88	428	0.996	EPA-12 Sediment	
$C_{15}EO_9$	1145	0.65	3084	0.977	Sediment 1	Cano and Dorn (1996a)
$C_{15}EO_9$	1900	0.62	5547	0.972	Sediment 2	
$C_{15}EO_9$	410	0.55	1455	0.954	Sediment 3	
$C_{15}EO_9$	525	0.56	1793	0.958	Sediment 4	
$C_{13}EO_3$	500	0.83	816	0.996	Sediment 1	Cano and Dorn (1996b)
$C_{13}EO_3$	490	0.89	674	0.998	Sediment 2	
$C_{13}EO_3$	110	0.97	120	1.000	Sediment 3	
$C_{13}EO_3$	110	0.89	151	0.998	Sediment 4	
$C_{13}EO_9$	450	0.66	1180	0.979	Sediment 1	Cano and Dorn (1996b)
$C_{13}EO_9$	590	0.56	2015	0.958	Sediment 2	
$C_{13}EO_9$	110	0.53	405	0.950	Sediment 3	
$C_{13}EO_9$	160	0.45	715	0.924	Sediment 4	

[a]See text for estimation procedure.

of the sediments tested. Increasing EO number showed an increase in the influence of the clay content of the sediment. These Freundlich isotherm constants are summarized in Table 5.

Freundlich isotherm values (Brownawell et al., 1997; Cano and Dorn, 1996a, b) were used to estimate a K_d for a linear relationship as follows. First, the Freundlich isotherm equation (Eq. (2)) was used to calculate solid-phase concentrations (C_s) from an input of aqueous-phase concentrations (C_w) in the range of environmental interest (0.1–50 µg/L) and the K_f and n constants cited in the respective paper. The water concentrations used for these calculations were 0.1, 0.5, 1, 5, 10, and 50 µg/L.

Next, Eq. (3) was rearranged and used to generate a regression with slope K_d in a linear form:

$$C_s = K_d C_w. \tag{5}$$

The aqueous concentration values used are consistent with the concentrations determined to give linear results in experimental work reported in this study. In Brownawell et al. (1997), the two lowest concentrations for each of the homologues tested are below 50 µg/L and lie on the linear

