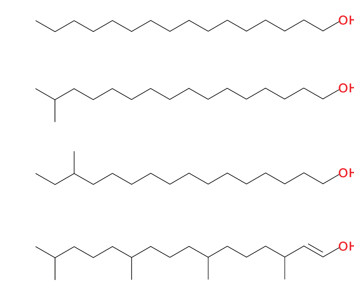
Using stable isotopes of carbon (^{13}C) and hydrogen (^{2}H) to determine the contribution and fate of detergent fatty alcohols in the environment

S.M. Mudge – Bangor University, Menai Bridge, Anglesey, UNITED KINGDOM

P.C. DeLeo - The Soap and Detergent Association, Washington, DC

C.V. Eadsforth - Shell Health, Chester, Shell Global Solutions, Central Product Safety-Environmental, Cheshire, UNITED KINGDOM



INTRODUCTION

Fatty alcohols are widely produced by bacteria, plants and animals for a variety of metabolic purposes and, in general, terrestrial plants produce long chain compounds with carbon chain lengths greater than 20. Marine organisms tend to have shorter chain compounds typically from C_{10} to C_{18}. Due to the synthetic pathway by which these compounds are formed, higher organisms tend to have even carbon numbered straight chains such as C_{10}, C_{12} and C_{14}.

Detergent formulations can include fatty alcohols as alcohol ethoxylates or alcohol ethoxysulphates. The chain length of the compounds used in these formulations has typically been in the C_{10} to C_{18} region with some mid-chain methyl branches possible as well as straight chain moieties. These alcohols may be sourced from both natural materials such as palm oils or *de novo* synthesis from oil components. The majority of these compounds are functionally identical to the natural fatty alcohols produced by bacteria, plants and animals.

Fatty alcohols may enter the marine environment from a range of sources (Figure 1) including natural production by animals and plants as well as the use of man-made products such as liquid detergents and cosmetics. Waste water treatment plants (WWTP) collect surface water drainage containing soils and plant materials as well as faecal matter, food waste and anthropogenic fatty alcohols used in cleaning or cosmetic formulations. These compounds may be altered during passage to the influent works of the WWTP, within the WWTP itself and also be removed with the solid phase sludges (biosolids) so the final effluent may have a different suite of compounds. The discharges would combine with the natural materials in the marine environment from runoff and *in situ* production.

The work reported here is part of study to quantify the relative inputs of these fatty alcohols from each source in the receiving environment.

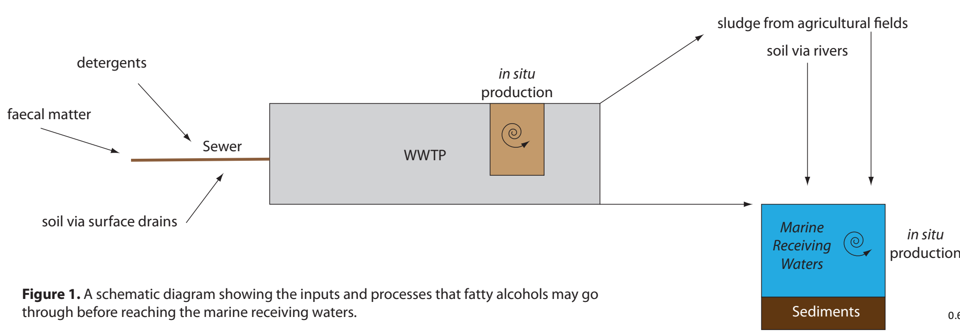
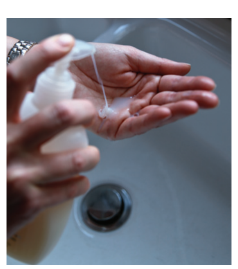


Figure 1. A schematic diagram showing the inputs and processes that fatty alcohols may go through before reaching the marine receiving waters.



SAMPLE COLLECTION AND PREPARATION

Soil samples were collected from land that would potentially contribute to the Menai Strait, North Wales. The marine sediment samples were collected along a transect from the discharge point of the WWTP (Figure 2). Liquid samples were collected from the various stages of Treborth WWTP (Figure 3).

All samples were extracted by reflux with 6% KOH in methanol, liquid - liquid separation into hexane and derivatisation with BSTFA. An internal standard (2-dodecanol) was added prior to reflux. Liquid samples were extracted after addition of KOH to the liquor.

Consumer products were selected after a qualitative survey of the different brands of liquid detergents available in the major supermarket serving the catchment of the Treborth WWTP. On the basis of this survey, four liquid formulations containing fatty alcohols were selected and provided simply labelled 1 – 4 for analysis. These fatty alcohols were extracted as their alkyl iodides (Figure 4).

