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Occurrence and risk screening of alcohol ethoxylate surfactants in three U.S. river sediments associated with wastewater treatment plants

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ABSTRACT

Alcohol ethoxylates (AE) are high production volume (HPV) chemicals globally used in detergent and personal care products and are truly a work-horse for the household and personal care industries. Commercial AE generally consist of a mixture of several homologues of varying carbon chain length and degree of ethoxylation. Homologues that are not ethoxylated are also known as aliphatic alcohols or simply fatty alcohols (FA). This group of homologues represents a special interest in the context of environmental risk, as these are also abundant and ubiquitous naturally occurring compounds (*e.g.* animal fats and in human feces). Hence, in a risk assessment one needs to distinguish between the natural (background) concentrations and the added contribution from anthropogenic activities. We conducted a weight-of-evidence risk assessment in three streams, documenting the exposure and predicted risk, and compared these to the habitat and *in situ* biota. We found that the parameters (*e.g.*, habitat quality and total perturbations hereunder total suspended solids (TSS) and other abiotic and biotic stressors) contributed to the abundance of biota rather than the predicted risk from AE and FA. Moreover, the documented natural *de novo* synthesis and rapid degradation of FA highlight the need to carefully consider the procedures for environmental risk assessment of naturally occurring compounds such as FA, *e.g.* in line with the added risk concept known from metal risk assessment.

1. Introduction

Alcohol ethoxylates (AE) are high production volume (HPV) chemicals used widely as 'down-the-drain' chemicals globally in detergent and personal care products. These workhorse surfactants' annual use in the U.S. alone was 381,000 metric tons in 2008 (Blagoev and Gubler, 2009). Commercial AE generally consist of a mixture of several homologues (114) of varying carbon chain length (C_x) and degree of ethoxylation (EO_n). Homologues that are not ethoxylated (C_xEO_0) are also known as aliphatic alcohols or simply fatty alcohols (FA). AE conform to the general structure:

$$CH_3(CH_2)_n(OCH_2CH_2)_yOH, \text{ where n is generally 11–15, 17 and y is 0–18.}$$

A conventional shorthand notation for a material is "C_xEO_n" where x is the alkyl chain-length and n is the degree of ethoxylation. FA are the special case to the formula where $n = 0$ (C_xEO_0). In most consumer product applications, the saturated alkyl group is essentially linear with a very small amount of branching. FA represent a special interest in the context of environmental risk, as these are also abundant and ubiquitous naturally occurring compounds (*e.g.* animal fats and in human feces; Mudge et al., 2012). Since these are lipophilic compounds, they inherently have the potential to partition into fats. Mudge et al. (2012) recently published that long chain alcohols can be sourced from both natural and anthropogenic sources. Hence,

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understanding the potential for bioaccumulation is dependent upon alcohol sourcing. Soluble alcohols correspond to an acute narcosis mechanism of action, increasing toxicity until they are insoluble and therefore not readily available to exert a non-specific disruption of the cell membrane (Schäfers et al., 2009).

The major disposal route of AE 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 AE in treated sewage effluent of interest to industry and regulators alike. AE are extensively biologically degraded by WWTP in excess of 95–99% (van de Plassche et al., 1997; Wind et al., 2006; Federle and Itrich, 2006). Nevertheless, as with all biological degradation processes, residuals do remain resulting in low levels which are ultimately released to the environment *via* WWTP effluent. Concentrations of total AE in WWTP effluents range from 1 to 23 μg L^{-1} in Europe, Canada and the United States (Matthijs et al., 1999; Eadsforth et al., 2006; Morrall et al., 2006). Sorption onto activated sludge particles is an important process in removing surfactants from sewage, with significant fractions of effluent AE found associated with effluent suspended solids. AE are the subject of several environmental risk assessments including those of Little (1977), Goyer et al. (1981), Talmadge (1994), and van de Plassche et al. (1999). These assessments are becoming increasingly sophisticated with numerous advancements in understanding analytical methods, exposure, fate, and effects in the environment. These surfactants have a strong affinity for sorption to solids such as activated sludge, river water solids and, ultimately, sediments (Kiewiet et al., 1996; Cano and Dorn, 1996; McAvoy and Kerr, 2001). A predictive equation for sorption coefficients for individual homologues has been reported (Kiewiet et al., 1996) and expanded by van Compernolle et al. (2006). This allows the extension of risk assessments to account for the bioavailable fraction using sorption data (Belanger et al., 2006). These risk assessments address the aquatic environment in WWTP receiving waters. Interest is now extending to the fate and effects of sorbed AE on the sediment domain at and below WWTP discharges. Moreover, in 2009 a special edition of *Ecotoxicology and Environmental Safety* was published based on the HPV assessment for the OECD of long chained aliphatic alcohols documenting the hazard profile of these compounds, which belong to the AE family (Sanderson et al., 2009). Dyer et al. (2006) conducted an assessment of AE in sediment samples, along with an example environmental risk assessment in which the approach as well as validated sediment analytical methods were introduced.

This study applied and extended those methods to a survey of three small stream systems in the mid-west of the US with the objective of characterizing the occurrence and risk of AE up- and down-stream of WWTPs in surface water, porewater and sediment. The streams are effluent dominated and their selection was based on type of wastewater treatment system, its wastewater characteristics (no or low industrial discharge), and sampling accessibility (see Section 2.2).

The aims of the study were the following:

1) Describe the finger-print (homologue distribution) of AE up and down-stream from three WWTPs;
2) Assess the ratio between FA (EO_0) and AE EO_{n+1};
3) Compare modeled exposure predictions to measured concentrations;
4) Assess the predicted risk to aquatic organisms;
5) Compare the predicted risk to observed biota *in situ* in a weight-of-evidence assessment.

2. Materials and methods

2.1. Analytical methods

The analytical methods and instrumentation applied in this study are described in detail in Dyer et al. (2006). There were 114 possible AE and FA ethoxymers in the range of interest (E_xO0 to E_xO18). Due to the great expense in quantifying all ethoxymers (alcohols and AEs with EO of 1 or more), a subset of 38 components was selected that represents both the shape and most toxic portion of the distribution. For alkyl chain lengths of 12 (C12), ethoxylates (EOs) of 0, 1, 2, 3, 6, 9, 12, 15 were measured. For chain lengths of C13, 14, 15, 16, and 18, EOs of 0, 1, 2, 6, 9, and 15 were measured. Ethoxylates of 0, 1, 2, 6, 9, and 15 were also measured for the deuterated internal standard.

2.1.1. Standard and reference materials

The following materials were used as standards and to spike sediments: NEODOL® 25-9 (an alcohol ethoxylate with alkyl chain lengths of C12 through C15 and an average ethoxylate number of 9), Shell Chemical LP (Geismar, USA), 7 GENAPOL® T110 (an alkyl ethoxylate with alkyl chain lengths of C16 and C18 and an average ethoxylate number of 13, Shell Chemical, LP), C12 linear alcohol (99%) from Chem Service (West Chester, USA) C13 and C14 (97%) individual linear alcohols from Sigma-Aldrich (St. Louis, USA), and C15, C16, and C18 individual linear alcohols (99%) from Sigma-Aldrich. A deuterated alcohol ethoxylate, provided by Shell Chemical LP, was used as internal standard. This AE consisted of a single alkyl chain length with the alkyl chain deuterated (C13D27) with an average ethoxylate number of nine.

