USNS Potomac Oil Spill Melville Bay, Greenland August 5, 1977

A Joint Report on Scientific Studies and Impact Assessment by the NOAA-USCG Spilled Oil Research Team and the Greenland Fisheries Investigations, Ministry for Greenland.

August 1979

U.S. DEPARTMENT OF COMMERCE National Oceanic and Atmospheric Administration United States of America

MINISTRY FOR GREENLAND Greenland Fisheries Investigations Denmark

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PREFACE

The spill of Bunker-C fuel from the USNS POTOMAC on August 5, 1977, in Melville Bay, Greenland, is among the few oil spills studied in Arctic waters. This report presents the studies and findings of the NOAA-USCG Spilled Oil Research and Grönlands Fiskeriundersögelser (Greenland Fisheries Investigations, Ministry for Greenland) teams which responded to study the spill. This spill is noteworthy for three reasons: 1) the spill occurred in the pristine waters of the Arctic which have very low background levels of petroleum hydrocarbons and a fragile ecology, 2) the fuel oil, (a blend containing 55 percent pitch with a specific gravity of 1.054) remained on the surface until it weathered sufficiently to sink, and 3) a fairly comprehensive sampling program was undertaken in spite of the remoteness and logistic problems, which served as the basis for comprehensive studies on the fate and impact of the spilled oil.

ACKNOWLEDGMENTS

This report represents the efforts of many people and organizations without whose support and dedication it could not have been generated.

The following scientists participated in the field investigations: P. L. Grose, Physical Oceanographer, NORA; J. S. Mattson, Marine Chemist, NOAA; E. I. Chan, Marine Ecologist, NOAA; G. Mueller, Arctic Biologist, University of Alaska; H. Petersen, Environmental Biologist, Greenland Fisheries Investigations (GF); S. A. Horsted, Fishery Biologist, GF; J. Christensen, Marine Ecologist, Marin ID.

The field program was supported by the U.S. Coast Guard Cutter WESTWIND, the Military Sealift ship MIRFAK, and the Greenland research vessel ADOLF JENSEN. While valuable support was received from all of the personnel on these vessels, specific acknowledgment of assistance is due to: Cmdr. D. Super, Captain: Marine Science Technician (MST) Chief L. Pierce; B. Grahm, MST2; and G. Davis, MST3; and Lt. Cmdr. J. Carruthers, Executive Officer, all from the WESTWIND as well as Captain J. Petersen and the entire crew of the ADOLF JENSEN. Many useful observations and oil samples were received from the U.S. Coast Guard Atlantic Strike Team and the U.S. Navy Superintendent of Salvage representatives involved in the cleanup effort.

The biological samples were sorted and analyzed by R. Maurer and J. Kane of the Narragansett Laboratory of the NOAA National Marine Fisheries Service and O. Norden Andersen of Marin ID, Denmark.

Chemical analyses were performed by Energy Resources Co. for the NOAA samples and by the Water Quality Institute and University of Gothenburg (Sweden) for the Danish samples.

Microbiological studies were performed by the Water Quality Institute.

Funding for the studies was supplied by NOAA's Environmental Data Service, U.S. Navy Superintendent of Salvage, and the Ministry for Greenland.

Publication costs were underwritten by the NOAA Hazardous Materials Response Program.

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1.0 INTRODUCTION

On the morning of August 5, 1977, the U.S. Navy ship POTOMAC, bound for Thule Air Force Base with a cargo of arctic-blend diesel fuel, was being escorted in intermittent dense fog by the U.S. Coast Guard cutter WESTWIND through the scattered sea ice of Melville Bay in the northeastern part of Baffin Bay off western Greenland. The WESTWIND moved into a large ice floe at 9 to 10 kn, followed by the POTOMAC. When both vessels were in the ice floe, a crewman on the POTOMAC sighted oil on the water at 0430 local time. The WESTWIND was immediately informed. The POTOMAC's position at the time of the sighting was 74°52'N, 61°13'W (Figure 1-1). It was discovered that the No 2 Bunker (deep port) tank, containing about 107,000 us gallons of Bunker-C fuel, had been "holed" by an iceberg or "growler". Almost all of the fuel in the holed tank was eventually spilled.