Table 6
Compilation of AE sorption data

C no.	EO no.	Sorbent	K_d (L/kg)	log K_d	f_{oc} fraction	K_{oc} (L/kg)	log K_{oc}	Reference
12	10	Activated sludge	2827[a]	3.45	0.430	6574	3.82	Kiewiet et al. (1993)
10	9	Sediment	166.5	2.22	0.11	1514	3.18[a]	Kiewiet et al. (1997)
12	9	Sediment	743.7	2.87	0.11	6761	3.83[a]	
14	9	Sediment	2195	3.34	0.11	19,953	4.3[a]	
14	9	Sediment	3322	3.52	0.11	30,200	4.48[a]	
16	9	Sediment	15,184	4.18	0.11	138,038	5.14[a]	
13	2	Sediment	618.6	2.79	0.11	5623	3.75[a]	
13	4	Sediment	761	2.88	0.11	6918	3.84[a]	
13	6	Sediment	1003	3	0.11	9120	3.96[a]	
13	8	Sediment	1353	3.13	0.11	12,303	4.09[a]	
13	3	Sediment	258[a]	2.41	0.023	11,073	4.04	Brownawell et al. (1997)[b]
13	6	Sediment	451[a]	2.65	0.023	19,356	4.29	
13.5[c]	9	Sediment	1146[a]	3.06	0.023	49,185	4.69	
13	6	Sediment	427[a]	2.63	0.023	18,326	4.26	
13	6	Sediment	3924[a]	3.59	0.03	129,079	5.11	
13	6	Sediment	2103[a]	3.32	0.012	175,250	5.24	
13	6	Sediment	2257[a]	3.35	0.008	296,974	5.47	
10	3	Sediment	41	1.61[a]	0.11	370	2.57	Kiewiet et al. (1996)
10	5	Sediment	48	1.68[a]	0.11	435	2.64	
10	8	Sediment	126	2.1[a]	0.11	1144	3.06	
12	3	Sediment	257	2.41[a]	0.11	2337	3.37	
12	8	Sediment	1230	3.09[a]	0.11	11,184	4.05	
14	3	Sediment	2951	3.47[a]	0.11	26,829	4.43	
14	5	Sediment	3467	3.54[a]	0.11	31,522	4.50	
14	8	Sediment	3548	3.55[a]	0.11	32,256	4.51	
16	5	Sediment	4786	3.68[a]	0.11	43,512	4.64	
16	8	Sediment	6166	3.79[a]	0.11	56,054	4.75	
12	5	Sediment	724	2.86[a]	0.11	6586	3.82	
15	9	Sediment	3084[a]	3.49	0.028	110,143	5.04	Cano and Dorn (1996a)
15	9	Sediment	5546[a]	3.74	0.016	346,625	5.54	
15	9	Sediment	1455[a]	3.16	0.003	485,000	5.69	
15	9	Sediment	1793[a]	3.25	0.002	896,500	5.95	
13	3	Sediment	816[a]	2.91	0.028	29,143	4.46	Cano and Dorn (1996b)
13	3	Sediment	674[a]	2.83	0.016	42,125	4.62	
13	3	Sediment	120[a]	2.08	0.003	40,000	4.60	
13	3	Sediment	151[a]	2.18	0.002	75,500	4.88	
13	9	Sediment	1180[a]	3.07	0.028	42,143	4.62	
13	9	Sediment	2015[a]	3.30	0.016	125,938	5.10	
13	9	Sediment	405[a]	2.61	0.003	135,000	5.13	

Table 6 (*continued*)

C no.	EO no.	Sorbent	K_d (L/kg)	$\log K_d$	f_{oc} fraction	K_{oc} (L/kg)	$\log K_{oc}$	Reference
13	9	Sediment	715[a]	2.85	0.002	357,500	5.55	
12	3	Activated sludge	1463	3.17	0.34	4571	3.66[a]	McAvoy and Kerr (2001)
12	6	Activated sludge	813	2.91	0.34	2570	3.41[a]	
14	1	Activated sludge	1690	3.23	0.34	5248	3.72[a]	
14	3	Activated sludge	4136	3.62	0.34	12,882	4.11[a]	
14	6	Activated sludge	2736	3.44	0.34	8511	3.93[a]	
14	9	Activated sludge	2955	3.47	0.34	9333	3.97[a]	
16	6	Activated sludge	10,371	4.02	0.34	32,359	4.51[a]	
12	3	Humic acid (DOC)	1021	3.01	0.5	2042	3.31[a]	
12	6	Humic acid (DOC)	1694	3.23	0.5	3388	3.53[a]	
14	1	Humic acid (DOC)	17,337	4.24	0.5	34,674	4.54[a]	
14	3	Humic acid (DOC)	13,151	4.12	0.5	26,303	4.42[a]	
14	6	Humic acid (DOC)	11,454	4.06	0.5	22,909	4.36[a]	
14	9	Humic acid (DOC)	9099	3.96	0.5	18,197	4.26[a]	
16	6	Humic acid (DOC)	45,601	4.66	0.5	91,201	4.96[a]	
16	3	Activated sludge	3901[a]	3.59	0.34	12,191	4.09	This study
12	3	Ohio River water suspended solids (ORW)	770[a]	2.9	0.1	7700	3.89	
14	3	ORW	5173[a]	3.71	0.1	51,730	4.71	
16	3	ORW	8969[a]	3.95	0.1	89,690	4.95	
14	1	ORW	2332[a]	3.37	0.1	23,320	4.37	
14	6	ORW	6406[a]	3.81	0.1	64,060	4.81	
12	3	ORW + act sludge	1742[a]	3.24	0.104	16,700	4.22	
14	3	ORW + act sludge	8565[a]	3.93	0.104	82,108	4.91	
16	3	ORW + act sludge	19,363[a]	4.29	0.104	185,623	5.27	
14	1	ORW + act sludge	4604[a]	3.66	0.104	44,136	4.64	
14	6	ORW + act sludge	7323[a]	3.86	0.104	70,202	4.85	
12	0	Gowey River water suspended solids (GRW) + act sludge	3002[a]	3.48	0.167[d]	17,981	4.25	
14	0	GRW + act sludge	8486[a]	3.93	0.167[d]	50,828	4.71	
16	0	GRW + act sludge	23,790[a]	4.38	0.167[d]	142,492	5.15	
18	0	GRW + act sludge	78,695[a]	4.9	0.167[d]	471,350	5.67	

