

HYDROCARBONS: NATURAL DISTRIBUTION AND DYNAMICS
ON THE ALASKAN OUTER CONTINENTAL SHELF

by

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ABSTRACT

Determination of the ambient kinds and amounts of hydrocarbons in sediment, organisms and water of Alaska's continental shelf have shown that this area is generally free of petroleum. Measurements made in the Gulf of Alaska, Cook Inlet, the Bering Sea, Norton Sound, the Chukchi Sea, and the Beaufort Sea indicate that the hydrocarbons present are predominantly of modern biogenic origin. Where non-biogenic hydrocarbons have been observed, these appear to be associated with natural oil seeps, coal outcrops, long distance atmospheric transport of combustion particulate and local pollution sources such as a small boat harbor.

Two potential mechanisms for the transport of petroleum from the water column to the benthos have been investigated. Sorption of dissolved hydrocarbons by Alaskan suspended sediments is a highly inefficient process for transport to the bottom. Movement of oil droplets to the bottom after incorporation into zooplankton fecal pellets is a process of highly variable efficiency depending on location and season.

INTRODUCTION

In the early 1970's, the federal government of the United States began to actively consider petroleum exploration and development on Alaska's outer continental shelf (OCS). In order to better understand and anticipate the environmental consequences of petroleum related activities in this area, an extensive program of scientific research has been implemented. The overall goal of this research has been to provide reliable information about the present state of Alaska's marine environments and their probable responses to pollution induced stresses.

This Final Report covers one project commissioned by the Outer Continental Shelf Environmental Assessment Program (OCSEAP). As implied by this report's title, the project's objective was to study the natural distribution and dynamics of hydrocarbons in Alaskan OCS areas under consideration for petroleum exploration and development. Work on this project began in 1975 and continued through 1980. During this period, a considerable number of specific tasks have been accomplished. These include several groups of measurements which provide "baseline data sets", indications of the ambient kinds and amounts of hydrocarbons (in the approximate molecular weight range 200-400) present in water, biota and sediment prior to petroleum exploration. This project has also included studies of dynamic processes by which hydrocarbons are transferred from the water column to the sediments. These studies have provided the basis for the estimation of the quantitative extent of two such transfer processes under conditions likely to prevail in Alaskan marine environments.

This Final Report consists of two principal parts. Part One presents results obtained since the preparation of the most recent Annual Report. Hence, this part is essentially an Annual Report for the final six months of the project. Part Two is a review of information obtained over the entire course of the project. This review first treats each geographic area for which "baseline data sets" have been obtained and then addresses the dynamics of hydrocarbon transfer.

PART ONE: SUB-PROJECT REPORTS

I. HYDROCARBONS OF NORTHEAST GULF OF ALASKA SEDIMENTS

One of the first tasks addressed in the course of assessing the probable environmental consequences of petroleum exploration on Alaska's OCS was the measurement of the kinds and amounts of hydrocarbons in benthic sediments in the northeast Gulf of Alaska (Shaw, 1975). In view of the substantial progress in analytical methodology, which has been made since these sediments were first analysed, we decided to reanalyse northeast Gulf of Alaska sediment samples which has been collected in 1974 and 1975. By doing this, we hoped to gain two kinds of information: (1) more detailed and accurate information about the ambient kinds and amounts of hydrocarbons present in Gulf of Alaska sediments in the mid-1970's; and (2) information about the consequences of 5-6 year's storage on the hydrocarbon contents of the sediments. As it turns out, our results do not allow a neat separation of these kinds of information. Some of the ambiguities that arise here are probably generic to the reanalysis of archived materials. Therefore, we discuss them in some detail as a model of the kinds of conclusions which can (and cannot) be drawn in this circumstance.

Methods

Sediments were collected at the times and places specified in Table I and Figure 1. All collections were made with a van Veen grab except Station 37 which, because of the greater water depth, was made with a Skipek grab. Samples were transferred from the interior of the grab (i.e., not material in contact with the grab itself) to pre-cleaned glass jars with aluminum foil lined lids. Samples were frozen within one hour of collection and stored at 0° to -30°C until analysis.

Approximately 80 g of accurately weighed homogeneous sediment were added to a solvent cleaned, tared cellulose extraction thimble (Whatman, 43x123 mm). Samples were reflux extracted using 150 ml distilled hexane plus 150 ml distilled methanol for 48 hours with stirring after 24 hours. The solvent was then separated from the sediment sample for further processing.

TABLE I
 SEDIMENT SAMPLING STATIONS USED IN THIS STUDY

Station (GASS)	Position		Depth (m)	Collection Date	% Water	% TOM (dry)
	N	w				
1	59°50.2'	149°30.5'	263	July 74	61	
6	59°07.2'	148°47.5'	151	July 74	44	3.9
25	59°02.5'	140°49.8'	179	May 75	38	4.2
28	59°26.5'	140°16.9'	239	May 75	54	4.0
30	59°44.1'	141°27.9'	43	February 75	30	1.1
37	59°16.2'	142°59.2'	1920	February 75	59	
41	59°55.1'	142°39.5'	119	July 74	34	3.4
42	59°55.1'	143°51.2'	93	July 74	30	3.1
44	59°35.0'	143°54.2'	181	February 75	34	4.0
49	59°37.5'	145°10.0'	186	February 75	48	4.4
52	60°07.6'	145°06.5'	53	February 75	49	3.6
53	60°23.0'	146°54.0'	279	February 75	28	
56	60°55.2'	146°36.8'	64	February 75	33	
59	59°17.1'	146°14.0'	334	July 74	50	3.7