Calm seas with waves of 0 to 2 ft and light winds of 0 to 7 kn kept the oil from dispersing for several days after the spill. While the WESTWIND escorted the POTOMAC to Thule with a water bottom in her holed tank, representatives of the U.S. Coast Guard (USCG) National Strike Force and the U.S. Navy Military Sealift Command flew to Thule aboard a USCG C-130, arriving on August 8. Immediately upon arrival, they left for the scene of the spill onboard the WESTWIND. From August 10 to 12, the C-130 flew over the entire area, carrying its airborne oil surveillance system for mapping the extent of the oil slick. Helicopters from the WESTWIND also participated in the search. The C-130 located the major concentration of the oil on August 12, and directed the Coast Guard helicopters and the icebreaker WESTWIND to the scene.



Figure 1-1. USNS POTOMAC oil spill site and surrounding area. The spill site is marked by + in Melville Bay.

2.0 SCIENTIFIC RESPONSE TO THE OIL SPILL

As is standard for oil spills, the scientific response to the POTOMAC oil spill was an ad hoc effort by concerned scientists. The U.S. and Danish responses were not fully preplanned nor were they coordinated before arrival on scene. This section summarizes the events and planning that culminated with their arrival on scene and the objectives for their responses. Summaries of the impact of the spill and the significant scientific findings are presented in Chapters 10 and 11.

2.1 NOAA Response

On August 11 and 12, the Office of the Chief of Naval Operations called upon the Office of Environmental Monitoring, National Oceanic and Atmospheric Administration (NOAA), regarding possible advice or assistance with the POTOMAC oil spill. After consultation within NOAA, the Navy was informed that the NOAA-USCG Spilled Oil Research Team (SOR) could lend assistance.

On August 14, a meeting was held at the U.S. Navy Military Sealift Command in Washington D.C. attended by representatives of the Navy Superintendent of Salvage, Chief of Naval Operations, and the NOAA SOR team. At this meeting a description of the water circulation in the vicinity of the spill was presented along with the most recent "pollution report" from on scene. This report stated that there had been a "fairly rapid dispersion and breakup considering [the] nature of [the oil]...the rainbow streamers [had] disappeared leaving chocolate mousse streamers ... [weather] calm ... sea conditions have not accelerated this breakup ... [the oil] will not float forever; it will breakup and dissipate through evaporation and [chemical] breakdown with subsequent dispersion into [the] water column, " and "oil within streamers on 12 Aug showed 50,000 gals of recoverable oil ... a 50 percent recovery would be optimistic." They cautioned against overconfidence, continuing "a [weather] change with [increased] wind could disperse the oil so widely that recovery could be reduced to 1-5,000 gals." The message finished with, "[c]onversely, the oil could be pushed ashore contaminating 20 miles of ice and coastline with 10-25,000 gals ..., " and since "impact would be in a

sensitive eskimo hunting area, ... the sensitivity of the incident vs. cost of [a cleanup] response dictates referral to mission coordinator for appropriate action."

Additional information for those present at this meeting was contained in a brief summary of typical physical properties of the spilled fuel; i.e., "typical" analysis as relayed by EXXON: specific gravity 0.974 at 60 F [0.987 at 30 F] ... oil will float [rather than] sink" As was to be learned later, these "typical" properties of the spilled oil were all that could be provided on short notice by EXXON because of a communications strike in Aruba.

