CONCENTRATION OF HYDROCARBONS ASSOCIATED WITH PARTICLES IN THE SHELF WATERS ADJACENT TO THE ENTRANCE OF CHESAPEAKE BAY

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SUMMARY

Particulate hydrocarbon concentrations were measured in 94 water samples from the 1980 Superflux II and BAPLEX cruises. The concentrations ranged from below the detection limit (>0.7 μg/ℓ) to 32 μg/ℓ. The mean for all samples was 5.6 μg/ℓ. Particulate hydrocarbon concentrations are higher in the Bay mouth and lower in the shelf waters adjacent to the entrance of Chesapeake Bay. No coherent particulate hydrocarbon distribution is seen with depth in the water column. The Bay is postulated as one of the possible chronic sources of particulate hydrocarbons for the adjacent shelf waters. Additional research on the sources of particulate hydrocarbons and the processes affecting their temporal and spatial distribution is needed in order to further evaluate this postulation.

INTRODUCTION

The objective of this preliminary study was to measure concentrations of particulate hydrocarbons at selected stations adjacent to the entrance of the Chesapeake Bay. This work supports the NOAA-NASA program entitled Superflux. The objectives of Superflux are to determine the characteristics of plumes and contents of plumes influencing living resources in shelf waters and to determine the extent to which these characteristics and influences can be sensed remotely. The particulate hydrocarbon concentration of plumes was measured. An attempt was made to determine if the outwelling of Chesapeake Bay contains hydrocarbons which may adversely influence the living resources in shelf waters.

Petroleum hydrocarbons are entering the marine environment at a rate of approximately 6 million metric tons annually (MTA) (ref. 1). The most publicized inputs come from tanker accidents, but this source accounts for only 4.9 percent of the total input (ref. 1). A significant portion of the annual input (13 percent) is added directly to the coastal environment from sewage treatment plants, coastal refineries, and coastal industries. Another substantial portion of the annual input (31 percent) is from river and urban runoff, which may eventually reach the marine environment (ref. 1).

Detailed examination of wastewater treatment plants shows that these facilities may contribute a quantity of hydrocarbons equal to that entering from direct oil spills (ref. 2). Hydrocarbons discharged from wastewater treatment plants are predominantly (95 percent) associated with suspended

material and about half of this input is removed to the sediment in the vicinity of the discharge; the other half is transported away from the discharge site (ref. 2).

The association of petroleum hydrocarbons and sediment appears to be related to grain size characteristics. Particles smaller than 44 μm adsorb more hydrocarbons on a weight basis than do sediment particles larger than 44 μm (refs. 3 and 4). The interaction of petroleum hydrocarbons with very fine-grained sediment may form neutrally buoyant aggregates. Both of these processes favor dispersal over sedimentation of hydrocarbons.

Chesapeake Bay experienced numerous chronic inputs of anthropogenic hydrocarbons similar to those outlined above. These hydrocarbons may be deposited near their source of input, or may be adsorbed to suspended materials and transported to the open ocean. These hydrocarbons may adversely affect the open ocean ecosystem.

MATERIALS AND METHODS

This research required collection and analyses of water samples for particulate hydrocarbon concentrations. A total of 92 samples were collected during Superflux II cruises aboard the NOAA ships Delaware II (June 17 to June 23, 1980) and Kelez (June 24 to June 27, 1980) for hydrocarbon analyses. Bay Plume Experiment, or BAPLEX, is an ongoing program involving several researchers in the Department of Oceanography at Old Dominion University. BAPLEX data are included in this paper to provide additional information regarding the characteristics of water masses at the mouth of Chesapeake Bay. A total of seven samples were collected during BAPLEX cruises aboard the R/V Holton (June 19 and June 24, 1980).

The hydrocarbon analyses were performed using accepted methods and included analyses of procedural blanks and standards. The analytical techniques have been described in detail elsewhere (refs. 4 and 5). Samples consisting of approximately 16 ℓ of seawater were filtered through preignited Gelman A/E glass fiber filters and are therefore operationally defined as particulates. The filter, along with the retained material, was saponified/extracted under reflux. The hydrocarbons in the saponification mixture were partitioned into the organic phase by addition of dichloromethane. After removing the dichloromethane the residue was eluted through an alumina-silic acid column to separate the hydrocarbons from other organics. The hydrocarbon fraction was then analyzed on a Hewlett Packard 5830 gas chromatograph (GC) equipped with a 25 M methylsilicone, fused silica, WCOT, capillary column. Analyses were done by temperature programming from 80° to 270° C at 10° C min. The areas of the resolved peaks and unresolved complex mixture were measured by planimetry. Comparison of the areas of the resolved and unresolved peaks and unresolved complex mixture to the area of the internal standards allowed for quantitative measurement of the amount of hydrocarbon present.