2.1.2. Reagents and solvents

All solvents were HPLC grade purchased from Honeywell Burdick and Jackson (Morristown, USA) and included methanol, dichloromethane, acetone, acetonitrile, tetrahydrofuran, and ethyl acetate. Water was obtained from a Millipore Milli-Q Plus water system. Triethylamine (99%) was purchased from Fisher Scientific USA (Waltham, USA) formic acid (95–97%) from Sigma-Aldrich (USA), formalin (ACS grade, 37% formaldehyde) from VWR (Radnor, USA), and the derivatization agent, 2-fluoro-N-methyl pyridinium p-toluenesulfonate (>99%, Pyr+) was purchased from Sigma-Aldrich (USA). All reagents and solvents were used as received.

2.1.3. Solid phase extraction cartridges

Varian Mega Bond Elut C-2 (2 g) 12 mL Part No. 1225-6056 Lot 032811, Varian HF Mega Bond Elut SAX (2 g) 12 mL Part No. 1425-6021 Lot 780700, Varian Mega Bond Elut SCX (2 g) 12 mL Part No. 1425-6019 Lot 772209 were used (Palo Alto, USA).

2.1.4. Optimized Sediment Extraction and Derivatization Procedure

An optimized procedure for extraction and derivatization of sediment samples was developed and reported by Morrall et al. (2006) and Dyer et al. (2006), as summarized below. All glassware was cleaned by sequential rinses with hot tap water (~55 °C), deionized water, methanol, acetone, dichloromethane, acetonitrile, and Milli-Q water. The glassware was then autoclaved at 110–120 °C for at least 1 h and stored in cleaned (as described for the glassware above) aluminum foil until used. Care was also taken to avoid contact with latex gloves, paper products, bare skin, or any other item potentially contaminated with soap or surfactants. For each sediment sample, approximately 20 g of wet sediment was freeze dried and then extracted with 30 mL of acetonitrile by manual shaking (2 min) and sonication (5 min), followed by centrifugation (5 min) at 874 *g* to separate the mixture. The supernatant was decanted and 30 mL of acetonitrile was added to the solids and re-extracted as before. The two extracts were combined and labeled as Fraction 1. The sediments were further extracted (twice) with a mixture of 30 mL methanol/ethyl acetate/water (78/20/2, v/v/v) using the same procedure as above. These extracts were combined and labeled as Fraction 2. SPE cartridges were set up in series, C2/SCX/SAX, and pre-conditioned by eluting with 100 mL Milli-Q water, 30 mL of acetonitrile, 10 mL (methanol/ethyl acetate/water (78/20/2, v/v/v)), 50 mL methanol,

50 mL acetone/methylene chloride (60/40, v/v), and 50 mL acetonitrile. Fraction 1 was passed through the cartridge series, followed by 5 mL of acetonitrile, and the total eluate collected. Fraction 2 was then passed through the SPE series, followed by 5 mL of the methanol/ethyl acetate/water solvent, and the total eluate collected separately from Fraction 1. The eluent of Fraction 2 was evaporated to dryness under nitrogen and then dissolved with the eluent of Fraction 1 to form the final extract. The extract was quantitatively transferred to a glass reaction vessel, and spiked with 12 μg of internal standard (C13D27 AE) followed by the addition of 100 μL of triethylamine and 300 mg of derivatizing reagent Pyr+. The reaction vessel was capped and stirred for a minimum of 2 h without heating. The derivatized sample was then taken to dryness under nitrogen. The resulting residue was dissolved in 1 mL of HPLC mobile phase (acetonitrile/Milli-Q water; 40/60, v/v) *via* sonication (1 min) and passed through a 0.2 μm PTFE syringe filter. Reagent blanks were analyzed to verify that the instrument and lab equipment were not contaminated with AE/FA. Reagent spikes were used to verify the stability of the refrigerated extracts in the preservation studies.

2.1.5. Calibration standards

Standard solutions of AE were prepared by serial dilutions of stock solutions, spiked with internal standard and derivatized as described above. Nominal spiking concentrations of 3000 ng L^{-1} total AE were used for water samples which corresponds to approximately 20 times the typical method blank. Water samples were spiked, allowed to equilibrate for several hours and carried through the analysis procedure. For sediment samples, upstream, presumably background sediment samples were fortified with either 450 ng total AE g^{-1} (Bryan and Wilmington) or 1100 ng total AE g^{-1} (Lowell) before freeze-drying and extracting the samples.

2.1.6. Liquid chromatography/mass spectrometry

All work was performed on a Hewlett Packard HP 1090 HPLC system coupled to a Micromass Quattro I Triple Quadrupole Tandem Mass Spectrometer operating in the positive ion electrospray (ESP) scan mode. The basic instrumental method used lower cost electrospray MS approach rather than requiring more complex MS/MS capability. Quantitation was performed using extracted ion chromatograms of the selected pyridinium derivative molecular (Pyr+) primary ion. Occasionally it was necessary to run in the MS/MS product ion mode due to matrix interferences; this was done only for qualitative identification purposes. The HPLC column used in this study was a Supelcosil TPR100, 200 × 2.1 mm. Injection volume for standards and samples was 25 μL and the flow rate was 0.2 mL min^{-1}. Mobile phase consisted of an acetonitrile/water gradient with 0.01 M formic acid. Initial gradient condition of 40% acetonitrile and 60% water was held constant for 5 min after the injection, then linearly increased to an acetonitrile concentration of 90% from 5 to 25 min, and finally to 100% acetonitrile from 25 to 30 min. The column was allowed to re-equilibrate at the initial conditions for 15 min before the next injection. Finally, the flow from the HPLC column was diverted to waste for the first eight to 10 min after the injection to avoid contamination (and loss of sensitivity) of the electrospray interface from early eluting components in the derivatized extracts.

2.1.7. Stability of AE and FA in sediment samples

Work by Dyer et al. (2006) determined the stability of AE and FA in sediments was acceptable if unrefrigerated for up to 3 days in 3% v/v formalin. Stability was extended to 14 days upon refrigeration (4 °C).

2.1.8. Detection and quantitation limits

The limits of detection (LOD) and limits of quantitation (LOQ) were determined by adding derivatized AE standards to the derivatized extracts of unspiked sediment. This mixture was analyzed to measure the response of derivatized standards in the presence of sample matrix. The responses equivalent to three times the signal to noise (S/N) for LOD and 10 times the S/N for LOQ were estimated for each ethoxymer monitored. These responses were then used to calculate corresponding LOD and LOQ concentrations of AE and FA in a sediment sample on a dry-weight basis. The LOD and LOQ were estimated values that were different for each sediment type and were affected by chromatographic interferences from the matrix, differences in mass spectrometer response factors for individual ethoxymers, dilution factors, and residual AE and FA levels of the test sample. The limiting factor in detection and quantitation limits for some ethoxymers were extracted background interference that can obscure or mask the AE and FA peaks in chromatograms. Typical laboratory method and field blanks ranged from 100 to 300 ng L^{-1} for water samples and 25–160 ng g^{-1} for sediments. The typical LOQ for an individual ethoxymer ranged from 0.5 to 10 ng L^{-1} for water samples and 0.5–10 ng g^{-1} for sediments.

