Steroids as Sewage Specific Indicators in New York Bight Sediments

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ABSTRACT

Sediments of the New York Bight were examined for steroidal compounds and found to contain relatively large amounts of coprostanol and 24 β-ethyl coprostanol. These steroids were found to be derived from sewage, and it is suggested that they be used as sewage tracers in marine sediments.

INTRODUCTION

The New York Bight has recently received much attention in the field of environmental pollution. The National Oceanic and Atmospheric Administration (NOAA) has been conducting a multidisciplinary study (Marine EcoSystems Analysis Program, MESA) to assess the impact of waste disposal in the Bight. Currently, the municipalities of New York City are dumping 3.7×10^6 metric tons/year of sewage sludge, 9.7×10^6 metric tons/year of dredge spoil, 2.0×10^6 metric tons/year of contruction rubble, and 2.2×10^6 metric tons/year of acid-iron wastes in the New York Bight (EPA, 1975). Additionally, undetermined amounts of sewage, sewage effluents, and chemical wastes are being released directly into the Bight or enter via the Hudson-Raritan river system (MUELLER and JERIS, 1975). Much of this waste material eventually settles to become part of the sediment in the Bight. GROSS (1972) stated that the major supply of sedimentary materials to the Bight was from anthropogenic sources. HATCHER and KEISTER (1975) suggest that most of the organic sedimentary matter in the Apex area is of sewage origin.

Recently some alarm has been expressed over the probable encroachment of black silty muds onto the beaches of Long Island (HARRIS, 1974). Pockets of black mud having a "mayonnaise" consistency similar to that of sewage sludge have been detected near the beaches (CHARNELL, 1974; HARRIS, 1975). HATCHER and KEISTER (1975) suggested that the ratio of total carbohydrates to total organic carbon serves as a

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semi-qualitative measure of sewage contamination. However, controversy subsequently arose due to the inability to positively determine specific identifiers which would classify the source of these black muds as sewage. By examining and comparing New York Bight sediments and sewage sludge, we now present steroids as suitable sewage tracers.

Steroids are minor constituents of both plants and animals (IKAN et al., 1975). Plants and more primitive species of the animal kingdom contain such a wide variety of steroids that taxonomic identifications are often made based on their steroid contents. In a comprehensive review on the occurrence of steroids in higher plants and animals, AUSTIN (1970) found cholesterol to predominate over other steroids.

Although steroids are minor components of plants and animals, they resist microbial degradation for much longer periods of time than other biolipids (RHEAD et al., 1971). ATTAWAY and PARKER (1970) found steroids present in a 2000-year-old sediment. Sediments as old as 130,000 years have been found to contain steroids (HENDERSON et al., 1971). This degree of preservation makes steroids useful biological markers for long periods of time.

Due to their taxonomic specificity, steroids may also provide distinctions between marine or terrestrial sources and anthropogenic sources such as sewage (ATTAWAY and PARKER, 1970; TABAK et al., 1972; KIRCHMER, 1971). This capability is quite useful, especially in the coastal zone where organic matter in sediments may be derived from a multitude of sources including sewage. In addition to being a mixture of plant and animal remains, sewage contains unique steroids derived from mammalian fecal matter (ENEROTH et al., 1964). These compounds are thought to arise from the reduction of sterols to stanols by mammalian intestinal microflora (ROSENFELD et al., 1954; MATTHEWS and SMITH, 1968).

The steroids found in human excreta are predominantly cholesterol, coprostanol, coprostanone, β-sitosterol, methyl cholesterol, and ethyl coprostanol (ENEROTH et al., 1964). Cholesterol, β-sitosterol, and methyl cholesterol have been identified in the marine environment (MATTHEWS and SMITH, 1968; ATTAWAY and PARKER, 1970; GAGOSIAN, 1975). However, coprostanol and ethyl coprostanol have not been detected in unpolluted marine sediments (ATTAWAY and PARKER, 1970; IKAN et al., 1975). Due to the miniscule contribution of marine mammals to oceanic biomass (RILEY and CHESTER, 1971), such mammalian fecal steroids would be present in the natural marine environment only in extremely insignificant amounts. While several microorganisms have been found to reduce cholesterol to coprostanol (EYSSEN et al., 1973; PARMENTIER and EYSSEN, 1974), their presence is unreported in the marine environment. However, if these organisms were active in marine sediments, we would expect to find detectable amounts of coprostanol due to the ubiquitous presence of cholesterol. Coprostanol has not been detected in uncontaminated marine sediments, and it is unlikely that its bacterial production is occurring. Discounting the natural production of coprostanol and 24 β-ethyl coprostanol, we believe their presence in the marine environment to be of contaminant origin. MATTHEWS and SMITH (1968) as well as EGLINTON et al. (1975) also suggest that these steroids are possible identifiers of sewage when detected in the environment. Coprostanol in the dissolved state has previously been used as a sewage tracer in fresh water systems contaminated by sewage effluents (TABAK et al., 1972; KIRCHMER, 1971; DOUGAN and TAN, 1973). We therefore examined the steroids of a suspected sewage-contaminated sediment of the New York Bight and a sample of sewage sludge. We were specifically interested in steroids of fecal origin.