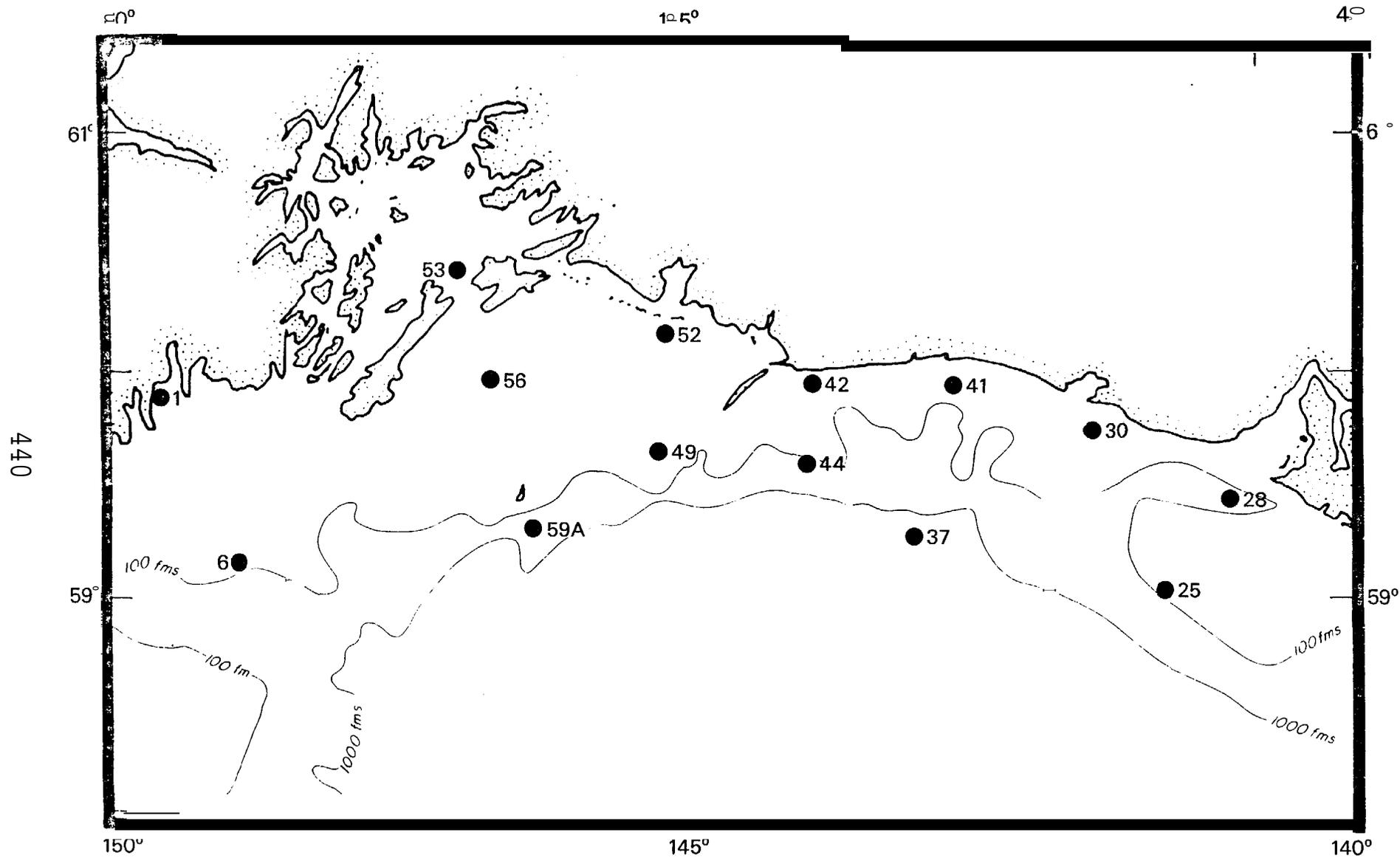


Figure 1. Sediment sampling stations used in this study.

The solvent mixture plus 50 ml distilled H₂O was extracted with 100 ml of distilled hexane 3 times, the hexane fractions collected, pooled, and dried overnight with Na₂S₄ (baked, 500°C, 24 hours). Samples were decanted from the Na₂SO₄ and concentrated by rotary vacuum evaporation to 1.5 ml, then further concentrated to approximately 1.0 ml with a stream of ultra-high purity N₂. Any residual sulfur that may have been present was removed by reaction with elemental copper.

The volume of the hexane extract was then determined by weighing the extract in a tared sample vial and computing from the density of the solvent. A 1% aliquot was air dried and weighed to determine non-saponifiable lipid content. All samples had 6-15 mg non-saponifiable lipid and each was eluted from a 9 mm I.D. x 27 cm column packed with 5 g of 6% deactivated silica (fully activated by baking at 120°C for 24 hours, deactivated with H₂O). Aliphatic hydrocarbons were eluted with 5 column pore volumes distilled hexane. Aromatic hydrocarbons were separated from the heavier weight esters by elution with 5 column pore volumes of 20% (V:V) methylene chloride in hexane.

The samples were analyzed on a Hewlett Packard 5710A gas chromatography (GC) with flame ionization detector. The analytical column was a SCOT glass capillary column, 30 m x 0.7 mm I.D. coated with a slurry of OV-101 (SCOT column from Scientific Glass Engineering, Inc., Austin, Texas). Samples were concentrated to approximately 0.5 ml with a stream of ultrahigh purity N₂. Total hydrocarbon weight was determined by transferring the sample to a tared vial and determining solution volume from the density of the solvent. Peak areas were measured with a Hewlett Packard 3385A digital integrator. Detector response was calibrated daily by injections of a standard mixture of aliphatic and aromatic hydrocarbons in hexane.

Selected samples were analysed further using a computerized gas chromatograph-mass spectrometer (GC-MS) system (Hewlett Packard model 5930/5933). These analyses were carried out on the second fraction from the silica column clean up to determine concentrations of polycyclic aromatic hydrocarbons (PAH) and their alkyl homologs. For this, a quantitative internal standard of fully deuterated naphthalene was added to the sediment extract. With

this, and an unlabeled external aromatic standard, PAH's were determined based on parent ion currents.

Results

Table II gives the sedimentary hydrocarbons of the 14 samples investigated as determined by flame ionization gas chromatography. These data include total saturates (operationally defined as hydrocarbons eluted with hexane in the silica gel clean up), total unsaturates (eluted with 20% methylene chloride in hexane), normal alkanes with 14 to 29 carbon atoms and the acyclic isoprenoids pristane and phytane. Pristane is the most abundant alkane in most of these samples. Pentadecane, heptadecane and nonadecane are also relatively abundant in most samples. Phytane was present in low relative concentrations in all samples except the two eastern most stations, 25 and 28. Most samples also contained normal alkanes with 20 to 29 carbon atoms; however, with little if any predominance of odd carbon chain lengths. Representative gas chromatograms are shown in Figure 2.

For seven of the sediment samples, the extract of unsaturates was further analysed by gas chromatography-mass spectrometry (GC-MS). Concentrations of aromatic hydrocarbons determined in this way are shown in Table III. This technique cannot distinguish among isomeric compounds. However, for seven aromatic ring systems, concentrations of compounds with 0 to 6 alkyl carbon substituents were determined. Table III also shows the highest aromatic hydrocarbon concentrations found in a blank determination (assumed sample size 50 g, dry weight). Other blanks run in the course of this work were generally one order of magnitude lower.

