Fingerprinting of Fatty Alcohols in Environment Samples

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Introduction

Fatty alcohols (Figure 1) occur in the environment from a range of natural and anthropogenic sources. Fatty alcohols are used in cosmetic and detergent formulations usually as sulphates or polyethoxylates. They are disposed of 'down the drain' and undergo degradation during sewage treatment and these degradation products may eventually make their way to the marine environment. Fatty alcohols are also produced naturally by a wide range of organisms. These compounds may be transported *via* several routes to the sediments of the marine environment. Some free fatty alcohols have been identified as potential pollutants (Aliphatic Alcohols [C_{6-22}] SIAR, 2006) as they typically have a greater aquatic toxicity (LC_{50} <1 mg.L^{-1}) than most of the ester and ether bound compounds. Comparison of fatty alcohol concentrations from waste water treatment plant (WWTP) effluent monitoring studies of alcohol ethoxylates (AE) (Eadsforth et al., (2006), Morrall et al., (2006)) with a laboratory continuous activated sludge study with AE (Wind et al., (2006)) has indicated that only a small fraction of fatty alcohols in WWTP effluents originates from AE entering the WWTP. To assess the risk associated with the use of fatty alcohol based surfactants used in detergents, the sources of the free fatty alcohols and the relative contribution of surfactants need to be determined. Due to the multiplicity of potential sources of fatty alcohols, further detailed molecular investigations are needed to determine the origin of various free fatty alcohols from natural and synthetic sources.

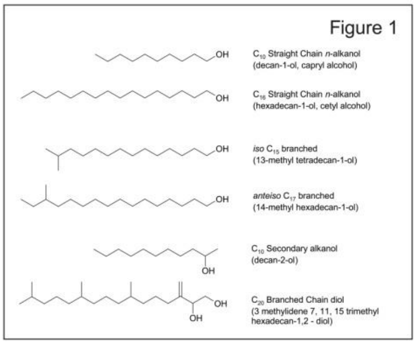

Figure 1

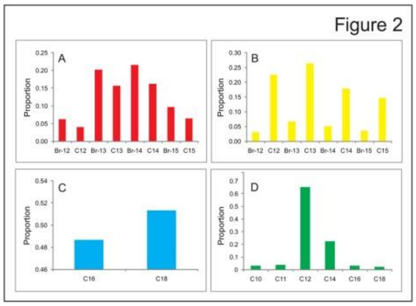

Figure 2

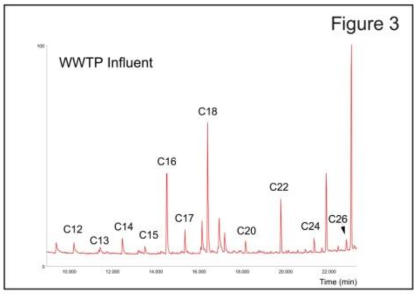

Figure 3

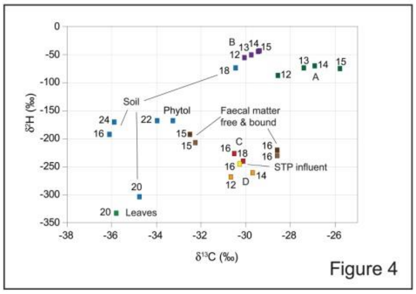

Figure 4

Experimental

The detergent range alcohols C_{12} – C_{18} (Figure 2 shows four mixtures used in formulations) are also produced by animals and plants so simple techniques such as signature analysis based on the profile of compounds do not unambiguously allocate source in this case. The most appropriate method for identification of the different materials may be through compound specific stable isotope analyses. All compounds contain stable isotopes of the elements and in the case of fatty alcohols these include ^{13}C, ^{2}H and ^{18}O as well as the more normal ^{12}C, ^{1}H and ^{16}O. The enzymatic and chemical reactions that the compounds undergo during synthesis can lead to preferential incorporation of one of the isotopes and so the final compounds have stable isotope ratios that differentiate between the manufacturing processes. The carbon and hydrogen isotopes were chosen for investigation in this work.

Samples of detergent fatty alcohols that are used in product formulations were obtained from manufacturers. Two of these are derived from oil while the other two are manufactured from palm products. Samples of soil, faecal matter, terrestrial plant matter and foodstuffs (which are known sources of fatty alcohols in WWTPs) were collected in the Bangor, UK area together with the WWTP influent, effluent and marine sediment. This treatment plant serves much of the community living beside the Menai Strait and has a catchment population of approximately 54000 giving a dry weather flow of 8222 m^3 per day. There are few industrial discharges to this plant as it serves a mainly domestic catchment. On return to the laboratory, these samples were immediately extracted and analysed for bound fatty alcohols (principally wax esters) as well as free unbound fatty alcohols. Figure 3 shows an example GC-MS trace of the bound fatty alcohols in WWTP influent.

Conclusions

* The most obvious difference in Figure 4 is the wide separation of the oil derived synthetic fatty alcohols (A and B) from those made from palm derivatives (C and D). These differences are principally in the δ^2H values although A is different from B in the δ^{13}C values. There are differences between individual members of the sequence in progression with the lower carbon numbers (*e.g.* C_{12}) having lower δ^{13}C values compared to the longer chain members of the sequence.

* The terrestrial soils which may enter an influent of the WWTP during periods of increased rainfall have a diverse set of stable isotope values. In general, they are all much lower in δ^{13}C as may be expected from their terrestrial origin. However, the C_{20} compound has a much lower δ^2H value compared to the other fatty alcohols. This value is consistent with the C_{20} values for terrestrial plant leaves where the fatty alcohols are likely to be in the wax cuticle protecting the plant from desiccation. The other odd compound in this sequence is the C_{18} fatty alcohol which is different in both the δ^2H and δ^{13}C values.

* The faecal matter was analysed as both bound and free fatty alcohols and consistent δ2H and δ13C values were obtained in the two fractions suggesting the same original source. The δ^{13}C values for the C_{16} fatty alcohol are greater than the other natural fatty alcohols in the analyses and are indicative of animal synthesis. The C_{15}, however, is different; this odd chain compound is typical of bacterial productivity and the carbon source may have a "plant like" origin or be the result of a different synthetic pathway which has a different discrimination for the carbon isotopes.

* The WWTP influent only had one compound with sufficiently high fatty alcohol concentrations to obtain both the δ^2H and δ^{13}C values. This free fatty alcohol had similar stable isotope values to that of the naturally produced raw materials (C and D). However, there is no evidence of any synthetic raw materials with significantly greater δ^2H values closer to -50 and -70‰ as the faecal matter had similar δ^2H values to the influent. The δ^{13}C values for the other components of the WWTP influent are indicative of animal production except for the C_{24} which has a value of -33.4‰ indicative of terrestrial plant matter.

* Of great interest, however, is the value of the C_{16} fatty alcohol in the sediment – essentially the receiving waters for the WWTP discharge. Although the hydrogen values could not be obtained, the carbon stable isotope value could (-24‰); this is significantly greater than the others measured in these samples and is indicative of marine faunal production and suggests very little anthropogenic or sewage derived fatty alcohol input.

" The initial investigations have confirmed that the stable isotope approach is valid for discrimination between point sources of fatty alcohols. A second phase of sampling in a Bangor catchment area has been completed. This involved soil and sediments, as well as samples from various treatment stages of a WWTP to assess the fate and potential origins of fatty alcohols within the treatment process. Samples have been analysed and are being processed."

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