[a]Form of the sorption coefficient reported in original publication.
[b]Linearized data from Table 5.
[c]AE mixture with an average carbon number of 13.5.
[d]f_{oc} estimated by Eq. (7) in text.

part of the sorption curve. For Cano and Dorn (1996a) surfactant concentrations were above the 50 μg/L range, whereas in Cano and Dorn (1996b) at least four data points fell below 50 μg/L. The linearized K_d values are summarized in Table 5 and compiled in Table 6, which is the data set used for the predictive equation.

3.3.2. Linear isotherm data

Kiewiet et al. (1993, 1996, 1997) and McAvoy and Kerr (2001) reported linear, or near-linear, sorption coefficients. These values were input into Table 6 without any manipulation. Kiewiet et al. (1993) reported a $\log K_{oc}$ value for $C_{12}EO_{10}$ in activated sludge. While the data fit a nonlinear Freundlich isotherm, they reported an n value close to one. Thus, the reported $\log K_{oc}$ was taken to be in the linear range of the sorption isotherm. Since, Kiewiet et al.'s study, the activated sludge had an f_{oc} value of 0.43, this high organic carbon content could explain the near-linear behavior of the isotherm.

Kiewiet et al. (1996) determined a suspended sediment water sorption coefficient, $\log K_{s/w}$ (equivalent to $\log K_d$ term used in this paper), at a single initial concentration after finding that the Freundlich isotherms at initial concentrations from 50 to 400 μg/L for these AE were near linear. The resulting Freundlich isotherm n values ranged from 0.8 to 1.3. This data set contains the broadest range of carbon number and EO units of all the data and is particularly useful because all values were determined using the same sediment as a substrate.

McAvoy and Kerr (2001) reported $\log K_{oc}$ values for several AE components to humic acids and activated sludge and these values were confirmed to be in the linear range.

3.3.3. Transformation between $\log K_d$ and $\log K_{oc}$ using f_{oc}

Once linearized, the sorption coefficient data were compiled as a set of K_d and K_{oc} values, as shown in Table 6. The two coefficients are related to each other

through the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}}, \qquad (6)$$

where K_d is the distribution coefficient or sorption coefficient, L/kg, and f_{oc} is the fraction of organic carbon.

As shown in Table 6, 46 coefficients were reported as K_d and 23 as K_{oc} (or as the corresponding logarithm value). The f_{oc} of the solids used as substrate for each determination is required to transform one value into the other. Brownawell et al. (1997) reported K_d values for a series of $C_{13}EO_{3,6, and 9}$ AE compounds using a single sediment with $f_{oc} = 0.0233$ and $C_{13}EO_6$ in a series of four sediments with different f_{oc} values (0.0233, 0.0304, 0.012, 0.0076). These f_{oc} values were used to transform the respective results to a K_{oc} value. Cano and Dorn (1996a) reported K_d for a mixture of commercially available surfactants in four sediments having f_{oc} values of 0.028, 0.016, 0.003, and 0.002 and these were used to calculate a corresponding K_{oc} value.

