RP054

The fate of high volume personal care product chemicals (fatty alcohols) in riverine environments: the effect of treatment type and Eco-region

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INTRODUCTION

Fatty alcohols are common ingredients of many personal care products (PCP) and cleaning agents; they have surfactant qualities and are frequently used as their ethoxylates. Typically, they are disposed of down the drain. Previous studies (*e.g.* Mudge *et al.*, 2010, 2012) on the fate of fatty alcohols passing through wastewater treatment plants (WWTPs) have indicated that the compounds in the influent were settled out and rapidly degraded such that the effluents had fatty alcohols principally derived from *de novo* bacterial synthesis. These discharges also made small contributions to the receiving waters which were dominated by terrestrial plant and algal compounds. The work reported here was undertaken to widen both the geographical range of the studies and the different technologies that are used in the WWTPs.

North America has been divided into 15 Ecological Regions ranging from the high arctic to tropical wet forests; these were proposed by Omernik (1987) and developed by the US EPA (http://www.epa.gov/wed/pages/ecoregions.htm). Although there are 15 regions, the bulk of the USA is encompassed by just six with two of these having restricted ranges along the west coast (Figure 1). The previous USA study conducted in Luray, Virginia was in Ecological Region 8.0 (sub-region 8.3, south eastern USA plains), part of the Eastern Temperate Forests (Mudge *et al.*, 2012). The bulk of the population in the USA live toward the East and West coasts with comparatively fewer population centres in the middle.

Figure 1. Ecological Regions of North America at level 1. While there are 15 regions across the whole continent, there are only six with a significant population in the USA. Modified from the USEPA.

Figure 2. A lagoon based WWTP system and an oxidation ditch in OH

Three different Eco-regions were chosen for this study:

- the Great Plains (Region 9) and the sampled zone was further sub-classified as region 9.4, South Central, Semi-Arid Prairies,
- the Eastern Temperate Forests (Region 8) and the sampled zone is further sub-classified as regions 8.1, mixed wooded plains; 8.2, central USA plains, and 8.4, Ozark, Ouachita-Appalachian forests,
- and the Marine West Coast Forests (Region 7) which has no further sub-classification.

It may be hypothesised that the different Eco-regions will have an effect on the indigenous flora and lead to different chemical signatures in both the material entering the rivers and streams as well as the bacteria in the WWTPs. These differences may lead to a change in performance between plants in the removal of compounds from the wastewater input and the fate of any subsequent discharge into the streams.

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APPROACH

Sampling sites were primarily chosen on the basis of their performance (in compliance) and treatment technology. Eight sites with at least four different treatment technologies were chosen in each of the three eco-regions - Oxidation Ditch, Activated Sludge, Percolating or Trickling Bed Filters (TBF), Lagoons, Rotating Biological Contactor (RBC) and Sequencing Batch Reactor (SBR). Time integrated samples of the influent, effluent and sediments downstream of the discharge point were collected at each location.

Each sample had an internal standard added, was saponified with KOH and the extracted lipids were derivatised with BSTFA to form the TMS - ethers of the fatty alcohols. Details of the methods can be found in Mudge *et al.* (2012).

The fatty alcohols were identified and quantified by GC-MS methods and the stable isotopes of ^{13}C and ^{2}H measured with a Thermo Delta V (Mudge *et al.*, 2012).

Table 1. Treatment type at the 24 WWTPs together with their inputs.