2.2. Site selection, wastewater treatment plants, and streams

Sites were selected based on criteria found in Sanderson et al. (2006). In summary, sampling efforts focused on moderately-sized, relatively efficient plants with primarily domestic/residential inputs. Periods of low dilution (7Q10, lowest 7 day average flow in 10 year period) in receiving streams were chosen to target conditions that are most favorable for surfactant presence in sediment. Hence, the following criteria for site selection were chosen:

- USEPA code 5 status — relatively high wastewater treatment efficiency (10–25 mg BOD L^{-1} in the effluent);
- A 7Q10 flow dilution factor between 1 and 3;
- Population base between 5000 and 50,000 people;
- Mean flow $< 8 \times 10^6$ L day^{-1} (2 million gallons per day (Mgd))
- <20% of industrial influent;
- Sites within a 300 mile radius of each other, which facilitated logistics for efficient sampling over distance/time.

Table S1 in the supporting materials summarizes the specific information on these locations.

Stream characterization and assessment are detailed in Sanderson et al. (2006). A habitat assessment and physical/chemical field data sheet were completed at each sampling location according to the procedure outlined in the RAPID bioassessment methodology by the United States Environmental Protection Agency (United States Environmental Protection Agency, 1999). Ten parameters were used to score habitat quality. All sampling was conducted in late September and early October of 2003. Sampling consisted of 30 locations (surface water and sediment): 6 upstream samples; 3 wastewater influent; 3 wastewater effluent; 6 in the streams at the outfall; 6 downstream; and 6 far-downstream.

2.3. Sampling

Surface water, porewater, sediment and benthic organism sampling was conducted according to the methods described in Sanderson et al. (2006). Samples were collected simultaneously — hence the biotic and abiotic backgrounds were identical to those in Sanderson et al. (2006). Physiochemical measurements were collected concurrently with benthic samples at each location including water temperature, dissolved oxygen, pH, conductivity, and oxidation/reduction potential. Sediment and porewater quality samples were analyzed for biological oxygen demand (BOD), chemical oxygen demand (COD), hardness, total suspended solids (TSS), total organic carbon (TOC), % gravel, % sand, % silt/clay, N, S, cation exchange capacity, and % H_2O according to standard ASTM Guidelines. Benthic sampling and identification were done according to United States Environmental Protection Agency (1999). Laboratory samples were preserved with 8% v/v formalin within

minutes of sampling (Sanderson et al., 2006) and analyzed within 14 days.

2.4. Predicted no effect concentrations (PNEC) for sediment dependent organisms

$PNEC_{aqueous}$ ($PNEC_{aq}$) for individual AE homologues as well as for the average AE structure based on the analytical "fingerprint" were developed (Belanger et al., 2006), and were used in this study to assess $PEC_{aq}/PNEC_{aq}$ ratios for effluent, surface waters and porewaters. The toxicities of AE were extensively studied in acute, chronic and experimental stream (mesocosm) tests. Several quantitative structure–activity relationships (QSAR) were developed from these studies and are summarized in tabular form in Belanger et al. (2006). Belanger et al. (2006) compiled results from 60 chronic tests on 17 species and then normalized results to monitoring data for AE mixtures, and Boeije et al. (2006) developed the AE QSAR, also known as the AE Workbook. Chronic toxicity was expressed as an EC_{10} per species (the concentration predicted to cause a 10% reduction in a relevant ecological endpoint, such as growth and reproduction). Species sensitivity distributions were constructed for each homologue and the HC_5 (hazardous concentration protective of 95% of species based on small effects (EC_{10})) was predicted. These HC_5 concentrations *per AE homologue* were used as the $PNEC_{aq}$ for this study. $PNEC_{sediment}$ ($PNEC_{sed}$) were estimated from $PNEC_{aq}$ using the equilibrium partitioning (EqP) approach (Eq. (1)) (DiToro, 1991). Distribution coefficients (log K_d) for AE ranged from 1.6 to 4.9 L kg^{-1} (van Compernolle et al., 2006). A predictive equation (Eq. (2)) for estimating homolog specific K_d of AE was developed (van Compernolle et al., 2006) and provided below:

$$PNEC_{sed} = K_d * PNEC_{aq} \quad (1)$$

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

"C" refers to the alkyl carbon chain length and "EO" refers to the ethoxylate chain length.

The partition coefficient for each ethoxymer was estimated using Eq. (2) and used to estimate the $PNEC_{sed}$ for each ethoxymer.

We applied an assessment factor of 10 to the chronic toxicity prediction for *Daphnia magna* to account for ecosystem level response in accordance to the approach by Slye et al. (2011); we also used the same additive assumption as Slye et al. (2011) to assess the total PEC/PNEC (toxic unit (TU)).

2.5. Interpolation of non-measured homologues in surface water, porewater and sediment solid samples using measured data and U.S. monitoring fingerprint

Not all homologues of the AE fingerprint were quantified in the monitoring. Estimation of total risk ratios was of course more realistic when the full fingerprint concentrations were applied to the PEC estimation. Hence, in order to gain a more complete picture of the fingerprint, homologue concentrations that were not measured were interpolated using the measured homologue values and the results of Morrall et al. (2006) and an approach similar to that reported by Popenoe et al. (1994). Morrall reported on the monitoring of 9 effluents throughout the United States, and reports an average effluent fingerprint. The average homologue fingerprint concentrations are given in Table S2.

Interpolation using the U.S. data was performed as follows. Reported concentrations from this study were tabulated from the analytical laboratory report. Any results that were reported less than the LOQ, 0.5 the LOQ was used for a measured concentration. The non-measured homologue concentration was then interpolated by using following equation:

$$C_xE_y^{Est} = C_xE_y^{US} x \left(C_xE_n^{Meas} / C_xE_n^{US}\right) \quad (3)$$

where:

C_x	carbon number of alkyl chain (same for U.S. and this study homologs)
E_y^{Est}	EO number of homolog to be estimated for this study.
E_y^{US}	same EO homolog measured in the average U.S. data.
E_n^{Meas}	EO number nearest homolog measured (or 0.5 = LOQ) in ng L^{-1} for aqueous samples and ng g^{-1} for sediment samples.
E_n^{US}	E_n^{Meas} of the U.S. distribution data.

An example data set including interpolated data is shown in S3. This interpolation was applied to both water column and porewater aqueous samples.

2.6. Impact and risk assessment framework

Ecological status of test sites were determined using the USEPA RAPID bioassessment method (United States Environmental Protection Agency, 1999) and impacts assessed *via* weight of evidence (WoE) approach based on Chapman and Anderson (2005). To achieve a semi-quantification, we modified Chapman and Anderson's (2005) three impact levels to 0, 1, and 2, the sum of impacts points then supported assessment of causality of observed differences and support addressing the hypotheses of the study. Where less than 20% alteration in benthos = 0 (minimal impact); >20% alteration = 1 (moderate impact); and ≫20% = 2 (high impact). The same 20% change regime used to derive habitat impact points (percent of upstream) was applied. For AE sediment exposure concentration criteria we used: less than the overall mean concentration for all streams = 0; greater than the mean but less than a factor of 2 = 1; and 2 or more-fold greater than the mean exposure concentration = 2. We also used the PEC/PNEC < 1 = 0; >1 but less than 2 = 1; ≥2 = 2. For biomagnification low-moderate potential = 0; moderate = 1; high = 2. The sum of all the weights provided a relative assessment of the potential impacts to benthic invertebrate communities and the individual weights provided potential diagnostic (Sanderson et al., 2006). We moreover, compared the PEC/PNEC ratios to the biota observed at the different locations (percent EPT taxa; percent tolerant taxa; and percent clingers), as these provided a measure of potential risk from AE and measured relative impacts to sensitive and tolerant taxa as well as ecologically relevant characteristics.