METHODS

Freeze-dried sediments and sewage sludge were Soxhlet extracted with a benzene:methanol (1:1 v/v) solution. Each extract was saponified in 0.5N KOH in methanol. The saponified solutions were then acidified with HCl, mixed with water, and extracted with CCl_4. The CCl_4 extracts were evaporated to dryness and the residues esterified with BF_3/methanol for preparation of the fatty acid esters which will be discussed elsewhere. Water was then added to each of the solutions which were subsequently extracted with hexane. The hexane extracts were placed on 30 x 1 cm silica gel columns and eluted with 0.5, 2.5, and 2.0 column volumes of hexane, benzene, and methanol, respectively. The methanol fractions were evaporated to dryness and treated with BSA (N, O, bis-trimethylsilylacetamide) to form the trimethyl silyl ethers of alcoholic compounds. The resulting solutions were chromatographed on a Tracor 550 using glass columns packed with 3% OV-1 on Chromosorb W (HP), and the temperature was programmed from 100° to 270°C at 4°/min. The peak areas were calculated with a Hewlett-Packard 3380A electronic integrator. Concentrations were estimated by injecting known amounts of solution and relating the areas of each component to the flame detector molar response for a cholesterol standard. The steroids were identified by retention data given by ENEROTH et al. (1964) and confirmed by combined gas chromatography-mass spectrometry (DuPont 490-B). The gas chromatographic peaks were checked for purity by scanning the mass spectrometer repeatedly as the peaks eluted. Although the chromatograms may be congested, the steroid peaks are sufficiently separated to allow quantitative analysis.

RESULTS AND DISCUSSION

One sediment sample was taken during a NOAA/MESA cruise in September 1973 from the topographic depression (Christiaensen Basin) in the Apex of the New York Bight, near the sewage sludge dumpsite. This sediment was observed to have a black "mayonnaise" appearance. The other sample (P-21) was taken in June 1974 aboard the R/V VENTURE, from within one mile of Atlantic Beach, Long Island. This sample had a similar consistency to that of the Christiaensen Basin sample, as it came from a localized accumulation of mud near the beach. The gas chromatograms for the BSA-treated methanol eluates of both sediments are presented in Fig. 1 (1 and 2). A large variety of compounds such as fatty alcohols and hydroxy fatty acids are present in addition to the steroid derivatives which are designated by letters. The major steroids found in both sediments are coprostanol (peak A), cholesterol (B), β-sitosterol (D), and 24 β-ethyl coprostanol (C). The sample mass spectra of these four compounds are presented in Fig. 2. The cholesterol and β-sitosterol are present in significant amounts and are generally dominant in marine sediments (IKAN et al., 1975). The presence of coprostanol and of 24 β-ethyl coprostanol immediately drew our attention. These steroids offer ideal sewage tracers, since they are found as major steroids in human excrement (ENEROTH et al., 1964; TABAK et al., 1972). Their natural contribution is unreported and is generally considered non-detectable in open ocean sediments. Their presence in New York Bight sediment samples links the source of the major organic component in these muds to sewage. The measured concentrations of coprostanol in the Christiaensen Basin and P-21 sediments are 4.8 and 5.2 ppm, respectively, indicating a similar level of sewage contamination. It is especially interesting that the near-shore mud (P-21) is as contaminated as that of the Christiaensen Basin, an area known to be heavily impacted by sewage (GROSS, 1972).

