Chemosphere 95 (2014) 3–8

Contents lists available at ScienceDirect

Chemosphere

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

Review

Molecular markers for identifying municipal, domestic and agricultural sources of organic matter in natural waters

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HIGHLIGHTS

- Molecular markers to determine sources of organic matter in waters is reviewed.
- Human and animal wastes are distinguishable by fecal sterols and bile acids.
- Artificial sweeteners identify input of human wastewater.
- LC–MS should facilitate analysis of molecular markers in environmental studies.

ARTICLE INFO

Article history:
Received 5 April 2013
Received in revised form 24 September 2013
Accepted 30 September 2013
Available online 4 November 2013

Keywords:
Molecular markers
Water pollution
DOC
Bile acids
Fecal sterols
Sweeteners

ABSTRACT

Molecular markers can be used to determine the sources of organic pollution in water. This review summarizes progress made during the last two decades in identifying reliable molecular markers to distinguish pollution from sewage, animal production, and other sources. Two artificial sweeteners, sucralose and acesulfame-K, are sufficiently stable to be molecular markers and easily associated with domestic wastewater. Waste from different animal species may be distinguished by profiling fecal sterols and bile acids. Other markers which have been evaluated, including caffeine, detergent components, and compounds commonly leached from landfills are discussed.

Contents

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http://dx.doi.org/10.1016/j.chemosphere.2013.09.104

1. Introduction

Robert Eganhouse (2004) has defined molecular markers as "organic substances that carry information about sources of organic matter or contamination". This review will focus on the use of molecular markers in determining anthropogenic sources of organic matter in natural waters. It presents the significant progress which has been made in this area since 1998, when two important reviews of previous developments in this area were published (Eganhouse, 1997; Takada and Eganhouse, 1998).

This review is organized by application, i.e., by sources of organic matter. The two main focuses of source allocation are the use of markers in specifically determining where waters are contaminated by human sewage and, a more comprehensive assignment of sources of organic pollution.

2. Landfill leachate

Municipal landfill leachate can contain very high levels of organic matter (e.g., see Castrillon et al., 2010). Schwarzbauer et al. (2002) used gas chromatography–mass spectrometry (GC–MS) to analyze seepage from a municipal landfill in Germany. Given the high degree of stability and similarly high concentrations of some compounds measured in the landfill seepage and leakage waters, these authors suggested compounds which might serve as markers of water pollution from municipal landfills: the pharmaceutical propyphenazone, the plasticizer N-butyl benzene sulfonamide (NBBS), and the insecticide N,N-diethyl toluamide (DEET). Clofibric acid, a plasticizer, and the herbicide mecoprop were also commonly detected. A continuation of this work used these five compounds to study lateral and vertical distribution of contamination as well as the long-term emission from the landfill (Heim et al., 2004).

3. Road runoff

Organic pollution from roads is a major source of polycyclic aromatic hydrocarbons (PAH) among other toxic pollutants (Mangani et al., 2005). Regarding the potential utility of PAH as road runoff markers, Kumata et al. (2000) note, "...the historical trend of PAHs is complicated by changes in the use of fuels or emission controls for power, residential heating, and industrial activities as well as that for vehicular emissions". Building on previous work of Spies et al. (1987), these researchers compared the tire rubber components 2-(4-morpholinyl)benzothiazole (24MoBT) and N-cyclohexyl-2-benzothiazolamine (NCBA), benzothiazolamines present in different vulcanization accelerators, as markers of road runoff in urban sediments in Japan (Kumata et al., 2002). Sediment cores were dated using Cs-137 and tetrapropylene-based alkylbenzenes. Deposition of these markers can be estimated from historical production. "Changeovers" in the concentrations of the markers in sediments coincide well with changes in the production history of vulcanization accelerators. The dated downcore profile of 24MoBT and NCBA showed positive correlation with the traffic data in the Tokyo Metropolitan Area.

Nitro-PAHs and triphenylene have been compared with sulfur-PAHs as markers of urban stormwater road runoff (Zeng et al., 2004). Concentrations of the compounds in a creek and a river receiving runoff, and effluents from four wastewater treatment plants (WWTPs) were compared; the group also investigated stability of the compounds in water and sediment. Based on abundance, source specificity, and persistence, dibenzothiophene and triphenylene were judged the most promising among the candidate markers. 24MoBT was found to photodegrade rapidly in the aqueous phase, and to not concentrate in sediment, limiting the potential usefulness of this marker. The ratio of 1-nitropyrene to total PAH has been found to be a useful indicator of road runoff from diesel fueled as compared with gasoline fueled vehicles (Murakami et al., 2008). Cluster analysis of tri-terpenes can distinguish atmospheric dust from road dust (Kose et al., 2008).

4. Sewage

4.1. Coprostanol and related compounds

Analytical markers of human sewage have been studied as alternative indicators of the potential presence of human pathogens. Murtaugh and Bunch (1967) first suggested coprostanol (5β(H)-cholestan-3β-ol), a product of the bacterial degradation of cholesterol in the human gut, be used as an indicator of fecal pollution. Other fecal sterols as well as bile acids have been enlisted in attempting to source human sewage input into waters (Bull et al., 2002).

Using analysis of fecal sterols to measure fecal pollution in Malaysia and Vietnam, Isobe et al. (2002) present a dramatic application of the utility of molecular markers in environmental analysis. In performing regional monitoring of sewage impact, sterols as molecular markers have two great advantages. The compounds are more stable in storage than are bacteria. Also, sterols concentrate in particulates, and so are collected from water samples on filters which can be easily transported. In this study ten sterols were measured at 59 sampling stations. The GC–MS analysis, including sample extraction and clean-up, required three days for ten samples. In urban areas, C27 sterols were abundant, with coprostanol and cholesterol predominating, whereas C29 sterols were depleted. These sterol profiles were typical of those previously observed in areas with heavy sewage impact. In samples from rural areas, C29 sterols, such as β-sitosterol, and stigmastanol were dominant. Only trace amounts of coprostanol were found in the rural samples, and this was attributed to contamination by non-human sources. A strong linear relationship was observed between concentrations of coprostanol and *Escherichia coli* in both Malaysia and Vietnam.

Fecal sterols have been used in more comprehensive pollution source identification, discussed below.

4.2. LAB/ABS

Linear alkylbenzenes (LABs) are manufactured for the production of the linear alkylbenzenesulfonate surfactants used in commercial detergent formulations. LABs are present as impurities in detergents, and hence are present in municipal wastewater. LABs concentrate in suspended particulate matter and sediment, where they are found generally in sub-μg L^{-1} or in μg g^{-1} concentrations (dry weight), respectively (Takada and Eganhouse, 1998). In secondary water treatment, microbial alteration results in depletion