The NOAA representatives disagreed with the optimistic predictions in the pollution report that the mass of the oil remaining at the surface would continue to diminish by 50 percent per week, until "residual tarballs remaining after 6 weeks would be 3 to 5 percent of the total spill." This disagreement was based on 1) the reported specific gravity of the spilled oil, and 2) the likelihood that the mass reduction observed in the first week was due to a total loss of the volatile fraction (b.p.< 250 C) of the "cutter stock". It was their opinion that continued reduction of the mass of the surface oil was unlikely, but that horizontal dispersive processes would quickly lower the possibility of recovering the spilled oil. Based upon the reported movements of the surface oil during the week that had elapsed since the spill and the analysis of the surface water motion in the Melville Bay - Cape York area, they predicted that within 2 weeks, or by about August 27, the surface oil would be so widely dispersed that no recovery would be possible.

The U.S. Navy Military Sealift Command decided to proceed with the cleanup effort even though 9 days had elapsed since the spill and they agreed that the overall effort would benefit from a scientific response that would include biologists, a physical oceanographer and a chemist. It was decided that four SOR Team members should accompany the Coast Guard Strike Team personnel on the C-5A flight to Thule. The scientific mission was threefold: 1) to advise and assist the On-Scene-Coordinator, the Strike Team, and the Navy to the maximum extent possible, 2) to conduct chemical, physical, and biological sampling for a rudimentary assessment of the ecological impact, and 3) to assist and collaborate with the Danish scientists aboard the R-V ADOLF JENSEN. The SOR team arrived in Thule at 0900 EDT on August 16, left for the scene of the spill aboard the USNS MIRFAK, and arrived at the WESTWIND's

position at 1300 EDT on August 17. The NOAA field effort was completed with the return of the WESTWIND to Thule on August 21.

2.2 Danish Response

At 0010 GMT on August 6, the Ministry for Greenland received a message that 390 tons of oil had been spilled by the USNS POTOMAC in Melville Bay, Greenland. The Ministry recognized that this opportunity to study an oil spill in Arctic water was of particular interest because of the ongoing oil exploration off West Greenland and the importance of hunting marine mammals and birds in this area by native hunters. Moreover, they wanted the opportunity to exercise and test recent contingency plans for oil spill research. The Minsitry, therefore, redirected the research vessel ADOLF JENSEN from its scheduled cruise to a special cruise into Melville Bay to study the oil spill. During the next 4 days, a cruise plan was generated and the required special equipment was staged onboard the ADOLF JENSEN. The cruise plan called for physical, chemical, and biological observations and was generated with inputs from the Water Quality Institute, Marin ID, the University of Gothenburg, and Greenland Fisheries Investigations, Ministry for Greenland.

The scientific staff for the cruise, two biologists and a marine mammal observer, left Copenhagen, Denmark on August 10 and arrived at Holsteinborg, Greenland the same day. In the meanwhile, the ADOLF JENSEN had been prepared for the cruise and sailed from Holsteinborg when the scientific party was aboard. Considering that there was only a weekend between the notice of the spill and the departure of the scientific team, that some of the scientific gear had to be sent from Sweden to Denmark, that the ADOLF JENSEN had to be directed from an area off Disko Island to Holsteinborg, and that the communications between Greenland and Denmark were very difficult because of a strike at the Greenland radio stations, the cruise to Melville Bay could hardly have been started earlier. The ADOLF JENSEN arrived at the scene of the spill on August 12 and the investigations started immediately. The cruise terminated on August 23 when the ADOLF JENSEN arrived at Egedesminde, Greenland.

2.3 On-scene Coordination

On August 17, the NOAA and Danish scientists met onboard the ADOLF JENSEN to exchange plans and discuss scientific coordination. At this meeting it was agreed that the chemistry sampling was all to be done from the ADOLF JENSEN because of better logistic support. Consequently, one of the NOAA team joined the ADOLF JENSEN with the required sampling and analytical equipment. It was also agreed that the NOAA team remaining on the WESTWIND would focus its efforts on the movement of the oil and on obtaining neuston and bongo tows for biological samples at or near the surface. The Danish team on the ADOLF JENSEN would concentrate on the subsurface biological sampling in addition to the chemistry. Daily contact was maintained between the two teams to ensure coordination and to discuss current findings.