Discussion

For the purpose of this discussion, it is convenient to divide the sediments into two groups. The main group consists of Station 01, 06, 30, 37, 41, 42, 44, 49, 52, 53, 56 and 59 (Figure 1). The eastern group consists of Stations 25 and 28. Marine organisms contribute hydrocarbons to the sediments of both groups as evidenced by the presence of pentadecane, heptadecane, nonadecane and pristane. Terrigenous plant material is a minor contributor to

TABLE II

HYDROCARBONS IN NORTHEAST GULF OF ALASKA SEDIMENTS AS DETERMINED BY FLAME IONIZATION GAS CHROMATOGRAPHY
EXPRESSED AS ng g^{-1} DRY WEIGHT BASIS

Pr = pristane, Ph = phytane, 14 = tetradecane, etc., t = trace

Station	Total	Total	14	15	16	17	Pr	18	Ph	19	20	21	22	23	24	25	26	27	28	29
	Saturates	Unsaturates																		
01	11400	1100	130	240	150	170	400	140	60	240	120	140	100	200	140	146	100	160	t	-
06	8400	3500	80	140	90	100	230	100	40	140	90	110	220	230	210	220	140	160	80	t
25	1300	90	4	7	3	5	6	4	-110	t	5	2	t	t	t	t	13	-	-	-
28	7300	160	10	20	10	10	20	10	-	10	10	20	10	20	t	40	t	50	-	-
30	830	180	14	20	18	20	40	22	9	24	22	23	25	25	49	47	36	36	t	-
37	1400	1300	80	100	60	60	140	50	20	60	30	30	50	60	40	40	20	20	t	-
41	3900	8100	69	110	76	83	190	72	29	73	58	54	50	68	52	51	28	t	t	-
42	7200	10600	130	170	89	93	250	82	37	88	71	71	66	61	51	110	75	93	t	t
44	14600	6600	64	93	64	68	18	66	26	78	64	68	59	100	86	89	60	75	t	t
49	3600	10400	32	95	84	110	320	110	58	160	110	120	110	160	150	160	130	200	93	120
52	5500	7600	31	66	36	44	120	35	18	52	31	26	25	26	20	25	18	32	33	45
53	4500	2000	38	74	41	50	120	38	16	64	36	41	35	78	47	84	36	14	t	46
56	4800	190	48	61	67	48	130	52	28	63	40	42	34	34	29	59	43	47	22	-
59	1100	1600	40	63	44	44	150	4021	42	34	33	32	62	48	50	t	t	t	t	t

TABLE III

AROMATIC HYDROCARBON CONCENTRATIONS IN SEDIMENTS IN ng g^{-1} DRY WEIGHT BASIS.

Column headings indicate ring system and the number of alkyl carbon atoms

Station	C_{10}H_8						$\text{C}_{12}\text{H}_{10}$						$\text{C}_{13}\text{H}_{10}$						$\text{C}_{14}\text{H}_{10}$																	
	0	1	2	3	4	5	6	0	1	2	3	4	5	6	0	1	2	3	4	5	6	0	1	2	3	4	5	6								
01	5	26	78	92	47	9	1	12	39	50	51	53	59	10	19	42	137	22	10	4	123	164	150	70	29											
28	2	3	8	6	1	3	3	12	5	10	-	9	1	2	4																					
42	25	71	137	135	63	28	9	22	54	68	79	77	-	23	23	63	54	32	47	36	23	159	220	182	108	50	16	5								
49	19	57	101	107	56	29	15	17	46	61	65	80	67	39	29	55	70	59	45	29	33	161	233	179	114	51	17									
52	27	81	144	133	70	29	12	27	58	77	82	94	-	31	37	62	84	47	33	37	22	190	240	191	116	50	20	13								
53	8	22	42	38	21	7	3	5	1	8	1	9	2	1	2	3	-	6	1	1	1	9	-	6	5	4	6	5	5	6	3	6	1	3	5	2
59	26	150	267	226	109	28	6	42	88	112	142	109	-	26	50	91	108	97	50	26	13	216	312	252	137	68	8									
High Blank	7	9	16	15	11	4	1	4	7	8	1	4	7	5	1	2	7	5	11	14	11	4	2													

TABLE III

CONTINUED

Station	$C_{16}H_{10}$							$C_{18}H_{12}$						$C_{20}H_{12}$							
	0	1	2	3	4	5	6	01	2	3	4	5	6	0	1	2	3	4	5	6	
01	38	47	43	25	12			25	34	11	12			19	9						
28	6	6	5					6	6	1	2	6		16	10	9	6				
42	44	72	71	50	22	9	6	44	50	-	38	19	6	67	68	37	19				
49	47	75	80	65	57	40	23	46	55	58	68	38	19	78	66	54	35				
52	46	76	75	59	28	18	11	43	55	51	42	27	11	74	49	34	16				
53	16	24	23	17	8	4	2	1	6	1	7	1	6	1	3	9	4	28	21	13	5
59	48	86	84	52	26	7	1	62	82	71	34	7	1	60	55	33	3				
High blank	3	5						1													

the sedimentary hydrocarbons as judged by the very slight predominance of odd chain length normal alkanes in the 20 to 29 carbon atom range.

The main group is distinct from the eastern group in that the former shows evidence of petroleum hydrocarbons. In the saturated fraction (Table II and Figure 2A) this evidence includes the presence of phytane and all normal alkanes from tetradecane through at least heptacosane with little if any dominance of odd carbon chain lengths. For the main group of sediments the presence of petroleum is further indicated by the wide variety of aromatic hydrocarbons in the 10-100 ng g⁻¹ concentration range (Table III and Figure 2B). The most abundant aromatic compound in most homologous series has 2 or 3 alkyl carbon substituents. These concentrations are higher than observed in other sediments remote from petroleum sources (Laflamme and Hites, 1978) and this distribution among homologous alkyl series is indicative of fossil rather than combustion derived aromatic compounds (Laflamme and Hites, 1978; Shaw *et al.*, 1979).

The two stations of the eastern group are distinctly different (Tables II and III, Figure 2C and D). Phytane is not detectable. Some of the higher normal alkanes are absent or only present in trace amounts. Station 28 shows aromatics at concentrations comparable to the highest blank. Thus, it appears that if petroleum is present at all in the eastern group, its concentration is at least an order of magnitude lower than in the main group.

Having established the presence of petroleum hydrocarbons in the sediments analysed, it is appropriate to consider possible sources. In these archived samples, it will be necessary to give careful consideration to the possibility of contamination between collection and analysis. First, however, we will consider environmental sources of the petroleum.

