

ALIPHATIC HYDROCARBONS IN SURFACE SEDIMENTS OF  
WILLAPA BAY AND GRAYS HARBOR, WASHINGTON

John B. Rapp, Keith A. Kvenvolden, and H. E. Clifton  
U.S. Geological Survey, Menlo Park, California 94025

U.S. Geological Survey

OPEN FILE REPORT

82-609

This report is preliminary and has not been reviewed  
for conformity with U.S. Geological Survey editorial standards.

## ABSTRACT

Willapa Bay and Grays Harbor are two adjacent estuaries along the coast of Washington state. Willapa Bay is a recreational area minimally affected by industry; Grays Harbor, on the other hand, is moderately industrialized. Aliphatic hydrocarbons in surface sediments from these two estuaries reflect the differences in human activities. For example, the mean concentration of aliphatic hydrocarbons for seven stations in Willapa Bay is 1,000  $\mu\text{g/g}$  (relative to organic carbon) while in Grays Harbor this mean concentration for six stations is 1,900  $\mu\text{g/g}$ . The difference is attributed mainly to the greater urban and industrial pollution in Grays Harbor. The gas chromatographic records of aliphatic hydrocarbons also reflect the extent of hydrocarbon pollution by the presence of a chromatographically unresolved mixture of hydrocarbons. This kind of mixture is more evident in sediments from Grays Harbor, and in both estuaries it is more concentrated in sediments collected nearest to urban centers.

## INTRODUCTION

The occurrence of aliphatic hydrocarbons in modern sediments has been known since the early 1950s when Smith (1952) first reported their presence in recent sediments from the Gulf of Mexico. During the next 20 years this observation was expanded upon as increased attention was given to the role of hydrocarbons in recent sediments to the origin of petroleum. (For a compilation of some of this work, see Haun, 1971, 1973). In the 1970s additional considerations were given to the significance of hydrocarbons in recent sediments. Starting with the investigations of Blumer and Sass (1972) and continuing with numerous other studies [for example, Farrington and Quinn (1973), Giger et al. (1974), Gearing et al. (1976), Palacas et al. (1976), Wakeham and Carpenter (1976), and Farrington and Tripp (1977)], emphasis changed from petroleum origin to petroleum pollution. It was increasingly recognized that recent sediments often contain petroleum-derived hydrocarbons resulting from pollution. In much of this work the aliphatic hydrocarbons have served as a guide to follow the fate and effects of petroleum pollution in recent sediments. In our study of Willapa Bay and Grays Harbor we have also selected the aliphatic hydrocarbons as an indicator of the effects of human activities on the hydrocarbon geochemistry of recent sediments in these two areas.

Willapa Bay and Grays Harbor are two major estuaries located in southwestern Washington (Fig. 1). The entrances to Willapa Bay and Grays Harbor are about 47 and 78 km, respectively, north of the Columbia River. Willapa Bay is a prime recreational area in a region of low population density. The largest town is Raymond, located on the Willapa River, which is the largest river emptying into the bay. Raymond has a population of about 3,000. Lumbering and shellfishing are the main forms of industrialization in the area. In contrast, Grays Harbor is an international shipping port. The cities of Aberdeen and Hoquiam have a total population of 30,000. Besides major shipping, lumber mills and pulp mills are potential sources of hydrocarbon pollution.

The contrasts of these two nearby estuaries makes them useful for studying the effects of industrialization on the hydrocarbon geochemistry of recent sediments. In this paper we compare the concentrations and distributions of aliphatic hydrocarbons in intertidal surface sediments on the periphery of both Willapa Bay and Grays Harbor. This comparison provides a measure of current background levels of aliphatic hydrocarbons in sediments against which future changes can be monitored.

## PROCEDURES

Samples of the upper 7 cm of intertidal sediment were taken by means of aluminum box corers that were cleaned with detergent and water, rinsed with distilled water followed by high purity acetone, and stored in sealed plastic bags until used for sampling. Figure 1 shows the location of seven sampling stations of the edge of Willapa Bay and six stations on the shores of Grays Harbor. Samples were collected at low tide while the sediment was exposed to the atmosphere and were frozen in the corer at the end of the day of collection. The samples remained frozen until analyzed for hydrocarbons. In addition to sediments, samples of algal mats and tidal flat grasses were

collected, frozen, and later extracted and analyzed in a matter similar to that of sediments.