3.0 FIELD PRCSRAM

The field program in response to the UENS POTOMAC oil spill was concentrated from August 13 to 21 for the vast majority of the sampling. Forty-six stations were occupied from the U.S. Coast Guard cutter HESTHIND and the Greenland research vessel ADOLF JENSEN. The locations of these stations are presented in Table 3-1 and Figures 3-1 to 3-4. Also noted in Table 3-1 are the sampling programs undertaken at each station. These sampling stations were the basis for the physical, chemical, and biological studies conducted by the NOAA and Danish scientists.

In support of the physical studies, 11 temperature provides were obtained to depths of 450 m using expendable bathythermographs (XBTs), eight stations collected hydrographic temperature and salinity data using Nansen bottles and reversing thermometers, and, at two stations, expendable current measuring probes were deployed. The physical programs were undertaken to determine the movement of the oil and are contained in Chapter 4.

Thirteen surface oil samples were collected for studies on the meathering of the surface oil. Aliquots of these samples were analyzed as part of the NOAA and Danish programs and are discussed in Chapter 5.

To ascertain the impact of microbiological degradation of the spilled oil, cultures were grown on various substrates from samples collected at five stations by Danish scientists. The results of these studies are contained in Chapter 6.

Water samples were collected at 18 stations to determine how much oil was accommodated into the water column. More than 56 samples at depths down to 30 m were obtained. The NOAA team collected their samples using a Niskin sterile bag sampler while the Danish team collected their samples with a 1.0 l diass bottle lowered in an stainless steel frame. These bottles were fitted with a teflon-lined cap unich was pierced by a spike when a messenger was dropped, allowing the bottle to be filled.

The boutles were not resealed before being brought back through the surface. Except for two reference stations acquired on the return to Thule by