3. Results

3.1. QA QC results

The reporting limits of AE for aqueous and sediment samples are summarized in Table 1. The reporting limits for aqueous samples range from 0.6 ng L^{-1} for $C_{18}EO_1$ to 28.9 ng L^{-1} for $C_{13}EO_0$. For the sediment samples the range is 0.1 ng kg^{-1} for $C_{18}EO_1$ to 5.8 ng kg^{-1} for $C_{13}EO_0$.

Recoveries for aqueous and sediment samples are summarized in Table 2. The EO_0 is significantly higher due to the ubiquitous nature of these materials in laboratory apparatuses. Blanks levels were, therefore, difficult to obtain during calibration. The spiked recoveries varied slightly between the three sites for the aqueous samples. At the lower levels of fortification, spike recoveries for sediments appear lower and more variable than observed in the initial method validation work. The aqueous recoveries for shorter chain lengths were generally higher than those for the higher chain lengths across the

Table 1
AE reporting limits for aqueous and sediment analyses, ng kg^{-1} (blank spaces (–) were not analyzed).

	C12		C13		C14		C15		C16		C18	
	Aq.	Sed.	Aq.	Sed.	Aq.	Sed.	Aq.	Sed.	Aq.	Sed.	Aq.	Sed.
EO0	25.9	5.2	28.9	5.8	24.9	5.0	24.6	4.9	26.6	5.3	30.5	6.1
EO1	2.5	0.5	2.6	0.5	2.1	0.4	1.8	0.4	0.3	0.1	0.6	0.1
EO2	3.9	0.8	4.0	0.8	3.3	0.7	2.7	0.5	0.7	0.1	1.8	0.4
EO3	5.6	1.1	–	–	–	–	–	–	–	–	–	–
EO6	11.8	2.4	12.2	2.4	10.1	2.0	8.4	1.7	4.3	0.85	10.1	2.0
EO9	16.7	3.3	17.3	3.4	14.4	2.8	12.0	2.4	8.9	1.8	21.0	4.2
EO12	16.5	3.3	–	–	–	–	–	–	–	–	–	–
EO15	10.8	2.2	11.2	2.2	9.3	1.8	7.7	1.5	10.3	2.1	24.3	4.9

sites. Even though the recoveries decreased with chain length the relative recoveries were quite consistent.

The sediment spiked recoveries were generally slightly lower than those for the water samples, but still consistent. The recoveries did not show the same tendency as in the water samples to decrease with chain length. The spiked sediment recoveries from the Wilmington location were not freeze-dried immediately resulting in a longer contact time (four days) between the spiked AE and sediment. This oversight resulted in highly variable recoveries between 0 and 839%. Hence, recovery results from the Wilmington location were outliers — they were therefore discarded and not used in further assessments.

3.2. Surface water AE and FA measured concentrations

The surface water total AE concentrations were generally low (76–921 ng L^{-1}) for both up- and down-stream of the wastewater plants (Table 3). There were no strong trends of AE concentrations from upstream to downstream. Lowell surface water concentrations were nearly constant. Bryan showed a slight increase at below the outfall, but the outfall concentration was only about 30% higher than the upstream value. The Wilmington trend was likewise weak, and the maximum total AE was actually in the upstream sample. A two way ANOVA showed no significant differences ($p = 0.05$) between sampling locations and between sites. In some cases, FA dominated the surface water samples (Lowell upstream and far downstream) while others were about equal. AE dominated in Bryan outfall and far downstream and in Wilmington upstream and far downstream.

Table 2
Control spike recoveries (%) for aqueous and sediment samples. Blank spaces (–) were not analyzed. Wilmington sediment samples were outliers due to late freezing and hence omitted.

Lowell	C12		C13		C14		C15		C16		C18	
	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed
EO0	46	17	38	23	15	19	11	11	8	17	14	26
EO1	61	30	120	–	42	44	20	37	27	41	23	41
EO2	59	34	52	–	31	33	28	31	18	32	20	38
EO3	113	41	–	–	–	–	–	–	–	–	–	–
EO6	100	27	84	26	57	37	40	39	26	35	17	34
EO9	112	44	122	37	59	35	45	36	40	36	20	33
EO12	87	28	–	–	–	–	–	–	–	–	–	–
EO15	92	26	75	21	73	30	56	35	39	34	30	37
Bryan	**C12**		**C13**		**C14**		**C15**		**C16**		**C18**	
	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed
EO0	53	6	39	10	23	10	16	5	15	7	24	20
EO1	60	52	NA	–	32	76	33	53	29	13	21	0
EO2	59	61	30	–	36	28	38	55	58	0	22	0
EO3	60	37	–	–	–	–	–	–	–	–	–	–
EO6	88	15	63	6	41	9	34	5	39	0	30	15
EO9	72	14	86	14	42	0	30	4	45	23	32	27
EO12	67	10	–	–	–	–	–	–	–	–	–	–
EO15	70	5	57	0	43	0	32	0	42	38	50	67
Wilmington	**C12**		**C13**		**C14**		**C15**		**C16**		**C18**	
	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed	Aq	Sed
EO0	44		25		11		7		8		26	
EO1	63		NA		27		21		23		22	
EO2	84		4		27		12		23		21	
EO3	78		–		–		–		–		–	
EO6	95		61		42		27		25		26	
EO9	74		88		45		31		34		31	
EO12	78		–		–		–		–		–	
EO15	79		62		63		38		37		42	

3.3. Porewater AE measured concentrations

Porewater concentrations for Bryan appeared to follow a similar trend as surface water AE concentrations, with increased concentrations at the outfall and downstream (Table 3). Lowell and Wilmington showed both slightly higher and lower AE concentrations downstream of the outfalls as compared to upstream, respectively. FA tended to be more prevalent in proportion to the other ethoxymers, especially in the Lowell far downstream site and at the Bryan WWTP outfall. Porewater concentrations of both AE and FA tended to be in greater levels than the corresponding surface water concentrations (Table 3). A two way ANOVA showed no significant difference ($p = 0.05$) between sampling locations and between sites. The Lowell far downstream and the Bryan outfall appeared to have very large alcohol concentrations *versus* the total AE. The Lowell result reflected the same trends as the surface water results, whereas Bryan showed the opposite whereas for the other samples the alcohols were more nearly equal to the ethoxymers. The distribution between AE and total AE and FA was on average almost 50/50, with Lowell far downstream and Bryan outfall (at 3.5 and 9%, respectively) as the exceptions. Lowell far downstream was a potential outlier with much higher FA levels in the porewater than in surface water, however, the AE level and ratio between AE and FA were more on par with the other sites.