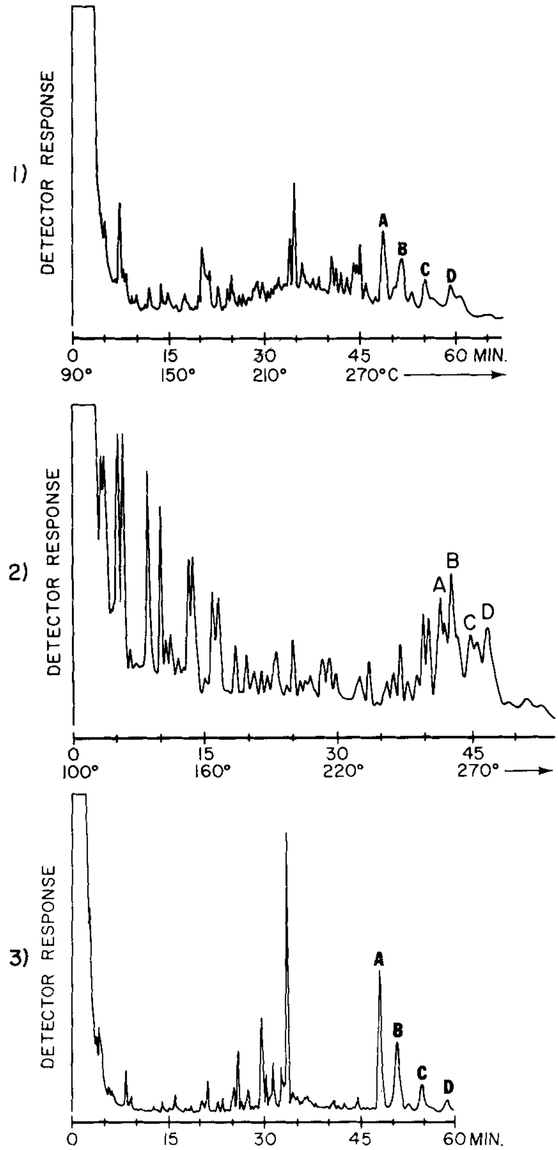

Figure 1. The gas chromatograms of the BSA-treated methanol eluate of the Christiaensen Basin mud (1), the P-21 sample (2), and the Ward's Island sewage sludge (3). A 6'x1/8" o.d. glass column packed with 3% OV-1 on chromosorb W(HP) was used in (1) and (3). A 6'x1/4" o.d. glass column packed with the same material was used in (2).

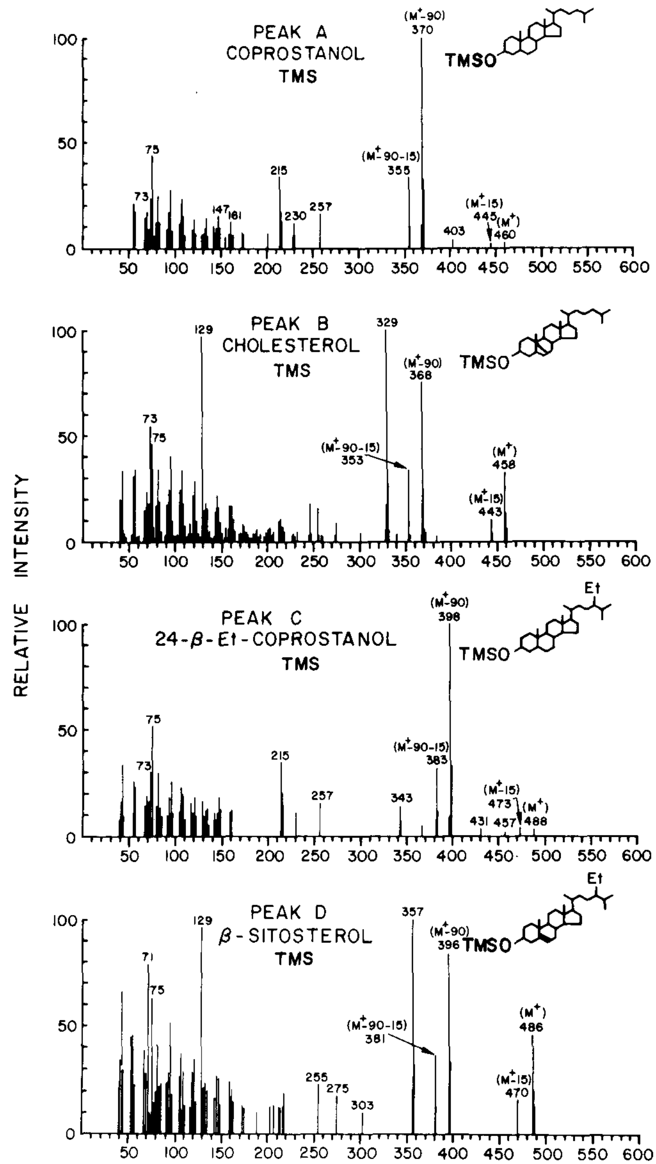

Figure 2. The mass spectra of the TMS derivatives of coprostanol, cholesterol, 24β-ethyl coprostanol, and β-sitosterol in the Christiaensen Basin mud sample.

To confirm our observations that sewage was the source of coprostanol, we analyzed a sample of sewage sludge from Ward's Island sewage treatment facility in New York City. The chromatogram of the BSA-treated methanol eluate is shown in Fig.1(3). In this fraction cholesterol and β-sitosterol are noticeably present, but the great quantity of coprostanol and 24 β-ethyl coprostanol confirmed our beliefs that sewage is the source of these steroids in the Christiaensen Basin and in the sample near the Long Island shoreline.

The coprostanol concentration of Ward's Island sewage sludge is 5800 ppm. Realizing that roughly 0.3×10^6 tons of sewage sludge sludge solids are added to the Bight annually (EPA, 1975), it is not too surprising to find relatively high levels of coprostanol in New York Bight sediments.

In conclusion, we point out that New York Bight sediments are contaminated with sewage resulting from either ocean dumping of sludge or from outfalls. Coprostanol or 24 β-ethyl coprostanol can be used to identify sewage contamination in sediments on both a horizontal and vertical sedimentary profile.

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