| Date | Time | Vessel* | Station | Latitude | Longitude | Map | Р | rog | ram | su | рро | rted* | ** | Comments |
|----------|------|---------|---------|-----------|-----------|------|---|-----|-----|------|-----|-------|----|--------------------|
| 1977 | GMT | | | N | W | fig. | X | Н | С | 0 | М | W | Z | |
| 10 Aug | | w | W-1 | 75° 02' | 60° 50' | 4 | | | | 0 | | | | |
| 12 Aug | | W | W-2 | 75° 06' | 61° 43' | 4 | | | | 0 | | | | |
| 13 Aug | 1130 | AJ | 5460 | 74° 53' | 61° 10' | 3,4 | | Н | | | | D | Z | Stramin & Hensen |
| | 2300 | AJ | 5461 | 75° 10' | 61° 23' | 3,4 | | н | | 0 | М | D | Z | Stramin & Hensen |
| 14 Aug | 1400 | AJ | 5462 | 75° 25' | 61° 44' | 3,4 | | | | 0 | М | D | | |
| 15 Aug | 2300 | AJ | 5463 | 75° 12' | 61° 23' | 3,4 | | | | 0 | | | | |
| 16 Aug | 1123 | AJ | 5464 | 75° 12' | 61° 30' | 3,4 | | | | 0 | | | Z | Stramin & Hensen |
| 1753 | 1155 | W | X-30 | 75° 13' | . 61° 24′ | 4 | Х | | | | | | | |
| 17 Aug | 0007 | W | X-31 | 75° 14' | 61° 26' | 4 | х | | | | | | | |
| | 0607 | W | X-32 | 75° 14' | 61° 05' | 4 | Х | | | | | | | |
| | 1215 | W | X-32 | 75° 14' | 61° 05' | 4 | Х | | | | | | | |
| | 1310 | AJ | 5465 | 75° 10' | 60° 38' | 3,4 | | | | | | | Z | Midwater Trawl |
| | 2100 | AJ | 5466 | 75° 20' | 61° 12′ | 3,4 | | Н | | 0 | | N,D | | |
| 18 Aug | 0009 | W | X-34 | 75° 21' | 61° 05' | 1 | х | | | | | | | |
| 1050 | 0300 | AJ | 5467 | 75° 34' | 61° 09' | 3,4 | | | | 0 | М | N,D | | |
| | 0634 | W | X-35 | 75° 21' | 61° 12' | 4 | Х | | | | | 73 | | |
| | 1205 | W | X-36 | 75° 20' | 61° 10' | 4 | Х | | | | | | | |
| | 1700 | W | 1 | 75° 30' | 61° 02' | 2,4 | Х | H | | | | | | |
| | 1900 | 'AJ | 5468 | 75° 42' | 60° 15' | 3 | | H | | | М | N,D | | |
| | 2100 | W | 2 | 75° 23' | 61° 53' | 2,4 | Х | Н | | | | | | |
| 19 Aug | 0500 | W | 3 | 75° 14' | 61° 10' | 2,4 | х | H | | | | D | Z | Stramin & Hensen |
| | 1448 | AJ | 5469 | 75° 44' | 61° 35' | 3 | | Н | | | | N,D | Z | Stramin & Hensen |
| | 1600 | W | B-1 | 75° 15' | 61° 15' | 4 | | | | | | | Z | Bongo 10,15,20 m |
| | 1700 | W | B-2 | 75° 15' | 61° 15' | 4 | | | | 0 | | | Z | Bongo 5,10,15,20 π |
| | 1830 | AJ | 5470 | 75° 35' | 61° 24' | 3 | | H | | 15.0 | | N,D | Z | Stramin & Hensen |
| 20 Aug | 0540 | W | WW-1 | 75° 16.5' | 61° 20' | 3 | | | | | | | Z | Neuston |
| - | 0635 | W | WW-2 | 75° 17.5' | 61° 15' | 3 | | | | | | | Z | Neuston |
| | 0723 | W | WW-3 | 75° 18.5' | 61° 12.5' | 3 | | | | | | | 7. | Neuston |