All samples were analysed by GC-MS to identify each fatty alcohol present in the samples (e.g. Figure 5) and generate the profiles. The samples were then analysed by Stable Isotope Ratio Mass Spectrometry using a Thermo Delta V instrument.

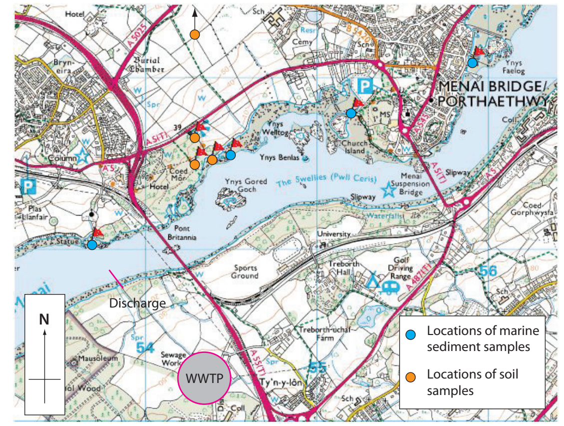


Figure 2. A map of the sampling locations. The WWTP discharges ~8000 m3 per day into the Menai Strait; marine sediment samples were collected in a transect away from the pipe towards the north east. Soils that may also contribute were collected from the adjacent land.

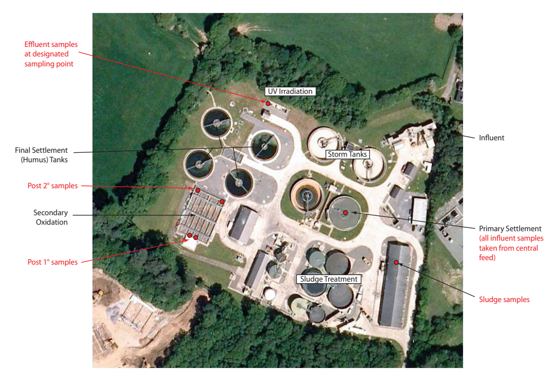


Figure 3. An aerial photograph (Google) of the Treborth WWTP indicating the sampling locations

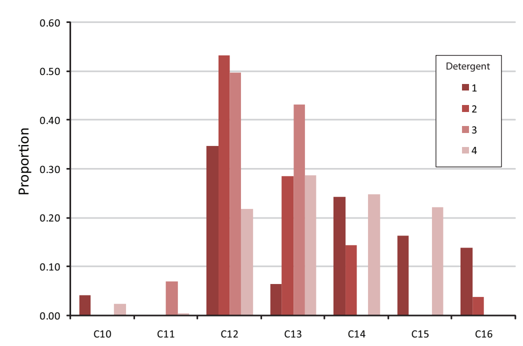


Figure 4. Detergent fatty alcohol profiles extracted from the consumer product as their alkyl iodides.

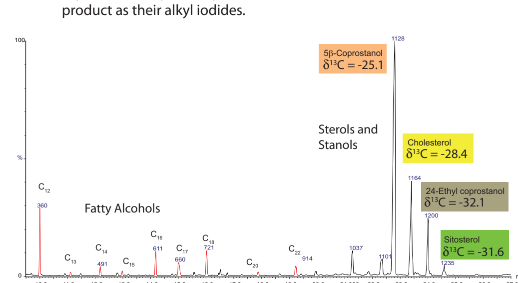


Figure 5. The GC-MS trace for an influent sample. The sterols and stanols are also indicated together with their $\delta^{13}C$ values showing significant differences between source.

RESULTS

Terrestrial vs. Marine (see Figure 6)

1. The fatty alcohols derived from the terrestrial biological sources (GREEN OVAL), most probably plants, had $\delta^{13}C$ values considerably smaller (-32 to -35‰) than the fatty alcohols extracted from the marine environment (-20 to -25‰). This even includes the short chain compounds (*e.g.* C_{14} and C_{16}).
2. The terrestrial fatty alcohols had a wide range of $\delta^{2}H$ values despite having a relatively narrow $\delta^{13}C$ range. The phytol, derived from chlorophyll, consistently had large negative values on this axis.
3. The marine sediment samples (BLUE OVAL) had a range of $\delta^{13}C$ values depending on the chain length of the fatty alcohol. The shorter chain fatty alcohols had the largest values (around -20‰) and this included the C_{12} which is not shown of the figure as there was no corresponding $\delta^{2}H$ value. The C_{16} and C_{18} had smaller values and potentially indicate a mixed marine and terrestrial source. The marine sources are probably algal synthesis using dissolved bicarbonate as the carbon source.