For analyses, portions of the frozen samples were removed from the corer and freeze-dried for two days to remove water. A filter trap between the vacuum pump and freezer coil prevented possible contamination of the sample during the drying procedure. A 100-g portion of dried sediment was extracted by shaking on a wrist action shaker with a total of 400 ml of pesticide quality dichloromethane in a specially prepared, ground glass-stoppered centrifuge bottle. After shaking, the sample was centrifuged, and the extract was decanted through a glass wool filter. Extraction was repeated two more times. The glassware for all procedures was washed carefully with detergent and water, rinsed thoroughly with distilled water, wrapped loosely with pre-cleaned aluminum foil, and heated overnight at 500°C to remove possible contaminants.

The combined, filtered extracts were concentrated to about 10 ml by means of a rotary evaporator. The concentrated extracts were filtered through activated copper dust to remove sulfur, then evaporated to near dryness to exchange pesticide quality n-hexane for dichloromethane. This solvent exchange step was performed three times.

The n-hexane solution was sonicated for 0.5 min. and then fractionated by column chromatography using a 10-mm ID column 25 cm long packed sequentially from bottom to top with activated silica gel (5 g Davidson No. 923 and 2.5 g Davidson No. 62) and 2.5 g deactivated (5% water) alumina. The column was eluted in sequence with 25 ml of n-hexane, 25 ml of benzene, and 25 ml of methanol to yield fractions containing aliphatic hydrocarbons, aromatic hydrocarbons, and polar organic compounds, respectively. Small aliquots of the total extract and of each fraction were evaporated to dryness and weighed on a microbalance.

Total organic carbon was determined on portions of the dried sediment by wet combustion following procedures of Bush (1970) (analyzed by Rinehart Laboratories, Wheatridge, CO 80001). Weights of the total extract and chromatographic fractions were compared to the amount of organic carbon in a sample and are expressed relative to organic carbon.

The hexane fraction from column chromatography was evaporated to a fixed volume of 0.4 ml, and a 1.0- $\mu$ l aliquot was analyzed by dual-column gas chromatography of a 6' x 1/8" 5% FFAP on 80/100 Gas Chrom Q column with flame ionization detection. After sample injection the column temperature was held for 1 minute at 85°C and then increased by 4°/min. to 240°C, at which temperature the column was maintained for 32 minutes. The dual columns were balanced to yield a zero-slope baseline during chromatography. Areas and retention times of chromatographic peaks were measured by electronic integration and the data were reduced by computer. The Arithmetic Index (AI) (Zweig and Sherma, 1972, p. 17) was used to report retention data of unknown peaks.

Van de Meent (1977) observed the formation of artifacts upon freeze-drying certain types of sediment. We investigated this possibility with several of our samples. The wet sediments were extracted with methanol followed by dichloromethane. The combined extracts were processed in the

normal manner and then analyzed. The chromatograms of these extracts were very similar to chromatograms of the freeze-dried sediment extracts indicating artifacts weren't formed from freeze-drying these sediments.

## RESULTS

Hydrocarbons are present in the surficial intertidal sediments at all thirteen sampling stations in Willapa Bay and Grays Harbor. To compare results from the two estuaries, we report our hydrocarbon data in  $\mu\text{g/g}$  relative to the organic content of each station (Table 1). This procedure reduces bias due to grain sizes that range from silt to fine sand. Average contents of extractable organic material (EOM), total hydrocarbons (Total HC) and aliphatic hydrocarbons (A HC) are significantly higher in sediments from Grays Harbor:

	EOM $\mu\text{g/g}$ (OC)	Total HC $\mu\text{g/g}$ (OC)	A HC $\mu\text{g/g}$ (OC)
Grays Harbor	12,900	4,000	1,900
Willapa Bay	4,900	2,200	1,000

The concentrations of aliphatic hydrocarbons relative to organic carbon are illustrated on Figure 1 by bar graphs at each station. The higher concentrations of these hydrocarbons are associated with sediments from stations located nearest to urban centers. In Grays Harbor the sediment samples nearest to the cities of Aberdeen and Hoquiam have the greatest amounts of aliphatic hydrocarbons; in Willapa Bay the sediment near the town of Raymond has the highest concentrations of aliphatic hydrocarbons.