Table 3-1. Scientific stations occupied during POTOMAC oil spill

| Date | Time | Vessel* | Station | Lat | itude | Long | itude | Map | P | rog | ram | su | рро | rted* | * | Comments |
|-------------------------------------|----------|------------|------------|--------|---------|-------|-------|---------|------|-----|------|----|-----|-------|------|--|
| 1977 | GMT | | | 1 | N | ī | W | fig. | | - | С | | | | Z | |
| 0 Aug | 0748 | W | WW-4 | 75° | 19.5' | 61° | 10.5' | 3 | | | | | | | Z | Neuston |
| 1999 - A. 1997 199 9 94. | 0827 | W | WW-5 | 75° | 20.5' | 61° | 14' | 3 | | | | | | | Z | Neuston |
| | 0850 | AJ | 5471 | 75° | 26' | 61° | 10' | | | H | | 0 | | N,D | Z | Stramin & Hensen |
| | 0945 | W | WW-6 | 75° | 22.5' | 61° | 04 ' | 3 | | | | | | | Z | Neuston |
| | 1045 | W | WW-7 | | 18.5' | 61° | 19' | 3 | | | | | | | Z | Neuston |
| | 1129 | W | WW-8 | 75° | | 61° | 17' | 3 | | | | | | | Z | Neuston |
| | 1200 | H | Α | 75° | 22' | 60° | 30' | 1,3 | | | С | | | | | Bad probe |
| | 1300 | н | В | | 15' | 61° | 00' | 1,3 | | | С | | | | | |
| | 2130 | AJ | 5473 | 75° | 16' | 61° | 15 | 2,3 | | | | 0 | | N,D | | Intercomparison |
| 1 Aug | 1300 | AJ | 5374 | 75° | 15' | 61° | 10' | 2,3 | | | | | М | D | | oil waste backgrou |
| | 0843 | W | WW-9 | 75° | 26' | 62° | 52' | 2 | | | | | | | Z | Neuston |
| | 1600 | AJ | 5475 | 74° | 55' | 60° | 12' | 2 | | | | 0 | Μ | D | | |
| | 1253 | W | WW-10 | 75° | 45' | 65° | 50' | 2 | Х | | | | | N | | Neuston |
| | 2200 | AJ | 5476 | 74° | 39 ' | 59° | 10' | 3 | | | | | | D | | |
| | 1600 | W | WW-11 | 75° | 53' | 67° | 58' | 2 | | | | | | N | Z | Neuston - |
| | | | | | | | | | | | | | | | | Reference station west of Cape York |
| 2 Aug | 0100 | AJ | 5477 | 74° | 211 | 500 | 37' | 3 | | Н | | | | р | Z | Stramin & Hensen |
| 2 Mug | 0100 | AJ | 5477 | /4 | 21 | 50 | 57 | 5 | | п | | | | D | L | Reference station |
| 8 Sept | | Local | | 75° | 2 | 61° | 2 | | | | | 0 | | | | Reference Station |
| 1 Oct | | Local | | 75° | | 61° | | | | | | 0 | | | | |
| I ULL | | LOCAL | | 15 | | UI | • | | | | | U | | | | |
| W= West | wind | AJ = Ado | lf Jensen | H | = Helid | opter | Loc | cal = (| 2011 | ect | ed | hv | 100 | al h | inte | rs |
| | | | | | | • | | | | | - uu | 25 | 100 | | | |
| *Progra | | | | | | | | | | | | | | | | |
| | | e Bathythe | | +1) | | | | | | | | | | | | |
| | | easurement | Nansen bot | ties) | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | | il sample | | | | | | | | | | | | | | |
| | crobiol | | NOAA | | and ch | | | | | | | | | | | |
| w - wa | ter samp | pres N. | -NOAA | D - Da | anisn | | × | | | | | | | | | |

Table 3-1. Scientific stations occupied during POTOMAC oil spill (Continued)



Figure 3-1. Locations of stations occupied by the WESTWIND. Areas where surface oil was found are indicated for three days.

the WESTWIND, all the water samples were acquired from either the ADOLF JENSEN or from her rubber dinghy a few hundred meters away to decrease the chance of contamination by waste discharges from the ADOLF JENSEN. The water samples were extracted using hexane as soon as possible after sampling (hours) and were independently analyzed using uv-fluorescence and gas chromatography-mass spectroscopy by both NOAA and Danish contractors. The results of these studies are presented in Chapter 7.

Zooplankton samples were collected using four different sampling devices at 22 stations. The NOAA team conducted if neuston tows with an 0.5 x 1.0 m frame fitted with a 0.505 mm mesh net. These tows each sampled 550 sq m of surface area. They also conducted two bongo tows with 61 cm frames fitted with 0.505 and .333 mm mesh nets. The first tow was for a distance of 0.96 km at 20, 15, and 10 m depth each, while the second sampled for 0.95 km at each depth of 20, 15, 10, and 5 m. The Danish team collected samples with a 2-m-diameter Stramin net fitted with a mesh of 500 threads/m and a Hensen net of 72 cm fitted with No. 3 silk mesh at each of their stations. The Stramin



Figure 3-2. Locations of stations occupied by the ADOLF JENSEN.



Figure 3-3. Detailed locations of NOAA and Danish stations in the area of highest oil concentration. See Table 3-1.

net performed oblique tows from 200 m depth for about 30 minutes at 1.5 kn speed, while the Hensen net was hauled vertically from 50 m at 0.33 m/s. The results of the species composition and contamination studies are contained in Chapter 8.

Limited observations on marine mammals (seals) and seabirds were made during the study period. Oiled skins of seals, shot later in the year by local Eskimo hunters, were made available to the Danish team for chemical analyses. These studies are presented in Chapter 9.