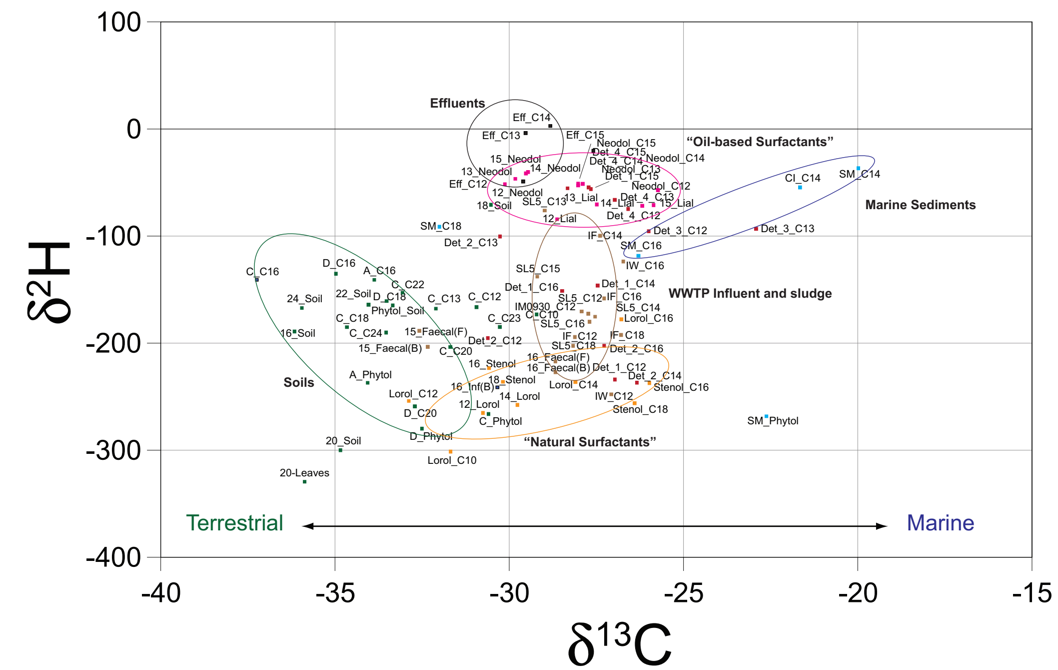


Figure 6. The two-dimensional stable isotope plot including all environmental samples and surfactants. The ovals group together samples from the same source type or location. The chain length of the individual fatty alcohols is also presented with each label.

Influent vs. Effluent (see Figure 6)

4. The fatty alcohols of the WWTP influent (BROWN OVAL) have $\delta^{13}C$ values that are common to faecal matter and both oil-based and natural based surfactants (LILAC OVAL). However, there is a big difference in the $\delta^{2}H$ values between the faecal and natural-based surfactants (ORANGE OVAL) on one hand and the oil-based surfactants on the other.
5. The influent appears to be a mixture of the faecal matter and natural-based surfactants (75%) with the remaining 25% of the C_{12} derived from the oil-based surfactants.
6. The effluent samples (BLACK OVAL) have considerably different $\delta^{2}H$ values to the other WWTP samples. The $\delta^{13}C$ and $\delta^{2}H$ values suggest that these compounds have been synthesised *de novo* within the WWTP by bacteria. It is possible that the some of the C_{12} may be derived from the oil-based detergents based on the $\delta^{2}H$ value.
7. Based on the mean concentration of the C_{12} in this effluent (~37 $ug.l^{-1}$) and the maximum authorised discharge (~8000 $m^{3}.day^{-1}$), this component may contribute up to 300 $g.day^{-1}$ to these receiving waters. However, there was no evidence of C_{12} with the correct $\delta^{13}C$ attributable to the effluent in the marine sediment samples except for one site, 1.7 km from the discharge point.

CONCLUSIONS

The two dimensional compound specific stable isotope ratio mass spectrometry has proven to be a useful tool in determining the sources of fatty alcohols in this complex multi-source environment. In this case, oil-based detergents may contribute up to 25% of the C_{12} fatty alcohol in the influent to this WWTP but this does not appear to be the same C_{12} that is present in the effluent. It is known that these compounds have short half-lives in sewage treatment facilities and these compounds may be synthesised by the very active bacterial population present in all stages of the system. In general, the sediments of the receiving waters also do not appear to have C_{12} derived from either the effluent or oil-based detergents but those derived from natural marine synthesis. Further work is in progress to quantify the contributions from a WWTP in a freshwater environment.