Organic carbon fractions of the river water and activated sludge solids used in the alcohol study described herein were measured (0.14 and 0.30, respectively). The f_{oc} of the river water-activated sludge mixture for use in calculating K_{oc} from the K_d was calculated as

$$f_{oc} = \frac{((f_{oc}^{AS} m_{AS}) + (f_{oc}^{RS} m_{RS}))}{(m_{AS} + m_{RS})}, \qquad (7)$$

where f_{oc}^{AS} is the fraction of organic carbon in activated sludge (0.3), f_{oc}^{RS} the fraction of organic carbon in river solids (0.14), m_{AS} the mass of activated sludge in the desorption test, and m_{RS} the mass of river solids in the desorption test.

Data reported as K_{oc} (Kiewiet et al., 1997; McAvoy and Kerr, 2001) had corresponding K_d values calculated using the reported f_{oc} values. For the activated sludge measurements of McAvoy and Kerr (2001), the f_{oc} value of 0.34 was confirmed by the authors (pers. comm.). The Kiewiet et al. (1996) f_{oc} value was also applied to the data in Kiewiet et al. (1997) since both papers are from the same study.

3.4. Review and synthesis of all data

Table 6 summarizes all of the sorption data from both this study and the literature sources cited. The original form of the sorption coefficient (K_d or K_{oc}) is highlighted with an asterisk. There is a wide range of C and EO combinations in the data set. A summary of the data in a matrix form is presented in Table 7. Bold-faced italics indicate where there are multiple values, and the number is the average of these values. Sorption coefficients summarized in this study cover a considerable cross section of the various alkyl carbon number and EO number combinations possible in AE and are presented in Table 7 in grid form to give a sense of how K_d changes with EO number at constant carbon number and vice versa.

Table 7
Summary of log K_d values vs. C_x and EO_y from Table 6

		Carbon number							
		10	12	13	13.5[a]	14	15	16	18
EO number	0		3.48			3.93		4.38	4.90
	1					*3.63*			
	2			2.79					
	3	1.61	*2.87*[b]	*2.48*		*3.78*		*3.98*	
	4			2.88					
	5	1.68	2.86			3.54		3.68	
	6		*3.07*	*3.09*		*3.80*		*4.34*	
	7								
	8	2.1	3.09	3.13		3.55		3.79	
	9	2.22	2.87	2.98	3.34	*3.65*	*3.41*	4.18	
	10		3.45						

[a] AE mixture with an average carbon number of 13.5.
[b] Values in *bold face close* are the average of two or more values from Table 6.

3.5. Development of the predictive equation

An Excel spreadsheet was populated with the log K_d and log K_{oc} data from Table 6 vs. the C and EO number for each surfactant. The regression feature within Excel was then used to estimate best-fit coefficients x, y, and b resulting in the following equation for log K_d:

$$\log K_d = 0.331C - 0.00897EO - 1.126 \quad (R^2 = 0.64), \qquad (8)$$

where C is the number of carbon atoms in the alkyl chain and EO is the number of EO units. The 95% confidence intervals for the coefficients are as follows: C coefficient (0.269–0.392), EO coefficient (−0.0422–0.0243), and intercept (−1.997 to −0.254).

A plot of measured log K_d vs. predicted log K_d using Eq. (8) is shown in Fig. 5A with each source represented by a different symbol. As noted under Section 2, some of the original data (23 of 69 values) were reported as K_{oc} or log K_{oc}. In these cases, the K_{oc} was transformed into the corresponding K_d by multiplying the K_{oc} value by the f_{oc} value reported in each study. Fig. 5B shows the same data as Fig. 5A except that originally reported K_d values are distinguished from K_d values transformed from originally reported K_{oc} values. Transforming log K_{oc} values to log K_d values maintains a consistent distribution of data.

The data in Table 6 were also used to build a predictive equation based on log K_{oc}, yielding the following equation:

$$\log K_{oc} = 0.322C + 0.0470EO - 0.196 \quad (R^2 = 0.53). \qquad (9)$$

The 95% confidence limits for the coefficients are as follows: C coefficient (0.246–0.398), EO coefficient (0.00592–0.0880), and intercept (−1.27–0.881).

