Forensic identification of the anthropogenic contribution of fatty alcohols to the environment by stable isotope analysis

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Introduction

To investigate the potential sources for fatty alcohols arriving at a WWTP and entering the receiving waters, a study was conducted in North Wales in the catchment of the Treborth treatment plant.

Fatty alcohols are produced naturally by most living organisms and may also be synthesized from various sources of oil. These compounds are used as ethoxylates or sulphates in many formulated consumer products such as detergents, which typically have a down-the-drain disposal and treatment in a waste water treatment plant (WWTP). Petroleum-based fatty alcohols are functionally identical to oleochemical-based (natural) fatty alcohols and are not easily distinguished by conventional means.

Fatty alcohols may enter the marine environment from a range of sources including both natural production by animals and plants as well as the use of man-made products such as liquid detergents and cosmetics. Terrestrial runoff may deliver long chain plant and insect waxes both associated with the parent biological material or after partial degradation in soils. Marine organisms may synthesise fatty alcohols directly or they may be formed *in situ* through the degradation of other organic matter. Waste water treatment plants collect surface water drainage containing soils and plant materials as well as faecal matter, food waste and anthropogenic fatty alcohol derivatives 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.

Stable isotope signatures of fatty alcohols may differ between biogenic fatty alcohols and synthetic fatty alcohols based on oleochemical and petrochemical precursors. Two dimensional stable isotope analyses (^{13}C and ^{2}H) had been shown to be a suitable analytical tool in an earlier study [Mudge & Meier-Augenstein, 2010] and so was used here to help with source attribution of fatty alcohols found in the WWTP and its discharge.

Materials and Methods

Samples

Soil samples were collected from land that would potentially contribute run-off to the Menai Strait, North Wales. Soils were collected as surface scrapes from an arable field, a pasture field, within a deciduous wood and within a coniferous wood. The location of the samples can be seen in Figure 1. In each case, ~200 ml of soil was collected. The marine sediment samples were collected in a similar fashion along a transect from the discharge point of the WWTP.

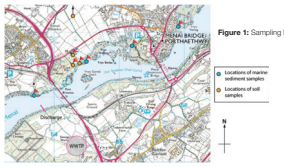

Figure 1: Sampling locations

Samples of raw fatty alcohols used in the formulation of detergents and cosmetics were provided from the manufacturers. These had been analysed in the initial study and analyses were repeated to ensure consistency between results. Commercial 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, North Wales. On the basis of this survey, four liquid formulations containing fatty alcohols, two hand dishwashing liquids and two liquid laundry detergents, were selected and provided.

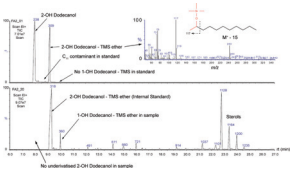

Figure 2: The upper panel shows the GC trace of the part derivatised standard together with the mass spectrum of the TMS ether. The lower panel shows the TIC of one of the samples including the derivatised standard

GC/MS analysis

All samples were analysed by GC-MS to identify and quantify the fatty alcohols; the internal standard was used to provide an internal calibration (Figure 2).

Compound specific ^{2}H and ^{13}C isotope analysis

All samples were taken to the Scottish Crop Research Institute in Dundee, Scotland for compound specific isotope analysis (CSIA) on a Thermo Delta V Plus Isotope Ratio Mass Spectrometer that was hybridized with a Thermo Ion Trap MS (ITQ 900) for simultaneous compound identification [Meier-Augenstein et al., 1994; Meier-Augenstein, 1995].

Results

The fatty alcohol profiles of the WWTP influent were dominated by the C_{12} straight chain moiety followed by the C_{16} and C_{18} compounds (Figure 3). The profile was weighted towards the even carbon short chain compounds with few plant derived long chain compounds present. This is typical of animal derived material. Small amounts of odd chain length and branched compounds were also present indicative of bacterial presence.

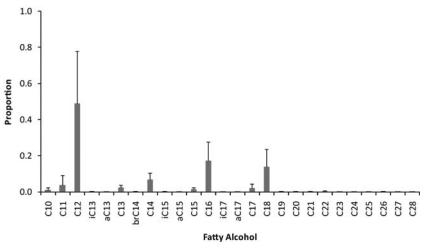

Figure 3: The mean fatty alcohol profile for the WWTP influent; error bars are one standard deviation.