3.4. Sediment AE and FA measured concentrations

The recoveries from sediments were variable due to the complex matrix of sediment and the resultant interferences in both the physical extraction and chromatographic peaks measured for some components. Sediment concentrations for Bryan repeated the trend of surface and porewaters, highest at the outfall and decreasing upstream and downstream also showed no clear trend with stream location (Table 3). Similarly, Lowell showed a greater sediment AE concentration far downstream than the upstream samples. FA dominated the sediments in the Lowell far downstream and Bryan outfall, similar to the porewaters for those sites. Otherwise, FA and AE appeared to contribute approximately equally to the total concentrations at the other sites. A two-way ANOVA showed no significant difference ($p = 0.05$) between sampling locations within sites and sites. The sediment concentrations were lower than both the surface water and porewater concentrations. The Lowell downstream and Bryan outfall had the lowest porewater to sediment ratios at 1.9 and 1.7, respectively. The distribution between total alcohols and AE was not significantly different from the other matrices.

3.5. Modeled influent and effluent AE and FA versus measured concentrations

The iSTREEM® model predicts concentration of influent, effluent, at the beginning of a river segment and at the end. The average concentration in a segment is calculated based upon mid-segment location, accounting for loss due to sorption, settling and biodegradation. For the purposes of this study, the average concentration was used as our “outfall” values to compare the predicted values to the measured

Table 3
Surface water, porewater and sediment concentration (MEC) of FA and AE and distribution.

	Location	FA (ng L^{-1})			AE (ng L^{-1})			Total FA/AE (ng L^{-1})			Percent AE of total FA/AE (%)		
		SW	PW	SW	SW	PW	Sed	SW	PW	Sed	SW	PW	Sed
Lowell	Upstream	164	160	37	76	230	79	240	390	116	31.6	59.0	68.1
	Influent	2,332,532			184,251			2,516,783			6.3		
	Effluent	933			2861			3794			75.4		
	Outfall	225	190	38	105	285	22	330	475	59	31.8	60.0	37.3
	Downstream	132	103	98	131	185	55	264	288	153	49.6	64.2	35.9
	Far downstream	226	6653	280	80	243	96	306	6897	376	26.1	3.5	25.5
Bryan	Upstream	242	479	21	706	268	29	948	747	50	74.5	35.9	58.0
	Influent	1,314,928			115,796			1,430,724			8.1		
	Effluent	197			506			703			72.0		
	Outfall	193	2785	1605	1093	276	188	1286	3062	1793	85.0	9.0	10.5
	Downstream	823	449	34	756	706	43	1579	1156	77	47.9	61.1	55.8
	Far downstream	162	216	34	592	180	35	754	396	69	78.5	45.4	50.7
Wilmington	Upstream	191	185	82	921	273	48	1112	458	130	82.8	59.6	36.9
	Influent	180,120			136,244			316,364			43.1		
	Effluent	780			401			1181			34.0		
	Outfall	417	270	22	315	300	20	732	570	42	43.0	52.6	47.6
	Downstream	497	821	37	489	416	33	986	1237	70	49.6	33.6	47.1
	Far downstream	282	595	65	424	363	93	706	958	158	60.1	37.9	58.9

homologues. The model is consistently conservative. The outfall prediction for Bryan although higher than expected, was within 10% of measured values (Table 4).

The influent wastewater concentrations of the measured homologues ranged from 3.16×10^5–2.52×10^6 ng L^{-1} (0.32–2.52 mg L^{-1}) in Wilmington and Lowell, respectively. The effluent concentrations ranged 703–3794 ng L^{-1}, lowest in Bryan and highest in Lowell (Table 4). Influents were dominated by FA (57 to 93%) relative to the total AE, and the effluents were somewhat lower (25–66%). The removal of AE (the difference between influent and effluent) was >98% and the removal of FA was >99%.

Based on 352 MM lbs in 2008 of U.S. AE used (Blagoev and Gubler, 2009), an AE surfactant per capita consumption was estimated using the iSTREEM® model. Average national consumption was calculated from 2008 AE use in grams (Blagoev and Gubler, 2009) by the estimated population for that same year (United States Census Bureau, 2012), to derive a rate of 1.44 g $capita^{-1}$ d^{-1} (Table S4). The model took into account the local population served and measured annual mean and low water flow to calculate influent concentrations. Due to short distances, and to report conservative predicted values, in stream loss was not accounted for in the model run. iSTREEM® modeling predicted an average influent concentration nationally of 3.54×10^5 ng L^{-1}. The predicted influent values for two of the sites were less than the national average (Table 4).

The predicted AE effluent values were higher than the measured concentrations but less than the national average of 48 ng L^{-1}. The WWTP at Wilmington had the highest predicted concentration of 2.16×10^4 ng L^{-1}, with the lowest measured concentration of 401 ng L^{-1}. The predicted concentration at Bryan was 1.78×10^4 ng L^{-1} and Lowell was 9.83×10^3 ng L^{-1}.

The influent, effluent and outfall predicted values were ranked nationally and percentiles determined for AE to compare the sites on a national scale. The influent concentration in the 5th percentile was less than 1.29×10^6 ng L^{-1}. The 10th percentile encompassed 1.29×10^6 to 1.66×10^6 ng L^{-1}, and the 25th percentile ranged from 1.66×10^6 to 2.45×10^6 ng L^{-1}. The ranges for predicted effluent concentrations for the 5th, 10th, and 25th percentiles respectively were $<1.33 \times 10^4$ ng L^{-1}, 1.33×10^4 to 1.72×10^4 ng L^{-1}, and 1.72×10^5 to 2.56×10^4 ng L^{-1}. The effluent PEC for Bryan and Wilmington was in the 25th percentile and Lowell in the 5th (Table 4), suggesting high dilution.

The AE outfall predicted concentrations varied depending on the water level. Nationally, the 90th percentile for mean flow is from

Table 4
Predicted and measured concentrations in surface water of FA, AE.

	Location	AE predicted** (ng L^{-1})	AE measured (ng L^{-1})	FA* predicted** (ng L^{-1})	FA measured (ng L^{-1})
Lowell	Influent	9.83×10^5	1.84×10^5	1.38×10^5	2.33×10^6
	Effluent	9.83×10^3	2.86×10^3	1.37×10^2	9.33×10^2
	Outfall	7.61×10^2 — mean flow 3.53×10^3 — low flow	1.05×10^2	18×10^0 — mean flow 84×10^0 — low flow	2.25×10^2
Bryan	Influent	1.78×10^6	1.16×10^5	2.50×10^5	1.31×10^6
	Effluent	1.78×10^4	5.06×10^2	2.50×10^2	1.97×10^2
	Outfall	9.04×10^2 — mean flow 8.61×10^3 — low flow	1.09×10^3	24×10^0 — mean flow 2.27×10^2 — low flow	1.93×10^2
Wilmington	Influent	2.16×10^6	1.36×10^5	3.03×10^5	1.80×10^5
	Effluent	2.16×10^4	4.01×10^2	3.02×10^2	7.80×10^2
	Outfall	1.19×10^3 — mean flow 9.93×10^3 — low flow	3.15×10^2	26×10^0 — mean flow 2.19×10^2 — low flow	4.17×10^2

* *In situ* degradation was not accounted for in this run.
** Predicted numbers are calculated values.

Table 5
PEC/PNEC ratios basis the approach of Belanger et al. (2006) using full interpolated fingerprint.