WWTP	Secondary Treatment	Influent MGD (litres per day x 10^6)	Population served (in thousand)
Oklahoma Sites			
Winfield (KS)	Oxidation Ditch	1.2 (4.6)	12
Stillwater	Activated Sludge	5.4 (20.5)	48
Edmond (Coffee Creek)	Oxidation Ditch	7 (26.6)	84
Deer Creek	RBC & Activated Sludge	15 (57)	82
Del City	SBR	1.5 (5.7)	25
Ada	SBR	2.5 (9.5)	15
Weatherford	Activated Sludge	1 (3.8)	10
Elk City	Lagoon	1.2 (4.6)	12
Ohio Sites			
East Liverpool	RBC	1.7 (6.5)	11
Alliance	Activated Sludge	4.0 (15.2)	23
Massillon	Oxidation Ditch + TBF	14.8 (56.2)	36
Summit/Stow/Fish Creek	Oxidation Ditch	3.5 (13.3)	40
Strongsville	RBC	1.0 (3.8)	15
French Creek	Activated Sludge	5.8 (22.0)	50
Danville	Lagoon	0.1 (0.4)	1.1
New Bremen	Lagoon + TBF	0.8 (3.0)	3.5
Oregon Sites			
Everett (WA)	TBF and Lagoon	13.5 (51.1)	150
Chehalis (WA)	SBR	1.5 (5.7)	9
Astoria	Lagoon	1.6 (6.1)	10
McMinnville	Oxidation Ditch	3 (11.4)	33
Molalla	Lagoon	1.1 (4.2)	8.1
Silverton	Activated Sludge	1 (3.8)	8.0
Stayton	SBR	1 (3.8)	10
Corvallis	Activated Sludge	6 (22.7)	55

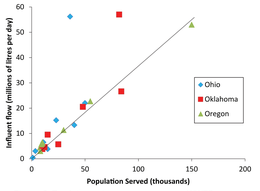

Figure 3. The influent flow measured at the WWTPs compared to the population served. The line is a trend line for illustration purposes and not a regression line. The two points substantially off the line had significant non-domestic inputs.

The three eco-regions sampled in this survey were all different, especially with regard to rainfall. OK was hot and dry; OR was cool and wet and OH was in-between. In the period running up to the sampling in OK, there has been a sustained period of drought and a reduction in the stream flows (Figure 4). This meant that at some locations, the WWTP liquid discharges made up the majority of the stream flows and so environmental concentrations of compounds in the discharge might have been greater than usual.

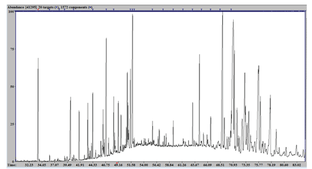

Figure 5. An example GC trace of a sediment sample from OK. The trace contains both fatty alcohols and several other compound groups.

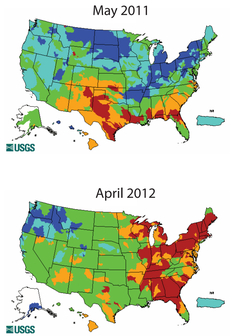

Figure 4. River flow conditions relative to the long term average. A significant deficit can be seen in the southern states over the sampling period in 2011 (top figure). Significant flows above the norm can be seen in OR during the 2012 sampling period. Data from the USGS

RESULTS

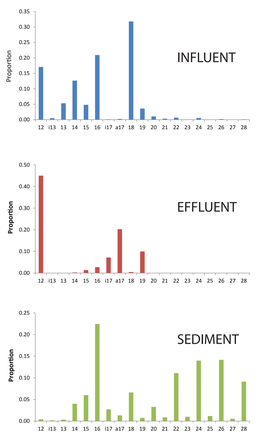

Figure 6. The fatty alchols mean profiles from OK sampling sites ($n=8$)

The mean fatty alcohol composition for samples collected in OK for the INFLUENT, EFFLUENT and SEDIMENTS can be seen in Figure 6. Similar traces were obtained for such samples in each Eco-region.

The INFLUENT samples had considerable amounts of the18 carbon fatty alcohol which was most likely produced within the pipe between the drain and the WWTP. The composition did not match the profile of the fatty alcohols used in the catchment (*e.g.* DeLeo *et al.*, 2011) and will be a mixture of the products, faecal matter and food waste.

The EFFLUENT had a different profile to the influent with increased amounts of the odd chain bacterial markers and the C_{12} fatty alcohol.

The SEDIMENTS were dominated by the terrestrial plant signal (long chain, even carbon numbers) together with algal short chain compounds. Notice the almost complete loss of the C_{12} from the effluent.

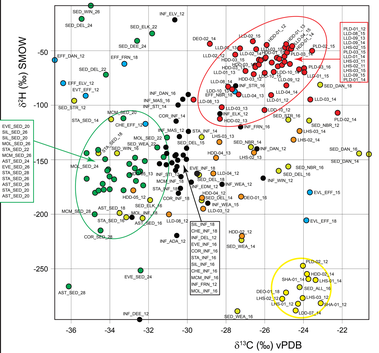

Figure 7. The stable isotope cross plot for all fatty alcohols measured in the three eco-regions together with the detergent derived fatty alcohols from the Luray study (DeLeo et al. 2011; Mudge et al. 2012). The data are colour-coded according to their likely source.

