Science of the Total Environment 470–471 (2014) 835–843

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The effect of secondary treatment and eco-region on the environmental fate of fatty alcohol based surfactants ☆

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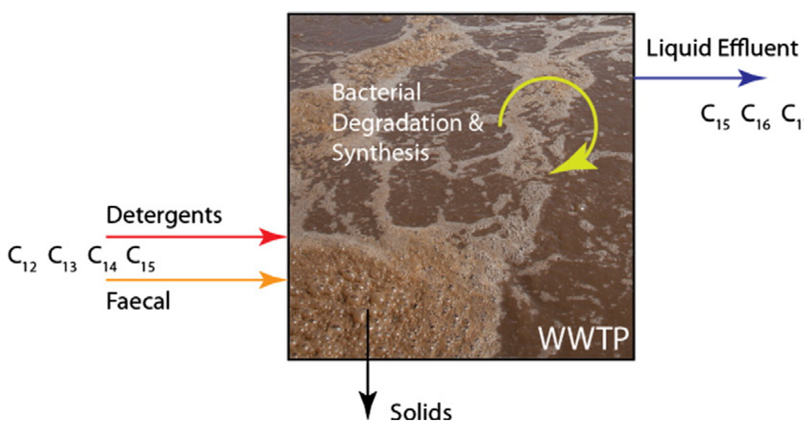
HIGHLIGHTS

- Secondary treatment technology does not alter the efficiency of removal of fatty alcohols.
- Stable isotope analysis shows fatty alcohols in the effluent are not those from the influent.
- The eco-region affects the influent composition and deuterium content of plant matter.
- Naturally occurring fatty alcohols dominate in the sediments of the receiving waters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2013
Received in revised form 23 September 2013
Accepted 25 September 2013
Available online 5 November 2013

Editor: Damia Barcelo

Keywords:
Detergents
Wastewater treatment plants
Eco-region
Sewage

ABSTRACT

Samples of influent, effluent and sediments of the receiving waters of eight WWTPs were collected in each of three eco-regions of the USA, a total of 24 facilities. Six different treatment technologies were included to determine the fate of anthropogenic fatty alcohols. The lipids were analysed by compound-specific stable isotope ratio mass spectrometry. There were significant differences in the profiles of the influent among eco-regions, due to differences in the products used within the catchment, the diets of the inhabitants, or in-pipe processes. The sediments of all the receiving waters had similar fatty alcohol profiles, with terrestrial plant matter dominating and secondary contributions from algal and bacterial synthesis. Any contributions from the WWTP liquid effluents were small (<1%) and not from the original fatty alcohols suite in the influent. These compounds might have the same chain lengths, but they have different stable isotopic signatures. The type of secondary treatment did not affect the removal of fatty alcohols and the sediments of the receiving waters were dominated by terrestrial plant inputs; the eco-region may affect the profile of the influents but not the stable isotopes. The ecological risk from the use of these particular chemicals, which are disposed of down the drain, is minimal.

1. Introduction

Fatty alcohols and their derivatives are widely used as surfactants in many detergents and personal care products. These high-production-

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http://dx.doi.org/10.1016/j.scitotenv.2013.09.078

volume chemicals have been assessed under REACH and similar global chemical management programmes, with data requirements driven by the need to understand the environmental sources, fate and effects of these compounds (Belanger et al., 2006, 2009). The principal chemical form of these compounds in product formulations is as ethoxylates with the number of ethoxylate units ranging from 0 to 18 (Morrall et al., 2006), as ethoxysulphates and sulphates (Federle and Itrich, 2006). The global market for these detergent alcohols reach 2.18 million tonnes in 2012 (Gubler and Inoguchi, 2013). The principal disposal route for all of these compounds is down-the-drain with subsequent removal in wastewater treatment plants.

The fate of the detergent fatty alcohols is of particular importance as regulators need to assess the risk to the environment from their use. Recent evaluation of river fauna communities based on risk calculations using alcohol ethoxylates in river water, pore water, sediments and benthic organisms (Sanderson et al., 2013) indicated that factors other than fatty alcohol contributions were responsible for the observed structure.

The fate of these chemicals has been investigated previously; analysis of multiple samples collected from two different catchments – one in the UK (Mudge et al., 2010) and one in the USA (Mudge et al., 2012) – led to the conclusions that fatty alcohols in the effluent from the two wastewater treatment plants (WWTPs) were not the same as the ones in the influent, and that the fatty alcohols in the sediments of the receiving waters were dominated by naturally occurring compounds, not those from the WWTPs. While these results are consistent and confirm laboratory investigations (Federle and Itrich, 2006; Itrich and Federle, 2004; Matthijs et al., 1995), the secondary biological treatments used in both cases were oxidation ditches.