	Sample/location	Surface water	Pore water	Sediment
Lowell	Upstream	0.007	0.008	0.029
	Influent	2.5	na	na
	Effluent	0.017	na	na
	Outfall	0.006	0.009	0.018
	Downstream	0.006	0.005	0.036
	Far downstream	0.005	0.012	0.079
Bryan	Upstream	0.015	0.014	0.017
	Influent	4.3	na	na
	Effluent	0.014	na	na
	Outfall	0.016	0.011	0.299
	Downstream	0.016	0.025	0.015
	Far downstream	0.016	0.010	0.020
Wilmington	Upstream	0.024	0.011	0.031
	Influent	3.6	na	na
	Effluent	0.016	na	na
	Outfall	0.011	0.013	0.010
	Downstream	0.016	0.021	0.017
	Far downstream	0.014	0.021	0.032

183 to 792 ng L^{-1}, at low flow it is 1.26×10^4 to 2.04×10^4 ng L^{-1}. The 95th percentile at mean flow is $\geq$793 ng L^{-1}, at low flow it is $\geq 2.04 \times 10^4$ ng L^{-1}. Modeling demonstrated the measured outfall concentrations corresponded to the 95th percentiles for Lowell, Bryan and Wilmington at mean flow. The predicted national average concentration at the outfall during mean flow was 2.68×10^5 ng L^{-1},

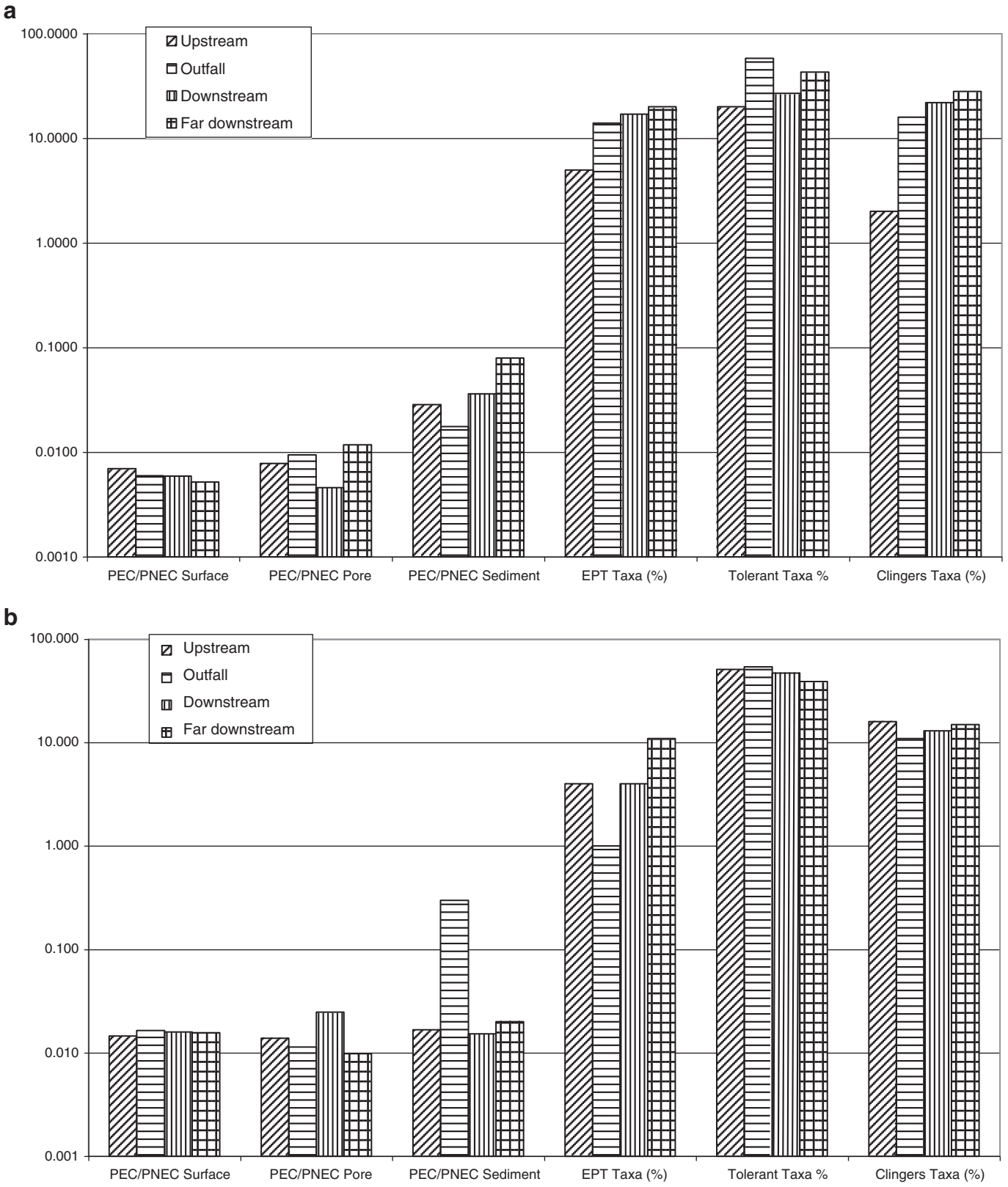

Fig. 1. PEC/PNEC ratios for surface water, porewater, and sediment solids *versus* percent indicator taxa out of total taxa, Lowell, IN (a), Bryan, OH (b), and Wilmington, OH (c).