Gas chromatograms (Fig. 2) reveal two important components of the aliphatic hydrocarbons in these estuarine sediments: (1) a resolved component consisting of a homologous series of n-alkanes ranging from about n-C<sub>17</sub> to n-C<sub>33</sub>, isoprenoid hydrocarbons (pristane and phytane), and unidentified compounds, and (2) an unresolved component consisting of a complex mixture of branched and cyclic alkanes that is not separated by the chromatographic techniques employed. The n-alkanes are predominantly odd-carbon-number molecules. A measure of the odd-carbon-predominance is given by the carbon preference index (CPI) calculated over the range C<sub>25</sub> to C<sub>31</sub> (Table 1) according to the method of Bray and Evans (1961). In addition to the n-alkanes, pristane and phytane (isoprenoid hydrocarbons) are present in sediments at most stations (Table 1). An unresolved complex mixture (UCM) of aliphatic hydrocarbons is particularly evident on the chromatograms from those stations near Aberdeen and Hoquiam on Grays Harbor and one station near Raymond on Willapa Bay. At other stations the unresolved complex mixture is less evident (Fig. 2). Estimates of the amounts of unresolved hydrocarbons [UCM (est)] are shown in Table 1. These estimates are based on the differences between concentrations of the resolved components and the weights of the aliphatic fractions.

## DISCUSSION

The highest concentrations of aliphatic hydrocarbons relative to organic carbon in sediments of these two estuaries are found near the centers of

urbanization. A major portion of these hydrocarbons is an unresolved complex mixture composed of branched and cyclic alkanes. This kind of mixture is commonly found in aquatic sediments, particularly those that are contaminated with petroleum-derived hydrocarbons (Farrington and Quinn, 1973; Wakeham and Carpenter, 1976; Gearing et al., 1976; and Boehm and Quinn, 1978). The fact that the unresolved complex mixture of aliphatic hydrocarbons is most evident at stations nearest to Aberdeen and Hoquiam in Grays Harbor and nearest to Raymond in Willapa Bay suggests that these hydrocarbons are petroleum-derived products that enter the estuaries through oil spillage, sewage effluents, and urban storm runoff. The unresolved complex mixture of aliphatic hydrocarbons is less evident in chromatograms (Fig. 2) from sediments at nine other stations located farther away from the urban centers. These hydrocarbons likely represent low-level contamination from the urban areas of the estuary or, less likely, represent a natural background of hydrocarbons derived from the reworking of older sediments as suggested by Giger et al. (1980) in his studies of Greifensee, Switzerland. The anomalously high values of total hydrocarbons, aliphatic hydrocarbons and unresolved-branched-cyclic hydrocarbons (UCM) for Long Island (Table 1) may be due to the fact that long sections of highway are drained into the bay at the sampling station and may represent petroleum-derived products from autos and the roadway asphalt.

Superimposed on the unresolved complex mixture of hydrocarbons are chromatographically resolved compounds consisting of n-alkanes, two isoprenoid hydrocarbons (pristane and phytane) and a number of unidentified hydrocarbons (Fig. 2). The distribution of n-alkanes is characterized by a dominance of odd-carbon-numbered molecules. Carbon preferences indices (CPI) calculated from n-C<sub>25</sub> to n-C<sub>31</sub> range from 6 to 12. An odd-carbon dominance of n-alkanes is a common feature of hydrocarbons in recent sediments from aquatic environments (Stevens et al., 1956; Cranwell, 1973; Giger et al., 1974; and Wakeham, 1976). The source of the hydrocarbons larger than about n-C<sub>20</sub> is probably terrestrial plants while the n-alkanes smaller than n-C<sub>20</sub> likely come from marine plants (Clark and Blumer, 1967). Extracts from an algal mat sampled at the Winter Ranch station contain significant n-C<sub>17</sub> as do extracts of grasses collected on the tidal flats on the eastern side of Willapa Bay. These kinds of sources undoubtedly contribute to the n-C<sub>17</sub> observed in the sediments. n-C<sub>17</sub> was identified in sediments at eleven of the thirteen stations, and, with few exceptions, is always present in higher concentrations than n-C<sub>18</sub> (Table 1). At four stations (Pickernell, Lynn Point, Long Island, and Winter Ranch) n-C<sub>18</sub> (AI=1800), if present, is not resolved on the chromatograms (Fig. 2) from another compound (AI=1792) that has been tentatively identified as a C<sub>20</sub> branched-chain monoene.