One possible source of petroleum in the northeast Gulf of Alaska is a series of onshore oil seeps extending from the Malaspina forelands (landward of Station 30) to the Katalla area (landward of Station 52) (Blasko, 1976). Although it has not been shown that this oil seep region extends offshore, the regional geology of the area does not exclude this possibility (Sharma, 1979). The unknown and probably variable quantity of petroleum entering the Gulf of Alaska from these seeps would be moved westward by the

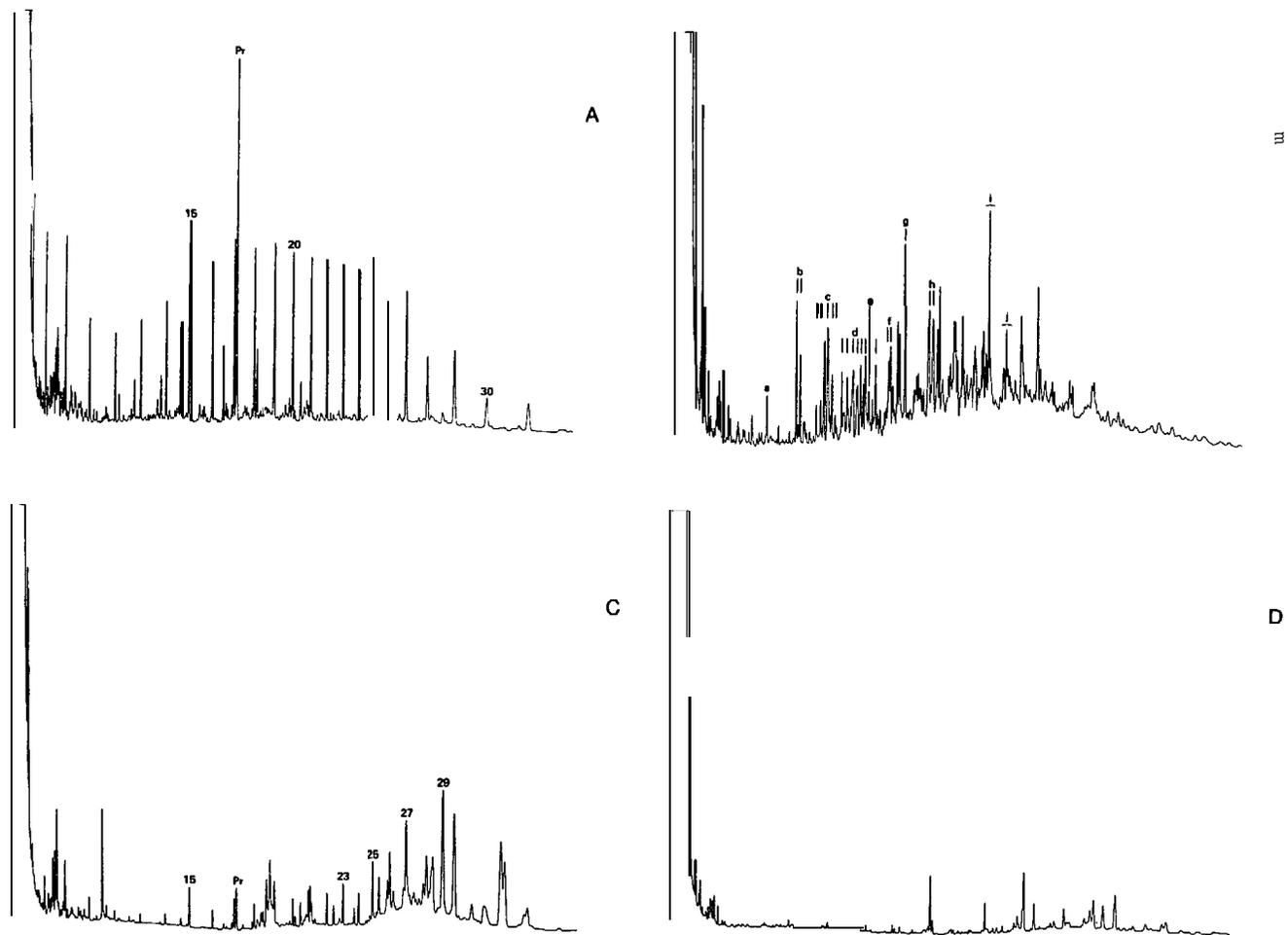


Figure 2. Representative gas chromatograms; A, Station 42 saturate fraction; B, Station 42 unsaturate fraction; C, Station 28 saturate fraction; D, Station 28 unsaturate fraction. In part B, a = naphthalene; b = methylnaphthalenes; c = C₂-naphthalenes; d = C₃-naphthalenes; e = fluorene; f = methylfluorenes; g = phenanthrene; h = methyl phenanthrenes; i = C₂-phenanthrenes; j = C₃-phenanthrenes.

general circulation of the area (Royer, 1979). Thus, petroleum from these seeps could be carried to the main group stations, but not the eastern group. This, of course, is the observed pattern. Although this source of petroleum to these sediments appears plausible, one puzzle persists. The petroleum in the main group sediments appears to be essentially unweathered. This is indicated by the high abundance of normal alkanes compared to the linear branched compounds, pristane and phytane, and by the absence of a prominent cycloalkane fraction (i.e., the lack of a large unresolved complex mixture). The sediments of the San Pedro Basin in the southern California borderland, a marine area of known oil seeps and anthropogenic petroleum additions, have an array of hydrocarbons much more characteristic of weathered petroleum (Venkatesan *et al.*, 1980). It is possible that this difference in degree of weathering is simply the result of environmental differences such as water temperature, oil seepage rate or microbial hydrocarbon degradation rate. But, the possibility that the hydrocarbons observed in the main group sediments are the result of contamination subsequent to collection also needs to be considered.

Given the logical basis of science, it is impossible to prove that contamination has not occurred in any sample where hydrocarbons are detected. The best that can be done is to present information which indicates that contamination is unlikely. In this way, we conclude that it is unlikely that contamination occurred during sediment extraction or analysis. This is based on two facts: (1) that three "system blanks" (complete analytical protocols executed without sediment sample) uniformly showed hydrocarbon levels well below those observed in the main group sediments, and (2) that, for the two eastern group sediments, a reasonable environmental explanation for the lower hydrocarbon concentrations exists (i.e., the observed distribution appears rational, not random). Two lines of evidence suggest that the likelihood of contamination during shipboard collection is also small. The main group sediment samples were collected on two separate cruises by different persons using different ships. Also, Station 37 was sampled using a Shipek grab, rather than the van Veen grab used elsewhere. The fact that none of these variables is reflected in the hydrocarbon distribution pattern argues against contamination during collection. However,

it may be significant that the two eastern group samples were the only ones collected in May 1975 (Table I).

The remaining opportunity for contamination is during frozen storage between collection and analysis. For these samples, this storage period extended over five to six years. Although we have found no change in the hydrocarbons of intercalibration sediments re-analysed after 1.5 years storage, we have no previous experience with sediments stored for five or more years. The principal argument against contamination during storage is the probabilistic one cited above as the second reason for doubting contamination during analysis. The argument (which also can be used against contamination during storage) is that if contamination were random, it is unlikely that of the fourteen samples analysed, the particular two that are uncontaminated would be those two for which a reasonable environmental explanation of low hydrocarbon concentration exists. In fact, if one assumes two uncontaminated samples distributed at random, their probability of appearing at any particular pair is only about 0.005 or one in two hundred.

II. HYDROCARBONS OF NEARSHORE BEAUFORT SEA INVERTEBRATE ANIMALS

In the summer of 1977 a suite of sediment samples from the nearshore Beaufort Sea was collected for hydrocarbon analysis. We found that in addition to aliphatic hydrocarbons of biogenic origin these sediments contained aromatic hydrocarbons of both fossil and combustion origin (Shaw *et al.*, 1979). Given the presence of aromatic hydrocarbons in Beaufort Sea sediments it was of importance to determine whether these compounds are being transferred to the biota of the area.