Terrestrial soils and plant matter were clearly separated from other samples by having a low $\delta^{13}C$ value, typically around -35‰. Similarly, marine derived compounds had $\delta^{13}C$ values around -20‰. In addition, fatty alcohol profiles differed significantly between soil samples and marine sediment samples (Figures 4 and 5). Samples from the WWTP had intermediate values which altered depending on where in the system samples were collected. The $\delta^{2}H$ values had a greater range from -350‰ to 0‰.

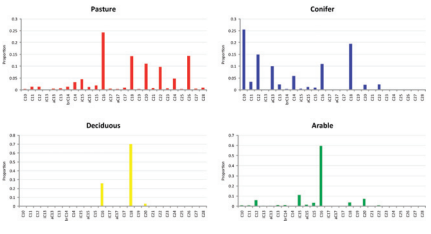

Figure 4: The fatty alcohol profile in the soil samples.

The limit of detection for ^{2}H CSIA was not as good as for ^{13}C CSIA. This reduced the number of stable isotope pairs to 91 compounds. The data from these analyses are combined with the data from the initial study to demonstrate the appropriateness of the method and the cross plot can be seen in Figure 6.

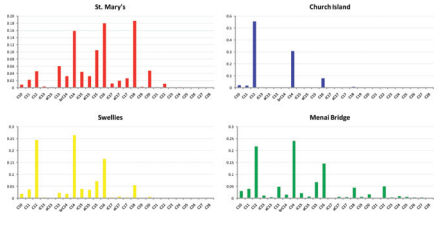

Figure 5: The fatty alcohol profile in the marine sediment samples. The samples are arranged in order of increasing distance from the WWTP discharge.

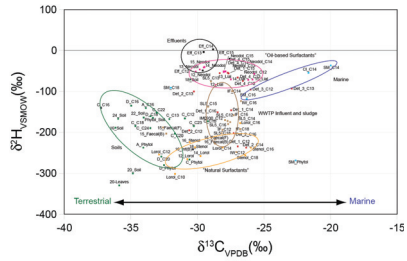

Figure 6. Cross plot of all the stable isotope pairs for all samples. The terrestrial soils are indicated by the green ellipse; the detergents and raw materials based on natural fatty alcohols are indicated by the orange ellipse; the oil-based detergents are within the lilac ellipse; the WWTP influent samples within the brown ellipse fall between the two detergent sources; the effluents have much greater $\delta^{2}H$ values and are located in the black ellipse at the top of the figure. The sediments of the marine receiving waters are shown in blue.

Conclusions

1. Two dimensional (^{13}C and ^{2}H) stable isotope analysis is a suitable analytical tool to separate the different sources of fatty alcohols that may exist in a WWTP and in the receiving waters from that WWTP. Isotopic abundance of ^{13}C alone may be good enough to separate terrestrial from marine sources but it does not separate faecal sources from either natural or oil-based detergents.
2. Natural plant based detergents have $\delta^{13}C$ values between -26 and -32‰ while oil-based detergents occupy a range between -25 and -30‰. The corresponding $\delta^{2}H$ values are -250‰ for natural sourced materials and -50‰ for oil-based detergents which enables these two sources to be separated.
3. Of the detergents analysed, samples 3 and 4 appear to exclusively derived from oil-based raw materials while detergents 1 and 2 have C_{12} and C_{14} components from natural sources combined with some oil-based longer chain fatty alcohols.
4. The effluents from the WWTP contain mainly short chain compounds with a chain length less than C_{16}. Their $\delta^{2}H$ stable isotope signature is different to the other potential sources examined and suggests bacterial synthesis during the treatment processes. On the basis of the maximum discharge rates and the mean C_{12} concentration in the effluent, this WWTP would contribute up to 300 g day^{-1} of fatty alcohols to the Menai Strait, the receiving waters.

The approach presented here clearly demonstrated the different sources and the fate of these compounds through the WWTP. In summary, the fatty alcohols in the environment were not derived from the WWTP effluents which in turn were not the same as the ones in the influent; the most likely source of fatty alcohols observed in sediment samples from the Menai Straight is *in situ* bacterial synthesis.

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References

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