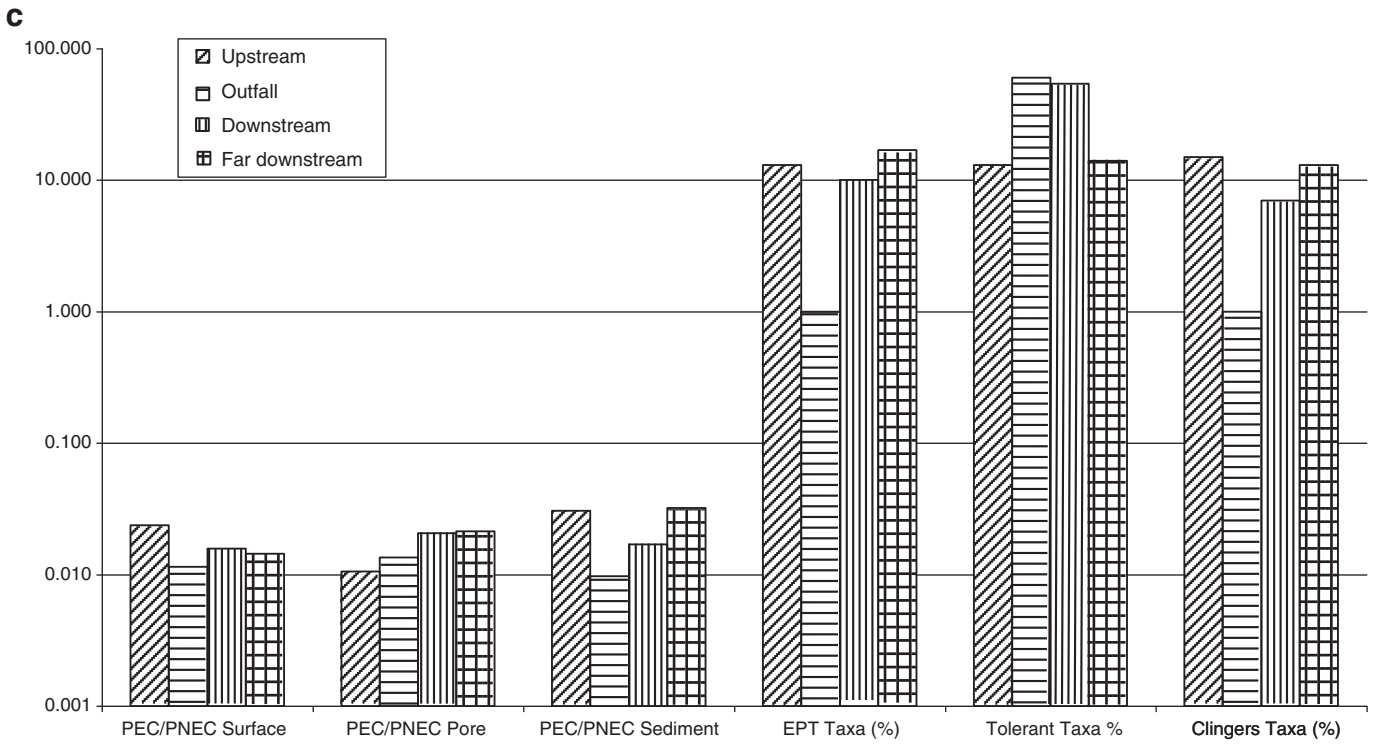

Fig. 1 (*continued*).

also in the 95th percentile. At low flow all three sites were within the 90th percentile. This is consistent with the national average of 8.58×10^5 ng L^{-1}.

FA that were modeled assuming 29,000 metric tons were used nationally (Blagoev and Gubler, 2009). The per capita consumption of FA was set to 0.202 g/cap/day. Details on the parameters used for the FA scenario are found in S4. The predicted influent concentrations ranged from 138 ng L^{-1} in Lowell to 303 ng L^{-1} in Wilmington. These values were substantially less than the measured concentrations which ranged from $1.80x10^5$ to $2.33x10^6$ ng L^{-1}. The national predicted average of FA was 4970 ng L^{-1}, also less than the measured values.

3.6. PEC/PNEC ratios

Aqueous phase PNEC values were calculated according to the method described in Belanger et al. (2006) using a probabilistic approach and estimating the HC_5 for each homolog based on the species sensitivity distribution over the toxicity tests summarized therein. PEC values were determined from the interpolated aqueous phase concentrations in the water column and in the porewater samples and risk ratios were calculated for both sets of aqueous data. Bioavailable fractions of AE were estimated by application of two previously reported adjustments to total measured concentration of each AE homologue, based on the background variables in S5.

Since the fraction organic carbon of the suspended solids was not determined, the log K_d equation was deemed more appropriate than the log K_{oc} equation. Hence, PEC values were estimated from the sediment concentrations (mg/kg) using an equilibrium partitioning approach based on log K_d data per homologue using the predictive equation developed by van Compernolle et al. (2006). Table 5 summarizes the PEC/PNEC ratios for surface and porewater and sediment solids.

Only the untreated influent to the sewage treatment plant had PEC/PNECs greater than unity. Effluent ratios were 0.016, 0.014 and 0.017 for Lowell, Bryan and Wilmington, respectively. Except for Lowell, where surface ratios were nearly an order of magnitude lower, the surface water PEC/PNECs were similar to the effluent ratios. Porewater ratios for all three sites were not significantly different from surface water ratios. Sediment values were more consistent for all three sites, which would make Lowell sediment PEC/PNEC ratios disproportionately higher relative to surface and pore values than for the other two locations. Bryan outfall sediment PEC/PNEC was dramatically higher, than any of the other results, but still well below unity. This result was driven by a high concentration of C_{16} and C_{18} FA.

3.7. Habitat, water, and sediment quality

Habitat quality, surface water, porewater, and sediment characteristics are detailed in Sanderson et al. (2006). For surface water, sediments, and porewater, no statistically significant ($p > 0.05$; Students t-test) differences of AE concentrations between the sampling locations relative to the reference location (upstream) were discernible. The average habitat quality for all locations was marginal with the Wilmington downstream and far downstream as the exceptions as sub-optimal.

3.8. Benthos

Sanderson et al. (2006) found no statistically significant ($p < 0.05$; Students t-test) differences between the sampling locations relative to the reference location (upstream) for any benthic endpoints in any of the streams. However, some differences (>20% of data) were found. In terms of total abundances, upstream location had the fewest benthic organisms, and that the outfall had the highest abundance values for Lowell and Bryan (in Wilmington the highest were the far downstream location). The total taxa richness across all streams was relatively consistent, mean = 27.5 ± 5.5 SD. However, the diversity (total abundance/total taxa) was highest in the upstream location for all streams. The percent Ephemeroptera, Plecotera, Trichoptera (EPT) taxa of the total taxa (mayfly, stonefly, and caddishfly (larvae)) were highest in the upstream or the far downstream locations for all three streams. Moreover, the percent total tolerant taxa was highest at the outfall locations for all the streams, and lowest at either the upstream or far downstream locations. As indicators of habitat

quality percent clinger taxa (insects having retreats or adaptations for attachment to surfaces in flowing water) were highest either upstream or far downstream. At the species level, twelve species were found only upstream, with a total abundance of 71 animals from all three locations. Of these 71 animals across all streams, only one species, *Boyeria vinosa* from the Aeshnidae dragonfly larvae family, were found only to be present upstream in more than one stream. In the Bryan upstream location, twenty six *B. vinosa* were identified and one *B. vinosa* was identified in the Wilmington upstream location, suggesting that this was the most sensitive species overall on a qualitative basis. The most tolerant species, on the other hand, was the chironomid (*Ablabesmyia* spp.), which was found to be the only species that occurred only in the outfall site in all streams ($n = 27 \pm 20$ SD) (Sanderson et al., 2006). These findings were consistent with stream mesocosm taxa sensitivities, where Chironomidae were less sensitive than Aeshnidae *Boyeria* sp. (Lizotte et al., 2002).

3.9. Impact and risk assessment

As described in Sanderson et al. (2006), all three sites were affected by human activity based on their chemical characteristics (S5).

Fig. 1 moreover illustrates the relationship between predicted PEC/PNEC (based on the full interpolated exposure predictions for each site divided by the QSAR results developed for AE) and the observed indicator taxa groups as percent of total taxa *in situ*.

With regard to the Lowell location, the highest PEC/PNEC was observed for the sediment far downstream; however at this site the greatest number of EPT taxa were observed. The lowest PEC/PNEC was observed in the downstream porewater at this location where we observed the highest percentage tolerant taxa. For the Bryan location, the highest PEC/PNEC was observed in the sediment at the outfall and had the fewest EPT taxa, and marginally highest number of tolerant taxa. At the Wilmington location the average lowest PEC/PNEC for all three sample matrices was observed at the outfall.

4. Discussion and conclusions

The first sections of the paper described how to find and fingerprint AE and FA up and down-stream of three WWPTs (Tables 1–2, S1). It was found that FA dominates the influent, most likely originating from many natural sources (fecal matter) (Mudge et al., 2012). The distribution AE and FA between the different locations and in the different matrices was varied due to multiple sources of FA at the locations (*e.g.* plant matter and run off) (Table 3) (Mudge et al., 2012). It is important to note that the consistency of recoveries among the different chain lengths for the aqueous samples lend confidence in the method despite low recoveries for some homologues.