In the summer of 1978 a suite of biota samples was collected from the nearshore Beaufort Sea to be analyzed with special attention given to the aromatic fraction.

Methods

Samples of approximately 10 g wet weight were digested in centrifuge tubes with 10 N NaOH at 90° for 3 hours and allowed to cool to room temperature (ea. 200). Hexane was then added, the tube was resealed and then

shaken vigorously for 2 minutes. The sample was then centrifuged at 2400 rpm for 10 minutes. The organic phase was subsequently removed with a 20 ml syringe and the extraction repeated twice. The hexane extract was dried over Na_2SO_4 and concentrated to 1-2 ml on a rotatory evaporator. This concentrate was further concentrated to 0.5 ml under N_2 before fractionation on a column of 5 g of silica gel (deactivated with 5% water). A saturate fraction was eluted with hexane and an aromatic fraction with 20% dichloromethane in hexane. Analysis of each fraction by gas chromatography was performed as described in the previous section.

Results and Discussion

Since the intent of this work was not only to obtain baseline information about the kinds and amounts of hydrocarbons in Beaufort Sea biota but also to assess the extent to which aromatic hydrocarbons previously identified in the area's sediments (Shaw *et al.*, 1979) are transferred to the biota, we attempted to obtain sessile or weakly motile organisms from locations whose sediments had previously been investigated. Although this objective was somewhat limited by logistic constraints, we were able to obtain sufficient data (Tables IV and V) to shed considerable light on the transfer question.

Three genera were investigated. The clams *Astarte* sp. were primarily *A. borealis* but included some *A. Montagu*. The clams *Liocyma* sp. were primarily *L. viridis* with a few *L. fluctuosa*. The isopods *Saduria* sp. were probably *Saduria entomon*. All of these invertebrates contain strikingly low concentrations of hydrocarbons. As shown in Table IV, pristane is the only identifiable alkane and squalene is the only identifiable olefin. These animals also contain small amounts of aromatic hydrocarbons as determined by gas chromatography-mass spectrometry (Table V). The suite of samples analyzed represents a considerable geographic range (Table IV) from Elson Lagoon just east of Barrow to Flaxman Island at the mouth of the Canning River. Although the size of this sample group was fairly small (13 analyses), the degree of uniformity in the results lends credence to generalizations drawn from this work.

TABLE IV

HYDROCARBONS IN BEAUFORT SEA ANIMALS AS DETERMINED BY GAS CHROMATOGRAPHY EXPRESSED
AS $\mu\text{g g}^{-1}$ ON A WET WEIGHT BASIS

Sample number	Taxon	Position		Location	Hydrocarbons				
		N	w		Pristane	Aliphatic DUCM	Total aliphatic	Squalene	Total unsaturated
1	<i>Astarte</i> sp.	71°17.5'	156°20.8'	Elson Lagoon	-			0.19	0.45
2	<i>Astarte</i> sp.	71°17.5'	156°20.8'	Elson Lagoon	-			0.32	0.69
3	<i>Astarte</i> sp.	71°17.5'	156°20.8'	Elson Lagoon	-			0.13	0.31
4	<i>Astarte</i> sp.	71°17.5'	156°20.8'	Elson Lagoon	-			0.17	0.28
5	<i>Astarte</i> sp.	70°16.1'	147°38.0'	Tigvaviak Island	-				
6	<i>Liocyma</i> sp.	71°17.5'	156°20.8'	Elson Lagoon	-		0.64	0.25	0.83
7	<i>Saduria</i> sp.	70°30.0'	148°04.0'	Cross Island	0.71	3.8	6.5	3.7	5.7
8	<i>Saduria</i> sp.	70°30.0'	148°04.0'	Cross Island	0.46	3.1	4.3	2.9	3.8
9	<i>Saduria</i> sp.	70°24.1'	148°32.6'	Stump Island	1.2	4.6	6.7	2.0	2.8
10	<i>Saduria</i> sp.	70°33.8'	149°30.0'	Pingok Point	1.1		1.6	3.6	5.7
11	<i>Saduria</i> sp.	70°33.8'	149°30.0'	Pingok Point	1.0		1.4	2.1	3.0
12	<i>Saduria</i> sp.	70°12.2'	146°41.4'	Challenge Entrance	1.3		2.6	1.3	6.6
13	<i>Saduria</i> sp.	70°11.2'	146°05.8'	Flaxman Island	0.5		0.8	1.4	3.4

TABLE V

AROMATIC HYDROCARBON CONCENTRATIONS IN BIOTA IN $\mu\text{g g}^{-1}$ WET WEIGHT BASIS

Column headings indicate ring system and number of alkyl carbon atoms

Sample	0	C ₁₀ H ₈			C ₁₂ H ₁₀		C ₁₃ H ₁₀		C ₁₄ H ₁₀		C ₁₆ H ₁₀		C ₁₈ H ₁₂		C ₂₀ H ₁₂	
		1	2	3	0	1	0	1	0	1	0	1	0	1	0	1
1	13	1.6	3.2	2.1	2.1	2.9			3.5	1.0	1.4		2.0		5.4	
2	14	1.7	2.4	1.5	1.7		0.54		2.6		0.8		0.1		0.2	
3	14	2.4	2.5	0.66	0.7		0.55		2.0	1.3	0.6		0.7		1.4	
4	31	7.2	7.9		2.8		2.4		4.5	4.2	3.1	2.2	1.6	1.3	3.3	
5	31	9.1	9.3	5.0	3.4		3.0		5.7		6.5	3.9		2.8		
6	23	11	16	38	2.7				5.7		3.0	1.8		3.2		
7	7.3	1.4	2.1		3.3	5.0	2.1	5.7	5.9	3.2						
8	21	6.4	3.1	1.7	1.0		0.8		2.4					0.9		
9	5.6	1.6	2.1	4.1	0.3			9.0	9.9							
10	13	3.2	3.5	1.0	1.3	1.9	0.6	1.7	2.1	0.9	0.6					
11	11				1.4			4.2	5.8		2.6			1.9		
12	8.3	4.0	5.2	2.3	3.4	2.5	0.9	2.0	1.6	1.5	0.6			0.6		
13	11	2.1	2.0	0.2	1.2	1.9	0.6	0.7	1.3	0.9	0.5					
Blank	7.2	0.7	0.3		0.7		0.2		0.7	0.3						

Our previous analyses of Beaufort Sea sediments indicated that the saturated hydrocarbon fractions were dominated by heptacosane and odd chain length normal alkanes with 23 to 31 carbon atoms whose respective probable origins are marine algae and terrigenous higher plants. None of these compounds were detected in any of the animal tissues analyzed. Since all three genera are consumers of particulate detritus, it seems reasonable to suppose that they are exposed to all of the hydrocarbons associated with the sediments. The fact that pristane (with its branched structure) is the only identifiable alkane which accumulates, may imply that normal alkanes are assimilated and rapidly metabolized by these organisms. The possibility of rapid metabolism is also consistent with the fact that only in *Saduria* were any aliphatic hydrocarbons whatever observed. In *Astarte* and *Liocyma* any aliphatics which may have been present were evidently below the detection limit of approximately $0.1 \mu\text{g g}^{-1}$. Squalene, which was found in all but one of the samples is a common metabolic intermediate; it is probably produced by the animals themselves rather than acquired through the diet.