A plot of measured log K_{oc} vs. predicted log K_{oc} using Eq. (9) is shown in Fig. 5B with each source represented by a different symbol. This correlation had a lower R^2 value than Eq. (8). This is likely due to the greater uncertainty in
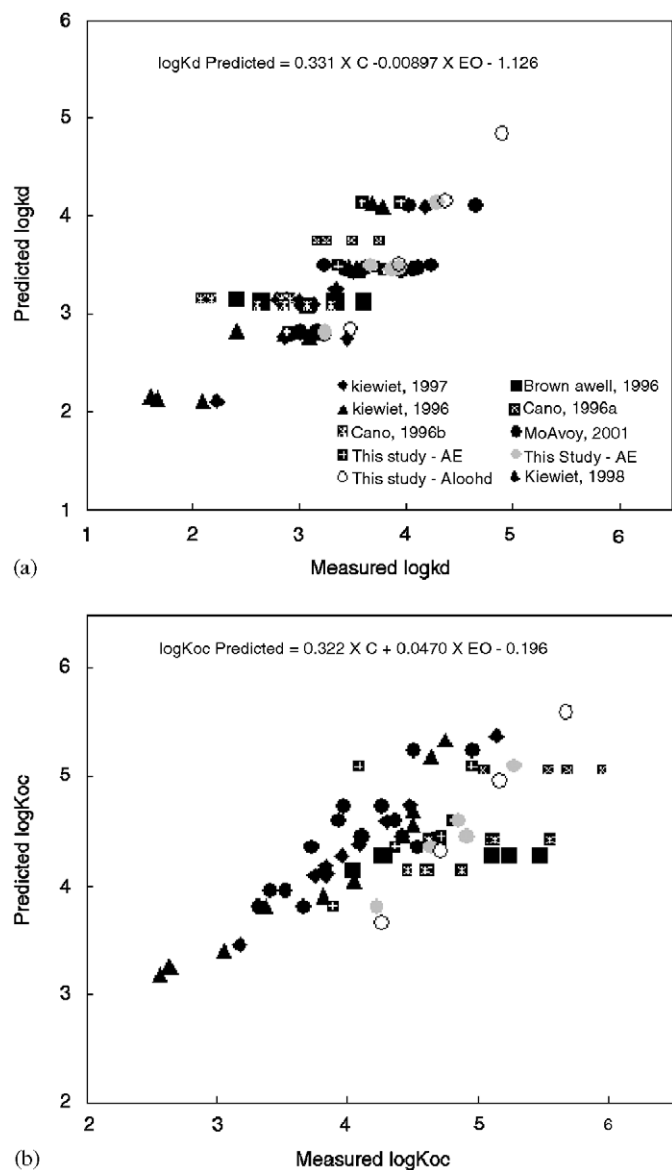
Fig. 5. Measured vs. predicted $\log K_d$ (A) and $\log K_{oc}$ (B) for AE and fatty alcohols.

introducing an f_{oc} normalization into K_d data when organic carbon may not be the only factor affecting sorption. Additionally, this required the transformation of 67% of the reported data to K_{oc} from its originally reported form K_d and thus uncertainty was introduced into a greater proportion of the data.

4. Discussion

The outcome of a realistic exposure assessment for AE surfactants in aquatic environments is influenced by sorption onto solids, which can reduce bioavailability and thus their ecological effects (Belanger et al., 2005). The sorption of surfactants to humic acids, e.g., has been given some attention as in the case of cationic alkyl trimethyl- and dimethyldioctadecyl ammonium surfactants. The presence of humic acids significantly correlated with a

reduced toxicity of these compounds to fathead minnows (Versteeg and Shorter, 1992). For the anionic surfactant linear alkylbenzolsulfonate this mitigating effect was less pronounced (Traina et al., 1996). Taking the impact of sorption into account for AE surfactants requires partitioning data of 144 specific homologues whose adsorption depends on carbon number and EO number.