As with any ad hoc scientific response, not all the desired information was collected during the field program. In retrospect, there should have been more direct measurements of the surface currents using the current probes, and it would have been desirable to have conducted the zooplankton sampling to account properly for diurnal variability. Probably the most important data not collected were numerous samples of the subsurface oil for weathering studies. However, given the short notice before departure, it is probably significant that the sampling was as complete as it was.

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4.0 MOVEMENT OF THE OIL

To assist the On-scene-Coordinator and to assess ecological effects, it was necessary to determine and predict the movement of the spilled oil. This was done by both direct measurements and modeling. The horizontal advection of spilled oil is influenced by the general circulation or permanent currents upon which the local effects of wind stress and waves on the oil are superimposed. These local effects tend to move the oil independently of the surrounding water. The approach used was to determine separate contibutions for the three time scales of motion -- days for the permanent currents, hours for wind stress, and minutes for the wave interaction -- and then draw conclusions based on their relative magnitudes. Extensive use was made of a report by Muench (1971) and supporting data from U.S. Coast Guard icebreaker cruises in 1968, 1969, and 1970 (Muench et al., 1971; Moynihan and Muench, 1971; and Muench, 1972).

4.1 Circulation And General Climatology Of Baffin Bay

Baffin Bay is a semienclosed body of water with limited access to the Arctic Ocean to the north and to the Atlantic Ocean to the south through Davis Strait. The waters in the bay consist of four layers: a surface layer extending to a depth of about 5 to 10 m generated by ice melt, a cold subsurface layer (< 0 C) from 20 to 100 m deep generated from the mixing of Arctic water and Atlantic water, a deeper layer of warm water (> 0 C) from 150 to 400 m deep originating from the Atlantic, and a bottom layer of cold water (< 0 C) below 500 m.

The circulation of Melville Bay is dominated by the West Greenland Current, which flows to the north along the west coast of Greenland. This current appears to be driven primarily by runoff and ice melt as the climatological winds are not very strong. The current primarily is contained in the upper layer of the bay (down to 20 m).

4.2 Currents And Horizontal Advection Of The Oil

4.2.1 Geostrophic Currents

Historical data (Muench, 1972) indicate that the predominant surface currents in Melville Bay are roughly parallel to the coast. In the area of the spill, the current is to the northwest, changing to west off Cape York. The geostrophic currents follow the contours of dynamic topography shown in Figure 4-1. Since these currents are based on isolated hudrographic stations acquired before 1971, the geostrophic currents were estimated during the spill from three hydrographic stations occupied on August 18 and 19 by the WESTWIND. At these stations, temperatures and salinities were measured with Nansen bottles and reversing thermometers at seven depths from the surface to 150 m. The locations of the stations are shown in Figure 3-4. The primary purpose of the stations was to define the density structure at the top and bottom of the subsurface Arctic water as an aid in predicting the location of the pil in the water column in the event the oil sank. Thus the acquired data did not adequately define the major density structure at the surface required for geostrophic calculations. Additional levels were interpolated for, based on the temperature-salinity relationship derived from the Nansen casts and the temperature structure derived from XBTs at each station. The density structure was found to be nearly constant below 40 m (Figure 4-2), in accord with historical data, and the surface currents were computed relative to a depth of 40 m. The calculations indicated a westerly flow (260°T) at 3 cm/s, which is only a crude estimate because of the interpolation used to supplement the Nansen data and the lack of sunopticity. The error bounds for the speed were estimated to be -3 to +5 cm/s and +/- 90 degrees for direction. Since the origin of the lighter surface water is ice melt, the derived current is consistent with the greater concentration of ice near the shore.

Several hydrographic stations were occupied by the Danish researchers from the ADOLF JENSEN, but simultaneous XBT data were not available to allow interpolation of the required additional levels to define the density structure. Also, all but one of the ADOLF JENSEN stations were more than 30 nmi from the area of the spill or were separated in time by more than 36 hours from the WESTWIND stations. The one comparable station (Station 5466) was consistent with the three WESTWIND stations.