The sediments of this region contain arrays of aromatic hydrocarbons whose alkyl homolog ratios indicate contributions from both fossil and pyrolytic sources (Shaw *et al.*, 1979). In these biota, the concentrations of aromatic hydrocarbons are quite low; sometimes scarcely above the blank values of Table V. However, the fact that the aromatic hydrocarbons of these animals are generally restricted to structures with either no alkyl substitution or a single methyl group suggests that pyrolytically generated compounds are being incorporated but not fossil materials. However, at the low concentrations observed, this conclusion must not be considered tentative. Nevertheless, it is clear that the animals investigated do not have substantial accumulations of aromatic hydrocarbons.

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PART TWO : PROJECT REVIEW

This part of this final report summarizes and reviews the results obtained during the course of this project, July 1975 through September 1980. The intent here is not to repeat the detailed discussions which have been presented in Annual Reports, but rather to provide a concise summary of those discussions together with indications about which Annual Reports and other open literature sources should be consulted for further detail. In this section an abbreviated citation form for this project's Annual Reports has been adopted. Thus (77) is used to indicate the 1977 Annual Report. The complete bibliographic data for these reports as well as the publications and theses resulting from this work are listed at the end of Part Two.

I. GULF OF ALASKA

Water

A suite of 18 unfiltered surface water samples from the Gulf of Alaska continental shelf between Yakutat (140°W) and Unimak Island (164°W) collected in 1975 indicated that these waters had total hydrocarbon concentrations at or below the low parts per billion ($\mu\text{g kg}^{-1}$) level. No evidence of petroleum was detected (76). An additional 43 water samples from the same area in 1976 (77) were generally similar. These latter samples showed generally higher concentrations in spring than in winter suggesting biological origin and, in some cases, had a normal alkane array which we have subsequently concluded may be bacterial (Shaw and Wiggs, 1979). Although the precision of these analysis is low, it appears that the continental shelf waters of the Gulf of Alaska are low in hydrocarbons and free of detectable petroleum.

Seston

Thirty-one surface tows covering 740 m² each were made in 1975 to determine the abundance of floating tar in the Gulf of Alaska (76). Of these,

only two contained small amounts of tar. Of an additional 19 tows made in 1976 (77), only three contained tar. These data give an arithmetic mean concentration of tar on the continental shelf of $3.8 \times 10^3 \text{ mg m}^{-2}$. This is two or more orders of magnitude less than the concentrations of tar reported along the world's major tanker routes.

Sediment

The results of the analysis of a suite of 14 sediment samples from the northeast Gulf of Alaska is described in detail in Part One of this report. These analyses indicate that some locations have small amounts of petroleum hydrocarbons, possibly the result of natural seepages in the area.

II. COOK INLET

Water

A suite of 20 unfiltered water samples was collected in lower Cook Inlet from Kennedy Entrance in the south to about Cape Ninilchik in the north and including both Kachemak and Kamishak Bays (77). The observed concentrations of total hydrocarbons ranged from 0.2 to 1.5 $\mu\text{g}/\text{kg}$ and the gas chromatograms indicated biogenic rather than petroleum origin. A suite of 29 filtered water samples and suspended matter samples was collected (79) as part of a time series measurement for plankton and as a reconnaissance of the petroleum production area of upper Cook Inlet. Of the 29 samples analyzed, 20 showed no detectable hydrocarbons. For the 9 samples containing observable concentrations of hydrocarbons, the gas chromatograms suggest that the origin is clearly not petroleum and may be bacterial.. The concentrations of hydrocarbons on suspended particulate matter were also low and appeared to be of bacterial and planktonic origin.

These results together with others presented here suggest that the intense tidal mixing of upper and central Cook Inlet rapidly disperse the petrogenic hydrocarbons which are added through oil production activities. Biogenic hydrocarbons (except for bacterial compounds which may be the

result of contamination from the collecting ship) are also absent in the upper Inlet. This is in keeping with the low productivity of the region. In the lower portion of Cook Inlet where turbulence and suspended sediment load are lower and biological productivity is consequently higher, low concentrations of biogenic hydrocarbons were observed.

Seston

Twenty seston tows were made between Kennedy Entrance and Cape Ninilchik (77). Only one tow (740 m²) contained a trace of floating tar (< 0.1 mg). This indicates that petroleum production and general commerce in Cook Inlet have not led to abundant floating tar there. This conclusion is reinforced by casual but extensive examination of stranded material on Cook Inlet beaches.

Sediments

Several determinations of hydrocarbons in sediments of Cook Inlet have been made (78, 79). These have primarily been intertidal materials from the lower part of the Inlet examined to provide background for biota analyses. Four sediment samples from Kachemak and Kamishak Bays were investigated (78) particularly to determine the character of aromatic hydrocarbons present. All four contained traces of aromatics whose alkyl homolog plots (Youngblood and Blumer 1975; Shaw *et al.*, 1979) indicated that both fossil (oil and coal) and combustion derived aromatics were present. A sample from Bluff Point (on the northern side of outer Kachemak Bay) was particularly rich in coal associated compounds. For comparison, a sediment sample from Port Valdez was also analyzed. It showed an alkyl homolog pattern indicative of only combustion derived aromatics. The aliphatic fractions of these samples showed arrays of normal alkanes typical of modern plants; there was no evidence of petroleum even in a sample from Iniskin Bay, one of the places within Kamishak Bay where natural oil seeps have been reported. Although the historic record of seeps in this area is extensive (Blasko, 1976), our work in Kamishak Bay has failed to detect any evidence of seeping petroleum in sediments, in organisms or visually

as oil entering the marine environment. Additional intertidal sediment analyses (79) indicated that the area whose hydrocarbon composition is strongly influenced by coal is limited to the northern side of Kachemak Bay (Homer-Bluff Point) and that the influence is very much reduced on the southern side of Kachemak Bay (Kasitsna Bay).

An experimental analysis of analytical and environmental variability of the hydrocarbon content of intertidal sediments was carried out for Mud Bay near Homer (78). From this work, we concluded that laboratory variability is of roughly the same magnitude as environmental variability occurring over tens of meters.

Bio ta

Over the past three years (78, 79, 80), we have determined the hydrocarbon compositions of 41 specimens of attached plants and 51 specimens of benthic animals from lower Cook Inlet.