Since it is impractical to measure a sorption coefficient for all AE homologues, a predictive equation provides a useful tool. Through a compilation of literature data and newly measured sorption coefficients, a $\log K_d$ predictive model based on alkyl chain carbon number and EO units has been derived:

$$\log K_d = 0.331C - 0.00897EO - 1.126 \ (R^2 = 0.64),$$

where C is the number of carbons in the alkyl chain (hyrophobe) and EO is the number of units in the ethoxylate chain (hydrophile). An equation that estimates $\log K_{oc}$ (i.e., normalized to fraction of organic carbon) had more variability ($R^2 = 0.53$) and was not as comprehensive. While in many cases f_{oc} is the solids characteristic most often influencing sorption of hydrophobic compounds (Di Toro and De Rosa, 1996), the presence of hydrophilic and hydrophobic moeties on the AE molecule appears to offer an exception.

The sorption of AE surfactants is complicated by the presence of both hydrophobic and hydrophilic moeties, which vary from $C_{11}EO_0$ to $C_{18}EO_{20}$. Each moeity interacts separately and together with a variety of solid matrices according to their structure and the solids characteristics. The predictive sorption equations in this study indicate that the carbon chain length on the alkyl chain (hydrophobe) most strongly determines sorption with a positive correlation between increasing carbon number and sorption coefficient ($\log K_d$). The coefficients for carbon in both the $\log K_d$ and the $\log K_{oc}$ predictive equations are quite consistent in this study (0.331 vs. 0.322, respectively) and agree with Kiewiet et al.'s (1996) reported value of 0.33 (Eq. (1)).

The observation that the $\log K_d$ equation has a higher R^2 than the $\log K_{oc}$ equation is unexpected under an assumption that sorption of AE depends strictly on hydrophobic effects driven by the alkyl side chain length and the fraction of organic carbon on the sorbing substrate.

This complexity of the sorption of AE is represented by the variability of the coefficient on the EO side chain length, which shows a negative correlation with sorption under the $\log K_d$ equation but a positive correlation under carbon-normalized conditions ($\log K_{oc}$). Others have also observed this negative correlation (Cano and Dorn, 1996a, b; Brownawell et al., 1997; McAvoy and Kerr, 2001). In contrast, the Kiewiet et al. (1996) equation shows a positive correlation. Authors observing a positive correlation have speculated that EO groups may be attracted to ionic sites on solids with high cation exchange capacity and possibly to organic carbon through van der Walls forces. Rheinlaender (as summarized in Klumpp and

Schwuger, 1997) demonstrated by X-ray measurements that nonionic surfactants could intercalate into clay layer interspaces. The author points out that, in nonionic surfactant adsorption on layer silicates, the hydrated ethylene glycol groups can interact with solid phases via ion–dipole interactions and hydrogen bonding. These attraction mechanisms compete with the hydrophilic nature of the EO group, which would tend to keep it in the aqueous phase.

The variation between positive and negative relationships of EO to sorption also may be attributable to the variations in the amount of organic carbon in the solids; high f_{oc} values may minimize EO effects while low f_{oc} values may allow other effects to exert more influence. The EO units appear to affect the rate of increase in $\log K_d$ with carbon number (Table 7). At EO_0 the $\log K_d$ increases at 1.4 log units/C unit, whereas at EO_3 the $\log K_d$ increases at 2.4 log units/C unit and at $EO_{5,6, \text{ and } 9}$ the increase is approximately 2 log units/C unit.

Thus, there remains an incomplete understanding of the interaction between EO groups and solids due to the fact that other features of solids (surface area, cationic exchange capacity, etc.) are not consistently taken into account across all the studies summarized herein. It may be possible that the $\log K_{oc}$ equation is more appropriate when the f_{oc} is relatively high, while $\log K_d$ is more applicable for solids with little organic carbon content. Although more work is needed to confirm this, our work suggests that an f_{oc} of approximately 0.07–0.1 is a reasonable breakpoint between the use of the two correlations.