The isoprenoid hydrocarbons, pristane (C<sub>19</sub>) and phytane (C<sub>20</sub>) were identified in most of the sediments studied here (Table 1). Phytane is present in sediments at all thirteen stations. Pristane was observed in sediments from ten stations. At three stations (Airport, Long Island, and Winter Ranch) pristane (AI=1670), if present, is masked on the chromatograms (Fig. 2) by a compound having almost an equivalent retention time (AI=1672) and tentatively identified as a C<sub>20</sub> branched-chain monoene. Thus, there are two unknowns that appear to be C<sub>20</sub> branched-chain monoenes that have distinctly different retention times corresponding to n-C<sub>18</sub> and pristane. Recently, two C<sub>20</sub> branched-chain monoenes were reported in sediments of Puget Sound, Washington (Barrick, 1980). Where both pristane and phytane are present in these sediments, pristane is always more abundant (Table 1). The

dominance of pristane over phytane is not unexpected because in recent marine sediments phytane is usually present in much smaller amounts than pristane (Blumer and Snyder, 1965), while both pristane and phytane are common in petroleum (Speers and Whitehead, 1969).

If our interpretations are correct, the sediments of Willapa Bay and Grays Harbor are contaminated to varying degrees with petroleum-derived hydrocarbons from urban and industrial processes. Sediments of Grays Harbor contain higher concentrations of these hydrocarbons. This observation correlates with the fact that Grays Harbor has a greater population and industrial development than does Willapa Bay. The unresolved complex mixture of branched-cyclic hydrocarbons, especially evident in sediments near the population centers of both estuaries, is the major evidence for this form of contamination. Fresh crude oil, containing n-alkanes, is not an obvious component of this contamination. If crude oil n-alkanes were present, the CPIs at stations where hydrocarbon concentrations are highest should be lower due to the contribution of crude oil n-alkanes that are characterized by low (near 1.0) CPIs (Bray and Evans, 1961). CPI values listed in Table 1 are all high, and there appears to be no difference in n-alkane distribution between sediments that are highly contaminated and those that have minimum amounts of the unresolved complex mixture of hydrocarbons. The contaminating hydrocarbons may include some phytane, because phytane concentrations are higher and pristane/phytane ratios are lower in sediments nearer to urbanization in both estuaries (Table 2). The pristane concentration listed in Table 2 does not provide a clear guide to possible sources. Most of the pristane is probably in the natural background of these sediments, although some may be part of the contamination.

The identified n-alkanes in sediments at all stations appear to represent the natural background of hydrocarbons in these estuaries. That is, if these areas were entirely unaffected by human activities, the chromatograms of the aliphatic hydrocarbons in all sediments would probably look like the chromatograms obtained at Palix and Pickernell. Although the sediments near the main cities on Grays Harbor and the town of Raymond on Willapa Bay appear to be contaminated with petroleum-derived hydrocarbons, the hydrocarbon concentrations of the most contaminated sediments (6,300  $\mu\text{g/g}$ ) are lower than the concentrations of the least contaminated sediments (11,000  $\mu\text{g/g}$ ) in Narragansett Bay, Rhode Island (Farrington and Quinn, 1973) and lower than the average concentrations (9,600  $\mu\text{g/g}$ ) in Rhode Island Sound (Boehm and Quinn, 1978). Urbanization and industrialization have added to the sediments of Grays Harbor and Willapa Bay a complex mixture of hydrocarbons. Continued development will probably add more of this kind of complex mixture to sediments of these estuaries.