The use of alkyl chain length and isotope signatures of carbon and hydrogen has been used to assess the removal of long chain alcohols as well as distinguish the sources of alcohols from detergents compared to environmental media such as wastewater and receiving water sediments. Recent studies by Mudge (2012) and Mudge et al. (2008, 2010, 2012) have clearly shown that long chain alcohols rapidly biodegrade in wastewater treatment facilities, the majority associated with fecal and detergent sources. In effluent, these alcohols have a signature that is unlike influent, a consequence of mixed-liquor in-situ (bacterial) synthesis. Not surprisingly, receiving water and sediment signatures also correspond to in-situ (algae, bacteria) production or terrestrial sources (runoff of feces and/or plant-based alcohols) instead of detergent-based sources. Therefore, long chain alcohols measured in receiving water and sediments are not sourced from detergents but from natural in-situ synthesis or terrestrial runoff sources. Mudge et al. (2012) reported that less than 1% of the total FA in a river study comparable to these streams was associated with detergents.

The predicted environmental concentrations of AE (*i.e.*, iSTREEM® values) for influent, effluent and outfall were found to be conservative, while the downstream measured concentrations were higher than predicted. This was likely due to the downstream being measured or calculated at different points in the stream from the sampling *versus* the model. The algorithm in iSTREEM® calculates the downstream value at the end of a predefined stream segment determined by a natural hydrological break, such as a tributary (Wang et al., 2005). The end of a segment in the model did not necessarily coincide with the distances the experimental samples were collected, 50 m and 1000 m from the outfall (Sanderson et al., 2006). The effluent concentration measured at all streams was less than or within the national interquartile average of 1000 to 23,000 ng L^{-1}. The predicted effluent concentrations at each site were also within the national average. This is consistent with the site selection requiring relatively efficient WWTPs. The result of the iSTREEM® modeling shows that the model can be used to prioritize sites to sample *a priori*, as well as *a posteriori* evaluate if the assumptions of relative worst-case exposure sites were accurate. Much of the FA measured in the streams was not from consumer products, as discussed above. Therefore the experimental values do not correlate to the predicted values. This is to be expected, but at the time of this sampling, anthropogenic FA contributions had not been quantified in freshwater. In conclusion, the model is not suited for compounds such as FAs with rapid and in sewer degradation, and *de novo in situ* synthesis.

As described in Wind et al. (2006) and Belanger et al. (2006), the FA played a significant role in the estimation of risk ratios for AE. Risk ratios can be determined utilizing the full measured concentrations of FA. It is also possible to "cap" the FA to that derived from AE biodegradation according to the results of Wind et al. (2006). This was done for the data evaluation reported herein. In this study (Wind et al., 2006) a continuous activated sludge (CAS) procedure was performed with synthetic sewage and a commercial AE mixture as the only surfactant substrate. Under this condition AE was the only surfactant source for FA. AE (including FA) also sorbed onto solids, and it was possible to adjust the PEC to the bioavailable fraction based on solids sorption K_d values using the equation described by van Compernolle et al. (2006). Since the measured values included both free and sorbed (*i.e.* unfiltered samples), the PEC was adjusted using the predictive equation and compared with the PEC based on total measured concentrations. Sorption was based on log K_d and the measured receiving water and porewater TSS concentrations.

The predicted risk of AE in surface waters and sediment were based on the models in the AE Workbook (Belanger et al., 2006; Boeije et al., 2006; van Compernolle et al., 2006) and as used in Slye et al. (2011). The total surface water PEC/PNEC ratio ranged between 0.024 (Wilmington upstream) and 0.005 (Lowell far downstream). All the porewater total PEC/PNEC ratios are less than 0.026. AE and FA sorb to sediments and particles; hence the sediment PEC/PNEC ratios are of interest. Use of the specific model (van Compernolle et al., 2006) resulted in total PEC/PNEC ratios that ranged from 0.010 to 0.299, for the Bryan and Wilmington outfalls, respectively (Table 5). As evident for the exposures in Tables 4, and S2, as mentioned under Section 3.7 the FA contributed significantly to the total predicted risk, while the detergent contribution of FA was less than 1% according to Mudge et al. (2012). The presence and assessment of AE, of which as a significant background of FA in surface waters are in many ways similar to the added risk approach for *e.g.* zinc and other heavy metals. In these cases, the added risk relative to the natural background exposure is accounted for (van Straalen and Souren, 2002; Bodar et al., 2005). In the case of FA the added risk is however further complicated by the fact that they are readily degraded and *de novo* synthesized, and varies over the season (*e.g.*, defoliation, temperature dependent bacterial activity). Furthermore, the results of the analysis by Schäfers et al. (2009) showed that the experimental determination of FA chronic toxicity is challenging to assess due to the rapid degradation/metabolism of the

FAs and sparse solubility of the higher chain-length FAs. FA toxicity generally increases with increasing chain-length with an optimum at C_{15} — longer chain-lengths less soluble and thus less toxic (Schäfers et al., 2009). It can be argued that assessment of FA should be treated separately from that sourced from detergent sources and, yet, conservatively assessed in this study.

The percent Ephemeroptera, Plecotera, Trichoptera (EPT) taxa of the total taxa (mayfly, stonefly, and caddishfly (larvae)) were highest in the upstream or the far downstream locations for all three streams indicating less perturbation at those sites (with the Wilmington far downstream location as the exception). Moreover, the percent total tolerant taxa were highest at the outfall locations for all the streams, and lowest at either the upstream or far downstream locations, which indicated perturbation in the outfall locations and less perturbation at the upstream and far downstream locations. As indicators of habitat quality percent clinger taxa (insects having retreats or adaptations for attachment to surfaces in flowing water) were highest either upstream or far downstream. In summary, the richness, composition, tolerance, and habitat measures relative to the macroinvertebrate benthos taxa and community indicator parameters pointed toward an increased perturbation (United States Environmental Protection Agency, 1999) in the outfall locations relative to the upstream and/or far downstream locations.

When comparing the observed biota at the different locations, with the predicted risks and habitat quality in a weight-of-evidence approach as outlined by Sanderson et al. (2006), there was no clear correlation between the predicted risk, the occurrence of biota and the habitat quality. Slye et al. (2011) and Sanderson et al. (2006), moreover also found that the surfactant PEC/PNEC ratios did not correlate with biota and hence, causality between surfactants and biota could not be established. DeZwart et al. (2006) in their analyses also found that habitat quality and surrounding activities were the primary drivers of impact on fish communities rather than the target surfactants in their study. The observed biota was of course a function of many parameters, hereunder habitat quality and total perturbations hereunder total suspended solids (TSS) and other abiotic and biotic stressors (Atkinson et al., 2009). Hence, overall, the PEC/PNEC ratios for detergent derived AE/FA suggest that minimal, if any, impact due to discharge of AE and FA from well operated activated sludge plants can be measured in these small streams. The PEC/PNEC results of this study agree well with those reported for other activated sludge effluents by Belanger et al. (2006).

Our paper highlights the low predicted risk of the AE and FA associated with detergent use. It moreover highlights the need to carefully consider the procedures for environmental risk assessment of naturally occurring compounds such as FA, which are moreover both readily degraded and *de novo* synthesized and sourced in the environment. An added risk concept could be considered with reference to both a PEC_{add} and $PNEC_{add}$ as outlined by Bodar et al. (2005).

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.05.047.

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