The $\log K_d$ values of the alcohols determined in this study appear to have responses somewhat different from those of the other reported AE homologues (Fig. 5). The predicted $\log K_d$ is lower than that measured for the C_{12} alcohol, whereas the predicted $\log K_d$ is somewhat higher than that measured for the C_{18} alcohol. The C_{14} and C_{16} alcohols fall more closely into the overall data set for all AE. However, the variation for all the alcohols is within the prediction confidence intervals for all the data. Thus, sorption of AE and their alcohols can be estimated using the same predictive model.

Freundlich isotherms of several surfactants reported in the literature frequently show nonlinearity factors of <1, implying that sorption affinity decreases with increasing surfactant concentrations. It has to be considered that this concentration dependency may affect the individual sorption assessment and that the sorption coefficient at environmentally relevant low concentrations is different from what has been measured in the laboratory at higher concentrations (Tolls and Sijm, 2000).

The importance of the sorption behavior of AE lies in the evaluation of environmental risk (Belanger et al., 2005). Sorbed AE is not bioavailable and thus should be considered such in predicting environmental exposure (i.e., bioavailability). Fig. 6 illustrates a case study of the role that sorption plays in developing the exposure assessment of AE based on the bioavailable fraction. A measured distribution
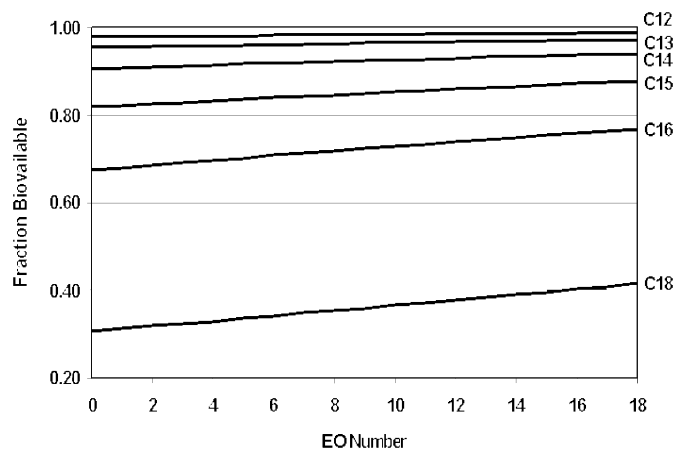

Fig. 6. Case example for bioavailable fraction when sorption is taken into account: 30 total SS mg/L, 0.32 f_{oc}, and no dilution.

of AE for a municipal wastewater treated effluent (Belanger et al., 2005) was prepared from monitoring data. These in-stream concentrations were then corrected for solid–liquid partitioning using Eq. (8) and assuming a stream SS concentration of 30 mg/L. No dilution of the effluent concentrations was taken into account. The values in Fig. 6 give the ratio for each AE homologue of bioavailable concentration with partitioning taken into account vs. the total nonpartitioned concentration. As expected from the $\log K_d$ values, the bioavailable fraction decreases significantly as the alkyl C number increases.

5. Conclusion

An equation for prediction of sorption coefficients for AE has been derived from a large subset of all possible AE homologues. This predictive equation has been found to be an important factor in environmental risk evaluations (Belanger et al., 2005). Regardless of the various factors discussed above, it remains a fact that AE can sorb strongly onto solids ($\log K_d$ ranging from 1.6 to 4.9), thereby reducing bioavailability in the aquatic environment. The example in Fig. 6 illustrates the importance of accounting for sorption when determining predicted exposure concentrations for risk assessments of AE in receiving water. It is, therefore, reasonable and justified to take sorption into account when assessing environmental exposure. While normalizing for the carbon content of the sorptive material (sediment, activated sludge, river solids) can be a useful exercise (Di Toro and De Rosa, 1996), the data herein indicate a stronger correlation in the predictive equation when the noncarbon-normalized sorption coefficient ($\log K_d$) is used.

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