Wastewaters are treated using several technologies and the secondary biological treatment processes may directly affect the degradation of compounds and may induce of different chemical products (McVicar et al., 2012). For instance, it is possible that the microorganisms present in a relatively static lagoon system lead to a different chemical suite in the effluent compared to an oxidation ditch or activated sludge system. Therefore, to ensure that the conclusions drawn from previous studies are valid across and wider geographical area, a range of WWTP technologies were included in the sampling design.

Previous work (Mudge et al., 2010, 2012) used the stable isotopes of carbon (^{12}C and ^{13}C) and hydrogen (^{1}H and ^{2}H) to develop chemical signatures of the organic compounds. These naturally occurring isotopes have slightly different ratios depending on the processes that the sources undergo during fatty alcohol synthesis. Therefore, there are measureable differences between the petrochemical and oleochemical surfactants along with many other natural sources. This approach was able to separate the different origins within the mixed source environment of the sewer system and receiving waters.

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 USEPA (2012). 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. The previous USA study (Mudge et al., 2012), conducted in Luray, Virginia, was in ecological region 8.0 (sub-region 8.3, south-eastern USA plains), part of the Eastern Temperate Forests. The bulk of the USA's population live toward the East and West Coasts, with comparatively fewer population centres in the middle.

It is possible that the different climates across the USA may lead to different microbial assemblages in the WWTPs or in the environment. Along with the different secondary treatment processes, this may influence the chemical composition of the final effluents.

2. Materials and methods

It can be argued that performance differences may occur over the range of climatic conditions in the USA, and also between the different secondary treatment processes available. Therefore, this work was undertaken to examine both of these potential factors in determining the fate of fatty alcohols in wastewater streams. Different eco-regions (climatic zones) were chosen for this study:

- The Great Plains (region 9), with the sampled zone further sub-classified as region 9.4, South Central, Semi-Arid Prairies. As the name suggests, the zone has low rainfall, wide-open grass plains typically grazed by cattle, and cool winter temperatures followed by hot, dry summers. Although the region extends northward into Canada, the major population centres are in the south and samples were collected in Oklahoma.
- The Eastern Temperate Forests (region 8) and the sampled zone are further sub-classified as sub-regions 8.1 (mixed wooded plains), 8.2 (central USA plains), and 8.4 (Ozark, Ouachita–Appalachian Forests). The region is distinguished by a moderate to mildly humid climate, a diverse forest cover, and a high density of human inhabitants (approximately 160 million). Activities include standard urban industries, agriculture, and forestry. In large parts of this region, the forests have been cleared and the land is now used for agriculture, especially corn and soybean farming. Samples were collected in Ohio.
- The Marine West Coast Forests (region 7.1), which has no further sub-classification. This region is described as highly productive, rain-drenched evergreen forests. The region includes the Willamette Valley, which runs from south to north between the Oregon Coast Range to the west and the Cascades Range to the east. The eco-region is drained mostly by the Willamette River and its tributaries, which flows into the Columbia River straddled by Portland, Oregon. The majority of the samples were collected in Oregon, with two sites in Washington (WA).

Previous work (Mudge et al., 2010, 2012) indicated that analysis of the influent, effluent and sediments in the receiving waters would be sufficient to determine the contribution that the different fatty alcohol sources make to the environment. The sampling plan, therefore, was designed to sample the three locations at each WWTP (influent, effluent and sediment) in the three different ecological regions across the four or five different secondary treatment techniques per eco-region depending on finding suitable WWTPs.

2.1. Sampling plan

Sampling sites were chosen on the basis of the performance of the WWTPs, with an influent flow of less than 152 million litres per day (equivalent to 40 million gallons per day, MGD) but greater than 3.8 million litres per day (1 MGD), a low effluent flow as a proportion of the receiving-water flow and <10% industrial contribution to the influent. This is the same screening process that was used in the selection of the Luray catchment in the initial study (Mudge et al., 2012). One of the objectives of the study was to determine whether the secondary treatment process for a facility influenced the magnitude and distribution of fatty alcohols discharged to the environment. Generally, samples from facilities covering at least four styles of secondary treatment were collected in each eco-region (activated sludge, oxidation ditch, lagoon and a fixed-film technology, either trickling filter or rotating biological contactor); these secondary treatment technologies were observed to be among the most common in the US EPA's quadrennial Clean Watersheds Needs Survey (http://water.epa.gov/scitech/datait/databases/cwns/). Facilities using fixed-film technology and meeting the other criteria could not be located in some areas, so sequencing batch reactor (SBR) facilities were sampled as an alternative technology that was observed to be prevalent. In order to include a sufficient number of lagoon facilities, the criterion >1 MGD influent flow had to be relaxed, because some lagoons were only available in small, rural communities and had lower influent flow rates. The data associated with the chosen WWTPs can be seen in Table 1.