From this work three principal conclusions can be drawn.

1. The only location at which we have observed petroleum hydrocarbon residues is the small boat harbor at Homer. We have not examined organisms from other harbors of Cook Inlet (Kenai, Seldovia, etc.) but we expect that petroleum enters the biota at those locations also. However, we have examined organisms collected in the oil seep areas of Kamishak Bay. These, like the sediments from that area, show no indication of petroleum. We do not know whether this absence of oil residues indicates that oil seeping into Kamishak Bay is efficiently dispersed and degraded or that the seeps previously reported in the Iniskin Peninsula area have reduced their flow in recent years.

2. In the Coal Bay to Bluff Point area of northern Kachemak Bay an array of hydrocarbons associated with coal exposed in the area has to a limited extent, entered the detritus based food web. Hydrocarbons in this array include odd chain length normal alkanes with 21 to 31 carbon atoms and a group of abietic acid derived diterpenoids including retene, simonelite,

f ichtelite, dehydroabietane and iosene. Although this same group of compounds is present in modern soils (Simoneit, 1977), our measurements (79) indicate that on the northern side of Kachemak Bay, this array is much more concentrated in detrital coal than in modern soil. Specimens of *Macoma balthica*, *Mytilus edulis* and *Strongylocentrotus droebachiensis* from this area showed all or part of this array. However, two factors complicate the situation: not every analysis of these species from this area showed the array and for those that did we do not know whether these hydrocarbons had been assimilated or were merely part of the gut contents.

3. By far the majority of the organisms examined contained only hydrocarbons consistent with contemporary biosynthetic origin. This included plant and animal materials from subtidal and intertidal locations in Kachemak Bay, Kamishak Bay and central Cook Inlet. In species for which hydrocarbon composition has been determined at other locations, the composition of Cook Inlet specimens were similar, at least in a qualitative sense. Quantitative differences within a species were observed between Cook Inlet and other locations, between locations in Cook Inlet and even between replicate analyses of materials collected at the same place and time. The most extensive example of this is our work with *Fucus distichus* (78, 79, 80). We expect that both seasonal and site-related differences contribute to this variation. We also concluded that variable hydrocarbon extraction efficiency probably related to an observed variability in efficiency of plant cell lysis contributes to the observed variability. However, the qualitative differences in hydrocarbon composition between petroleum contaminated *F. distichus* at Homer Spit and unoiled specimens collected at other locations were sufficient to make the two easily distinguishable.

III. BERING SEA

Biota

A considerable variety of organisms from the pelagic environment of the southeastern Bering Sea have been collected and analyzed (77, 78). The

animals investigated include **invertebrates, fish, birds and mammals**. No hydrocarbons from petroleum or terrigenous plant sources were detected in any of the tissues analyzed. The analyses showed that the source of hydrocarbons in the Bering Sea pelagic environment is biosynthesis in that environment t. This is in keeping with the current understanding of productivity and carbon flow in this area.

Seston

Twenty tows were made for floating tar in the southeast Bering Sea in 1975 (76). Only one of these revealed any tar. An additional 13 tows were made in Norton Sound in 1976 (77). No tar was found in any of these samples. Taken together these 33 tows imply an arithmetic mean concentration of 2.7×10^{-4} mg tar m^{-2} of the Bering Sea.

Water

Five analyses of unfiltered surface water were carried out on samples collected in Norton Sound in 1976 (77). These showed total hydrocarbon concentrations at or below the $\mu g\ kg^{-1}$ level. The analytical data indicated **biogenic** origin.

IV. CHUKCHI SEA

Water

Six analyses of unfiltered surface water were carried out on samples collected in 1976 (77). These showed total hydrocarbon concentrations at or below the $\mu g\ kg^{-1}$ level. The analytical data indicated **biogenic** origin.

Seston

Twelve surface tows of 740 m^2 each for floating tar were made in 1976 (77). No tar was found in any of these collections.

V. BEAUFORT SEA

Water

In 1976 (77), 14 surface water samples were collected in the Beaufort Sea from a U.S. Coast Guard Ice Breaker. Three of these samples showed evidence of petroleum hydrocarbons, but these may have been contamination from the collecting ship itself.

Sediment

A suite of 20 nearshore sediment samples was collected for hydrocarbon determination in 1977 (78). Analysis showed that, although the alkane composition suggests only biogenic sources, complex mixtures of polycyclic aromatic hydrocarbons are present. Among the stations analyzed, distributions of aromatic hydrocarbons characteristic of both pyrolytic and fossil sources were observed. The geographic distribution of pyrolytic compounds and other lines of evidence suggest that their source may be long distance transport of anthropogenic combustion products. Fossil aromatic hydrocarbons are present at some locations at sufficient concentrations to mask any pyrolytic which may be present.

Biota

As described in Part I of this report, a suite of 13 invertebrate animals from the nearshore Beaufort Sea was analyzed to determine the kinds and amounts of hydrocarbons present. These analyses showed low concentrations of a small number of biogenic hydrocarbons and very low concentrations of aromatic hydrocarbons from pyrolytic sources.

VI. THE ASSOCIATION OF PETROLEUM HYDROCARBONS AND SUB-ARCTIC SEDIMENTS - A POTENTIAL POLLUTANT TRANSFER MECHANISM

Based on published data as well as results from our own laboratory, we have developed a simple predictive model of the amount of petroleum likely to be transferred from the water column to the benthos by sorption

and sedimentation with suspended sediments. Our model is based on experiments performed with naturally occurring glacially derived sediments from southcentral Alaska. Since these sediments are unlike many lower latitude sediments in that they are chemically unweathered and low in carbonates and organic carbon, our results will not necessarily apply to environments whose sediments are not glacial in origin. In applying these results to any environment it must also be recognized that they are concerned with a single process whereas in the environment other processes including evaporation, uptake, and degradation by biota, and photooxidation are simultaneously occurring.

Several assumptions have been necessary in the development of the model and its application. In all cases for which we were not confident that we had accurate data, we chose values which lead to an over estimation of the extent of sediment-oil association. Thus the model represents an upper bound rather than an accurate prediction of the association. Even this approach leads to the prediction that interaction with suspended sediment can result in the sedimentation of only a small proportion of oil in seawater. Thus, we conclude that for the range of conditions investigated this process is not a major transport pathway for petroleum in the marine environment.

Sediment-hydrocarbon association experiments were carried out using particulate matter collected from the water column of the Gulf of Alaska and radio-labeled decane and biphenyl which were chosen to represent the two major compound classes in petroleum - the alkanes and the aromatics. The highest concentration of hydrocarbon tested was a biphenyl preparation of three times the saturated solution concentration; the range of concentrations examined was near or below saturation for both compounds. Thus, the model may only be applicable in environmental situations where petroleum is present in solution. Such situations might include permitted discharges or a spill at some distance from the slick itself. It is probably not appropriate to extrapolate the model to higher oil concentrations where most of the oil exists as droplets or larger particles. These may associate with sediments by mechanical coating giving quantitatively very different results than the dissolved fraction.