**ACKNOWLEDGMENTS**

The C<sub>20</sub> branched-chain monoenes were tentatively identified by gas chromatography and mass spectrometry. We thank the Hewlett-Packard Corporation for analyzing our samples in a demonstration of their product capability, and Don Anders, U.S. Geological Survey, Denver, Colorado, for providing independent, confirming mass spectra.

#### REFERENCES

- Barrick, R. C., Hedges, J. I., and Peterson, M. L. (1980). Hydrocarbon geochemistry of the Puget Sound region--I. Sedimentary acyclic hydrocarbons. *Geochim. Cosmochim. Acta*, 44, 1349-1362.
- Blumer, M. and Snyder, W. D. (1965). Isoprenoid hydrocarbons in recent sediments: Presence of pristane and probable absence of phytane. *Science*, 150, 1588-1589.
- Blumer, M., and Sass, J. (1972). Oil pollution: persistence and degradation of spilled fuel oil. *Science*, 176, 1120-1122.
- Boehm, P. D., and Quinn, J. G. (1978). Benthic hydrocarbons of Rhode Island Sound. *Estuarine and Coastal Marine Sci.*, 6, 471-494.
- Bray, E. E., and Evans, E. D. (1961). Distribution of n-paraffins as a clue to the recognition of source beds. *Geochim. Cosmochim. Acta*, 22, 2-15.
- Bush, P. R. (1970). A rapid method for the determination of carbonate carbon and organic carbon. *Chem. Geol.*, 6, 59-62.
- Clark, R. C., Jr., and Blumer, M. (1967). Distribution of n-paraffins in marine organisms and sediment. *Limnology and Oceanography*, 12, 79-87.
- Cranwell, P. A. (1973). Chain-length distribution of n-alkanes from lake sediments in relation to post-glacial environmental change. *Freshwater Biol.*, 3, 259-265.
- Farrington, J. W., and Quinn, J. G. (1973). Petroleum hydrocarbons in Narragansett Bay--I. Survey of hydrocarbons in sediments and clams (*Mercenaria mercenaria*). *Estuarine and Coastal Marine Sci.*, 1, 71-79.
- Farrington, J. W. and Tripp, B. W. (1977). Hydrocarbons in western North Atlantic surface sediments. *Geochim. Cosmochim. Acta*, 41, 1627-1641.
- Gearing, P., Gearing, J. N., Lytle, T. F., and Lytle, J. S. (1976). Hydrocarbons in 60 northeast Gulf of Mexico shelf sediments: a preliminary survey. *Geochim. Cosmochim. Acta*, 40, 1005-1017.
- Giger, W., Reinhard, M., and Stumm, W. (1974). Petroleum-derived and indigenous hydrocarbons in recent sediments of Lake Zug, Switzerland. *Environ. Sci. Technol.*, 8, 454-455.
- Giger, W., Schaffner, C., and Wakeham, S. G. (1980). Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. *Geochim. Cosmochim. Acta*, 44, 119-129.
- Haun, J. D. (1971). Origin of Petroleum. *Am. Assoc. Petrol. Geol. Repr. Ser.*, 1, 192 pp.

- Haun, J. D. (1973). Origin of Petroleum. Am. Assoc. Petrol. Geol. Repr. Ser., 9, 210 pp.
- Palacas, J. G., Gerrild, P. M., Lore, A. H., and Roberts, A. A. (1976). Baseline concentrations of hydrocarbons in a barrier-island quartz sand, northeastern Gulf of Mexico. *Geology*, 4, 81-84.
- Smith, P. V., Jr. (1952). The occurrence of hydrocarbons in recent sediments from the Gulf of Mexico. *Science*, 116, 437-439.
- Speers, G. C., and Whitehead, E. V. (1969). Crude petroleum. In *Organic Geochemistry--Methods and Results*, G. Eglinton and M. T. J. Murphy (eds.). Springer-Verlag, Berlin, 638-675.
- Stevens, N. P., Bray, E. E., and Evans, E. O. (1956). Hydrocarbons in sediments of the Gulf of Mexico. *Am. Assoc. Petroleum Geologists Bull.*, 40, 975-983.
- Van de Meent, D., Maters, W. L., de Leeuw, J. W., and Schenck, P. A. (1977). Formation of artifacts in sediments upon freeze-drying. *Organic Geochemistry*, 1977, vol. 1, 7-9.
- Wakeham, S. G. (1976). A comparative survey of petroleum hydrocarbons in lake sediments. *Marine Pollution Bull.*, 7, 206-211.
- Wakeham, S. G., and Carpenter, R. (1976). Aliphatic hydrocarbons in sediments of Lake Washington. *Limnology and Oceanography*, 21, 711-723.
- Zweig, G., and Sherma, J., eds. (1972). *Handbook of Chromatography*, II. CRC Press, Cleveland, 343 pp.