RESULTS AND DISCUSSION

Sampling dates and locations for Superflux II and BAPLEX cruises are shown in reference 6. The Superflux II samples were collected over a 10-day period (June 17 to June 27, 1980) and at random stages during the tidal cycle. BAPLEX samples provide relatively synoptic data as all samples except one were collected within a 2-hour window during ebbing tide.

Procedural blanks were analyzed periodically to determine background levels of hydrocarbons. All sample concentrations reported here have been corrected for the concentrations found in the procedural blanks. A standard n-alkane mixture was injected daily to insure that the GC was operating properly. Analyses of the ships' fuel oils indicated that they are not a major source of hydrocarbons found in these samples.

When oil enters the environment it can undergo many complex reactions collectively called weathering. Weathering reactions, including evaporation, dissolution, photochemical oxidation, microbial degradation, and adsorption. The extent of weathering reactions depends upon the environmental conditions that the oil encounters, such as temperature, wind speed, current velocity, microbes present and type and site of particles present (ref. 1). The overall result of weathering is preferential loss of specific hydrocarbons (ref. 1). Samples from Superflux II and BAPLEX cruises show GC patterns characteristic of weathered oils, indicating that they have been in the marine environment for a few days or longer.

Particulate hydrocarbon concentrations were measured in 87 Superflux II and 7 BAPLEX samples. The results are summarized in table 1. Total particulate hydrocarbon concentrations for Superflux II samples ranged from below the detection limit, <0.7 μg/ℓ to 32 μg/ℓ, with a mean of 5 μg/ℓ. Total particulate hydrocarbon concentrations for the BAPLEX samples ranged from 4 to 20 μg/ℓ with a mean of 13 μg/ℓ. The nine surface samples collected at stations in the Bay mouth (BAPLEX stations 0, 1, 2, 3 and 4 and Superflux II stations 800 and 801) had a mean hydrocarbon concentration of 15 μg/ℓ, or approximately double the mean for all surface stations (7 μg/ℓ). Therefore, in June 1980 the mean surface concentration of particulate hydrocarbons was highest in the Bay mouth and lower in the shelf waters adjacent to the entrance of the Chesapeake Bay.

Superflux II station 800 1-m depth particulate hydrocarbon concentrations measured on June 17 and 24, 1980, were 32 and 7 μg/ℓ, respectively. These samples were taken 1 week apart and at different stages of the tidal cycle. No consistent trend of hydrocarbon concentration was seen with depth in the water column. These findings indicate that the processes effecting the transport, concentration and/or dispersal of hydrocarbons with depth are very complex. Interpretation of the data is complicated by the long time period (10 days) and random tidal stages during which these samples were collected.

Literature values for particulate hydrocarbon concentrations range from 1.3 to 4 μg/ℓ in the Gulf of St. Lawrence (ref. 7), 16 to 40 μg/ℓ near a spill

in Chedabucto Bay (ref. 8) and 0 to 4 µg/ℓ 1 year after that spill (ref. 9). Thus, the range of particulate hydrocarbon concentrations found during this study (<0.7 to 32 µg/ℓ) was of the same order of magnitude as samples collected for other coastal areas.

Total hydrocarbon concentrations of surface water samples collected in October 1973 from shelf waters adjacent to Chesapeake Bay ranged from 39 to 56 µg/ℓ (ref. 10). Hydrocarbons were also present in samples collected on Superflux II cruises in June 1980. Other data from the Superflux II cruise suggest that particulate materials originating in Chesapeake Bay are transported to the adjacent shelf waters (ref. 11). This evidence suggests that the outwelling of Chesapeake Bay may provide a chronic input of anthropogenic hydrocarbons to the adjacent shelf waters.

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TABLE 1.- HYDROCARBON CONCENTRATIONS

Samples	Number	Concentration (µg/ℓ) Range	Mean
Superflux II	87	>0.7 to 32	5.0
BAPLEX	7	4.1 to 20	13.4
Surface[a]	43	>0.7 to 32	6.6
Surface-bay entrance[b]	9	4.1 to 32	15.0

a = All surface (>1 m) samples collected from Superflux II or BAPLEX

b = Surface samples for Chesapeake Bay entrance (see text)