We assume that once sorbed to sediment, hydrocarbons never desorb. Work in our laboratory provided qualitative evidence that in fact substantial resorption occurs when an oiled sediment particle enters clean water.

We assume that the concentration of petroleum (in ppm) associated with sediment is 30 percent of the original aqueous concentration (in ppm). Our laboratory work showed that for either decane or biphenyl, this is roughly the percentage of hydrocarbon which associates with sediment when the water is initially saturated with hydrocarbon. Since decane and biphenyl are structurally quite different and since together they represent the two major classes of hydrocarbons in petroleum, we assume that this relation holds, at least crudely, for all oil. We do know that for subsaturation concentrations of biphenyl or decane, the percentage of hydrocarbon associated with sediment is smaller. However, for simplicity and in keeping with our upper bound approach we assume 30 percent applies at all concentrations. It is very important to note that 30 percent is the relation between the hydrocarbon concentrations in water and sediment. This is very different than saying that 30 percent of the petroleum is on the sediment since the amount of sediment in water rarely exceeds $1 \text{ g } \bar{x}^{-1}$.

We assume that the concentration of petroleum associated with sediment is independent of the concentration of suspended sediment (sediment load). Laboratory experiments have shown that this is the case for typical Alaskan sediment loads. This assumption means that in any particular application of the model, the concentration of petroleum which is carried to the benthos is unaffected by variation in sedimentation rate.

We can apply the model to actual or hypothetical discharges of dissolved hydrocarbons in southcentral Alaska to predict an upper bound for the amount of petroleum sorbed and sedimented by mineral particles. We have done this for the permitted discharge of treated ballast water at the trans-Alaska oil pipeline terminal at Port Valdez, Alaska. The operating permit for the ballast water treatment facility specifies the following effluent characteristics: petroleum, 8 ppm; daily discharge, $1.6 \times 10^5 \text{ m}^3$.

If, as a quite unrealistic worst case, we assume no dilution at all, then the concentration of petroleum on sediment is predicted to be 2.4 ppm. Furthermore, we can estimate an upper bound to the total amount of hydrocarbon sedimented within Port Valdez. Shaw and Baker (1978) have reported seasonal sedimentation rates determined by sediment traps at several locations in Port Valdez. The highest sedimentation rate reported was 0.6 mg / cm² .hr during the summer at a station near the mouths of glacially fed rivers. If we assume that this sedimentation rate applies to the entire 105 km² area of Port Valdez, then the daily sedimentation is:

$$\frac{0.6 \text{ mg}}{\text{cm}^2 \cdot \text{hr}} \times \left(\frac{105 \text{ km}^2}{\text{km}} \right) \times \frac{105 \text{ km}^2}{\text{Port Valdez}} \times \frac{24 \text{ hrs}}{\text{day}} \times \frac{1 \text{ ton}}{10^9 \text{ mg}} = 15 \times 10^3 \text{ tons sediment}$$

If, as predicted above, this sediment contains 2.4 ppm of sorbed petroleum, then the total petroleum sorbed in a day is 0.036 tons. This can be compared to the total daily amount of petroleum discharged which is (assuming a density of 1 for the oil):

$$1.6 \times 10^5 \text{ m}^3 \times 8 \times 10^{-6} \times \frac{1 \text{ ton}}{\text{m}^3} = 1.28 \text{ tons}$$

Thus only 0.036/1.28 or 3 percent of the oil is predicted to associate with sediment.

The most important point to note here is that in order to reach this prediction we consistently made assumptions which tend to overestimate the extent of oil-sediment interaction. The essential conclusion is therefore that interaction with sediments is not a major pathway for the dispersal of oil from a release such as the discharge of treated ballast water at Port Valdez.

Fjords, such as Port Valdez, with their fairly restricted circulation and relatively slow flushing rates provide the most favorable conditions in southcentral Alaska for sorption of oil by suspended sediments. In more open locations, mixing can be much more efficient. For instance, at one nearshore location in central Cook Inlet a dilution of 10⁴ was observed within 25 m (Rosenberg *et al.*, 1969). A discharge at this location with

the same hydrocarbon concentration as the Port Valdez ballast water treatment facility would, at 25 m from the outfall, result in a hydrocarbon on suspended sediment concentration of 240 ppt.

Our model probably cannot be extrapolated beyond the hydrocarbon concentration range and suspended sediment type for which it was developed. Even within its area of applicability the model deals with only a single physical process, not the sum of all petroleum dispersing processes in the marine environment. The model shows that sedimentation *via* sorption to suspended mineral particles is not a major pathway for the dispersion of petroleum in the marine environment.

VII . HYDROCARBON TRANSPORT *via* COPEPOD FECAL PELLETS - A POTENTIAL POLLUTANT TRANSFER MECHANISM

Copepods and other zooplankton non-selectively ingest small particles from the water column and excrete relatively large and therefore more rapidly sinking fecal pellets. Consequently, when oil droplets are present in the water column, copepods have the potential of enhancing the transfer of oil to the benthos. We have constructed a simple numerical model of this process in order to estimate its importance and its sensitivity to environmental variables under Alaskan conditions (Else, 1981).

The model is based on several assumptions:

- o Copepods feed on food and oil particles in proportion to their concentration in the water. This is, there is no selectivity for or against oil.
- o Behavior and metabolism (including fecal pellet production rate) are unchanged by the presence of oil.
- o Each" copepod feeds until it ingests its daily food ration necessary for maintenance; oil droplets ingested during this process will be excreted.
- o The total ingested mass may not exceed twice the daily ration.
- o Animals will cease to feed when the concentration of oil droplets exceeds that of food particles.

Using these key assumptions and published information about copepod abundance we have modeled the transfer of oil particles to the benthos as a function of season in the southern Bering Sea and at Port Valdez, Alaska.

The model predicts that, at the maximum, in the Bering Sea 200 mg of oil $\text{m}^{-3} \text{day}^{-1}$ could be ingested by copepods and excreted as fecal pellets. A slightly smaller rate is predicted for Port Valdez. The times of year presenting greatest opportunities for this transfer are the spring bloom with high numbers of phytoplankton and zooplankton, and the summer. Summer months enable a greater percentage of the initial oil droplets to be ingested (as much as 60% the first day) than does the spring bloom situation, given an oil spill of equal magnitude. The low phytoplankton levels in winter months increase the chance of oil droplets outnumbering the food supply to such an extent that the animals *will* cease to feed. The increase in fecal matter mass due to the incorporation of oil is greatest in winter, and may quadruple the biogenic mass.

It appears that the importance of this mechanism for the transfer of spilled oil from the water column to the benthos is highly variable. At certain key seasons and locations this may be a major oil dispersal pathway; at others it is probably negligible.

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