TABLE 1.

## Geochemistry of Sediments from Grays Harbor and Willapa Bay, Washington

Station	OC + %	EOM + µg/g (OC)	Total HC + µg/g (OC)	A HC + µg/g (OC)	n-C <sub>17</sub> µg/g (OC)	n-C <sub>18</sub> µg/g (OC)	Pristane µg/g (OC)	Phytane µg/g (OC)	Pristane µg/g (OC)	Phytane µg/g (OC)	CPI (nC <sub>25</sub> -nC <sub>31</sub> )	Resolved UCM(est) + A HC + µg/g (OC)	Resolved UCM µg/g (OC)
<u>Grays Harbor</u>													
Hogan	2.20	14,500	2,900	860	8.8	3.5	7.5	2.6	2.9	6.8	230	630	
Airport	2.19	11,800	4,000	2,100	4.7	2.8	*	2.4	-	7.8	280	1,800	
Aberdeen	0.84	14,600	6,300	3,700	6.1	4.0	5.5	3.9	1.4	8.8	320	3,400	
Mile 3	1.81	15,000	5,200	2,600	15.9	4.2	4.7	4.1	1.1	7.4	650	2,000	
Arbor	2.07	13,600	3,000	1,300	5.3	2.1	4.2	2.0	2.1	10.0	330	1,000	
South Bay	0.79	7,800	2,300	900	4.8	2.4	11.0	1.7	6.5	7.1	190	700	
<u>Willapa Bay</u>													
Raymond	2.83	8,000	4,700	2,600	1.3	1.4	2.8	1.4	2.0	9.4	210	2,400	
Cameo	1.78	6,000	800	360	1.0	0.5	0.83	0.31	2.7	10.3	70	290	
Palix	2.90	3,700	1,700	770	0.9	0.6	0.60	0.22	2.7	11.9	130	640	
Pickernell	1.39	3,900	1,600	620	*	*	0.88	0.34	2.6	8.1	150	470	
Lynn Pt.	2.22	3,500	1,600	760	*	*	1.6	0.52	3.1	8.7	160	600	
Long Island	2.25	5,200	2,800	1,300	2.0	*	*	0.92	-	6.2	150	1,200	
Winter Ranch	2.11	4,000	1,900	820	5.8	*	*	0.31	-	7.3	180	640	

+ OC = Organic Carbon: Data reported as µg/g (OC) is normalized to organic carbon (OC)

EOM= Extractable Organic Material

HC = Hydrocarbons

A HC= Aliphatic Hydrocarbons

UCM (est)= Total wt. aliphatic hydrocarbons minus chromatographically resolved aliphatic hydrocarbons

\* Compound not resolved by GC from unknown compound

#### FIGURE CAPTIONS

Figure 1. Location of sampling stations in southwestern Washington. Bar graphs indicate the concentrations in  $\mu\text{g/g}$  (ppm) relative to organic carbon of aliphatic hydrocarbons at each station. Concentrations are highest near urbanization and lowest away from population centers.

Figure 2. Gas chromatograms of aliphatic hydrocarbons in sediments at stations along the edges of Willapa Bay and Grays Harbor. Peaks representing two n-alkanes, n-C<sub>17</sub>, and n-C<sub>27</sub>, are indicated. Other symbols are: pr = pristane, ph = phytane, and a, b, c are unknowns having AIs of 1672, 1705, and 1792, respectively.