Dark green circles indicate long chain (C20+) compounds from terrestrial plants found in sediment samples. Pale green/yellow circles indicate short chain compounds typically from algal synthesis found in sediment samples. Blue circles are used for all effluent compounds. **Black circles** denote fatty alcohols in influent samples. Red circles indicate the petroleum derived detergent fatty alcohols from the Luray study. Yellow circles are the oleochemical fatty alcohols in detergents from the same Luray study. Orange circles are used for detergent derived fatty alcohols that have stable isotopic signature that suggests a blending from both petrochemical and oleochemical sources.

Stable isotope analysis clearly demonstrates that the fatty alcohols in the influent (black circles) have a different geochemical signature to the same chain length fatty alcohols in the effluent (top left of Figure 7) and these are very different from the sediment fatty alcohols which are either terrestrial (dark green) or algal (light green) in origin.

These results are consistent with similar studies conducted in Luray, VA (Mudge et al., 2012) and the UK (Mudge et al., 2010).

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DISCUSSION

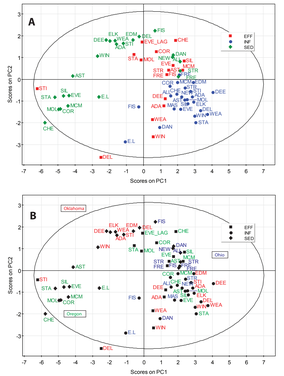

Figure 8. A. A scores plot of the fatty alcohol profile data from all sites and samples as proportions after log10 transformation. The data are colour-coded according to their sample type. **B.** The same data as in A but the data are colour-coded according to their location.

If all the fatty alcohol profile data are considered for the three eco-regions, significant patterns emerge. The scores plot from a PCA after log transformation can be seen in Figure 8. The data are presented according to their sample type in A or colour-coded according to their location in B.

The sediment samples tend towards the left of the figure (A) while the influent samples tend towards the right. The effluents occupy a more central location but are more closely related to the influents than the sediments. The separation is not completely clean as several of the OH sediments are intermingled with the effluents. This is due to the unusual relative absence of long chain fatty alcohols in these samples.

The score data can also be presented according to the Eco-region (B). In this case, it is clear that the samples are not clustering together by location and that the sample type is the major factor controlling the position of the samples in this figure.

Figure 9. Values of δ^2H in precipitation across the USA (Redrawn from Hoefs, 2009).

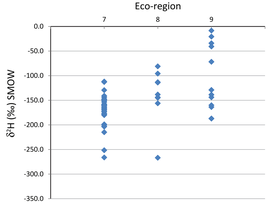

Figure 10. The spread of sedimentary fatty alcohol δ^2H values for the three eco-regions.

The bulk of the WWTP influent samples occupy a very narrow range with regard to the $\delta^{13}C$ values around -31‰. There is a wide spread of δ^2H values from -20 to -300‰ although there is not the same Eco-region trend as with the terrestrial plant fatty alcohols. The position of these influent fatty alcohols coincides closely with the values measured for faecal material undertaken as part of the initial phase of these investigations. The mean projection of the free and bound faecal fatty alcohols was -30 and -200‰ for $\delta^{13}C$ and δ^2H respectively. The differences in the δ^2H values may be due to Eco-region differences that may be ascribed to eating habits (*e.g.* Liu *et al.* 2006; Fraser and Meier-Augenstein 2007; Ehleringer *et al.* 2008) as the stable isotopic composition of the food consumed in the USA is relatively homogeneous or climatic (rainfall) patterns (Figures 9 and 10) or different contributions from petrochemical-derived surfactants in detergents and personal care products. There is very little overlap between the influent stable isotopic signatures and the other samples in this cross plot. It may be concluded from this study that:

a. the fatty alcohols entering the WWTPs are degraded within the plant indepedent of the secondary treatment type and Eco-region,
b. differences in the stable isotopes can be related to the different source materials and location,
c. the fatty alcohol contribution that PCP and detergent products make to the environment via WWTPs is negligible.