Exposure Assessment of Sewage Treatment Plant Effluent by a Selected Chemical Marker Method

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Abstract. Organic chemicals unique to sewage effluent can be useful as markers of an effluent plume. Samples were collected at a domestic wastewater outfall near Cocoa, Florida, and chemically characterized. Receiving waters were analyzed to determine the chemical components in the effluent most suitable for the assessment. The saturated hydrocarbon fraction and sterol fraction appeared to be of greatest utility for such purposes, and the concentrations of these fractions were determined for water, particulate matter, and sediment. Concentrations of the marker compounds decreased rapidly with increasing distance from the outfall.

In the United States, the discharge of municipal waste via sewage outfalls into rivers, estuaries, and coastal waters has been a source of continuing environmental concern. Sewage effluent contributes to eutrophication and may contain many potentially hazardous materials such as pesticides, petroleum hydrocarbons, polychlorinated biphenyls, heavy metals, pathogenic bacteria and viruses (VanVleet and Quinn 1977; Shigenaka and Price 1988). To delineate areas adversely influenced by sewage constituents, areas which have been exposed to the sewage plume, must be accurately identified. In the typical, poorly flushed coastal lagoon of the southeastern United States, traditional methods of determining the areas of sewage transport are the distribution of nutrients or of coliform bacteria. Recent studies, however, have shown that these methods sometimes yield confusing results (Morel and Schiff 1980; Yde et al. 1982). Hence, a technique that may be used in addition to the traditional methods for delineating a sewage plume is needed. If possible, the technique would identify a constituent that is unique to the sewage plume and/or where a group of plume constituents are found in a significantly different composition or concentration measured following dilution in the receiving water; the constituent(s) would thus mark the transport of the sewage plume. The objective of this study is to characterize the behavior of selected organic constituents in the sewage plume, whether they are soluble, adsorbed onto particles, or in sediment and the utility of these constituents for marking the plume. Through interpretation of the results the areas impacted by sewage constituents may be delineated.

Chemical markers of the sewage plume may be derived from excreta, domestic runoff, initially treated industrial discharges, improper disposal, or from treatment processes (i.e., bacteria). Two such markers, fecal sterols (Murtaugh and Bunch 1967; Hatcher and McGillivary 1979), and hydrocarbons (Brown and Wade 1984) have been used as markers of sewage plumes. The fecal sterol coprostanol (5β-cholestan-3B-ol) is formed exclusively by enteric bacterial reduction of unsaturated sterols (e.g., cholesterol) in humans and higher mammals. Because of coprostanol’s unique feature, the presence of coprostanol in the aquatic environment may indicate fecal contamination from domestic sewage even when other methods are unreliable (e.g., where chlorination has rendered coliform measurements unreliable). Coprostanol has an adsorptive capacity (KD = 10^5 ml/g) (Holm 1986) similar to many hydrophobic contaminants (i.e., pathogenic organisms, heavy metals, harmful organics) and may be utilized in studies where the source of a contaminant is unknown. If levels of coprostanol correlate to levels of a contaminant of concern, then a sewage outfall source of the contaminant may be indicated. However, careful evaluation must be made when using coprostanol as it may reflect fecal contamination from sources other than sewage treatment plant effluent such as runoff from feedlots or releases from ships. Normal alkanes and aromatic hydrocarbons have been detected in Chesapeake Bay in both particulate and water phases associated with sewage treatment plant effluent (Brown and Wade 1984). These hydrocarbons could be used as sewage plume markers if the levels from the outfall were significantly different in composition and/or concentration than the background levels of the receiving water. Other compounds, present in the outfall, derived from either natural or anthropogenic sources and having unique characteristics as those described above could be used to mark the area of the sewage plume and thereby delineate an adversely influenced area.

In this study, samples were collected at and near a do-
mestic wastewater outfall and at a site approximately 800 m away from the outfall near Cocoa, Florida. The water, particulate, and sediment phases were chemically characterized to determine the most suitable chemical(s) in each phase for the assessment. Further sampling continued for an array of stations away from the outfall to evaluate the extent of plume transport.

The study location is the Indian River Lagoon, Florida (Figure 1). The Lagoon is spanned by bridges and causeways which connect the mainland to the barrier island. Four inlets to the sea are maintained by the Army Corps of Engineers. The waterway has a channel depth of 3 m, while the rest of the lagoon is shallow averaging 1 m in depth. During normal tidal cycles, the inlets exchange around $4 \times 10^9$ liters of water between the river and the ocean, less than 5% of the river’s volume. Tidal flushing is limited to an area two to three km on either side of the inlets, the influence beyond that is negligible. The specific location of this study was at the Cocoa, Florida, publicly owned treatment work (POTW) outfall (Figure 2). The plant is presently equipped to treat a maximum of $9 \times 10^6$ L per day (MLD) of secondarily treated wastewater. The effluent is discharged into the Indian River from a reinforced concrete pipe 25 m from shore under 2 m of water. Effluent was observed rising to the surface in two locations approximately 1 m apart. Currents appear to be nonexistent in the area. Both the quantity of effluent load into the lagoon and the effects of circulation are significantly less than those cited in other studies assessing sewage effluent exposure. Because of this feature, the results of the study may be more useful in interpreting the characteristics of plume constituents than those areas where circulation is of greater intensity.

**Materials and Methods**

Samples were collected in November, 1985, at and near the Cocoa POTW outfall and at an area 800 m from the outfall site. Sample sites were at 3 m increments. Water and particles were collected in precleaned amber-glass bottles held 0.5 m under the sea surface from the bow of a small boat. The water samples were preserved with HgCl$_2$ solution (1%) and kept in the dark on ice until returned to the laboratory where they were vacuum-filtered, using preweighed and cleaned glass microfiber filters (pore size 1.9 $\mu$m). The filter and particulates were stored at $-20^\circ$C until extraction. Filtered water samples were kept in the dark at 20$^\circ$C until extraction. Each sediment sample was a homogeneous composite of three box cores. The top 8 cm of the sediment core were used for the composite. Sediment samples were placed in glass jars and sealed with solvent-washed aluminum foil lined caps. The jars were filled completely to eliminate headspace and kept on ice until returning to the laboratory where they were stored at $-20^\circ$C until extraction.

The method used for all extractions was similar. Sediment samples were thawed and mixed to ensure homogeneity. Sediment and particulates were Soxhlet extracted using a MeOH/toluene azeotrope and partitioned with $3 \times 20$ ml aliquots of dichloromethane. An experiment was accomplished to test for the necessity of saponifying the samples (saponification converts bound sterols to free sterols) but was found to be unnecessary using the method described (Holm 1986). Water was extracted in a separatory funnel with CH$_2$Cl$_2$. NaCl solution (10%) at pH 2 (acidified with HCl) was added to all extracts to reduce emulsion formation. Extracts were reduced in volume by a rotary flash evaporator under vacuum at temperatures not exceeding 35$^\circ$C. To fractionate the sample into useful compound classes, gradient elution column chromatography was performed, using a glass column (1-cm x 10-cm) packed with silica gel over alumina (1:1), both deactivated with 5% water by weight. Sodium sulfate was placed over the silica gel to desiccate residual moisture in the sample and the column was rinsed with hexane, dichloromethane, and methanol. The reduced extract was