Figure 4-1 Dynamic topography of the surface with respect to 1,500 decibars (from Barnes, 1941). Contour interval is 0.05 dynamic meters (from Muench, 1972).



Figure 4-2. Vertical density distribution at three hydrographic stations.

Nine additional XBT stations in the area indicated that the top of the subsurface Arctic water (0 C isotherm) was between 10 and 30 m deep. However, as the sensity at temperatures near 0 C are dominated by salinity effects, these XBT data did not yield any further information for estimating the geostrophic current.

4.2.2 Direct Measurements

On August 20, an attempt was made to measure surface currents directly with three Richardson current probes deployed from a helicopter. Only one was partially successful; the other two failed to release any subsurface floats. From the single float released from the one partially successful probe, the surface current was computed to be approximately 8 cm/s in a southwesterly direction (220°T). This current would correspond to the currents at 1 m depth and is relative to the net transport of the entire water column. Based on measurements of the elongation of the dye patches caused primarily by Stokes drift and only slightly by windage, the uppermost surface waters (5 cm) were calculated to be moving at 2 cm/s relative to the water at a depth of 1 m and at a right angle to it (125°T).

4.2.3 Wind Stress Currents

A second method for assessing the magnitude of the surface currents is to model the currents from wind observations. The wind model indicates that the wind driven surface currents were directly downwind with a speed of about 3 percent of the wind speed. Wind observations were made on the WESTWIND at 6-hour intervals while the ship was in the vicinity of the spill. These wind data and visual estimates of wave heights are contained in Mattson and Grose (1978).

Figure 4-3 shows the wind runs for the two periods when the WESTWIND was



Figure 4-3. Wind runs for 10-12 and 15-19 August. The nominal position is 75°15'N, 61°W.

at the scene of the spill. From these runs, one can model that the oil would have moved only 12 nmi in a nortwesterly direction (340°T) from August 10 to 12 and about 12 nmi in a southwesterly direction (120°T) from August 15 to 19. Oil locations for August 15 and 17 (Figure 3-4) indicate a net drift of 4 nmi to the northwest (310°T), and (for this time period) the model predicts a drift of 2 nmi to the south (160°T) at an average speed of 2 cm/s. From this difference between the slick locations and the wind model results, one can infer a general circulation of 6 cm/s in a northwesterly direction (320°T).

4.2.4 Summary of Currents

Estimates of the three time scales that contribute to the local surface current are as follows:

1-General circulation.

a-Historical values of less than 29 cm/s to the west.

b-Geostropic currents of 3 cm/s to the west (260°T) measured realtive to 40 m depth.

c-Inferred currents from the wind model of 6 cm/s to the northwest (320°T)

2-Surface currents at 1 m.

a-Current of 8 cm/s to the southwest (217°T) measured with Richardson probe.

b-Average currents of 2 cm/s from wind stress in various directions.

3-Surface currents at 5 cm (measured Stokes drift of 2 cm/s).

4.2.5 Horizontal Advection of Oil

Large errors, on the order of a factor of 2, are associated with all the measurements described above. However, there is no doubt that the surface currents are of small magnitude. The two shorter time scales probably contribute less than 5 cm/s and tend to average to 0 because of the random directions. The long-scale motions appear to be westerly at about 5 cm/s, which indicate that the oil was not transported far from the site of the spill, i.e., less than 40 nmi over a 2-week period.

The elongated slick pattern was probably caused by spillage over a period of time (1-hr duration at 8 km = 8 mmi length). Once generated, this pattern was then advected by local currents in random directions, depending primarily on winds with a net set to the northwest from the permanent currents. Oil observed in neuston tows northwest of the main spill site during the return to Thule on August 20 probably stemmed from continued leakage by the USNS POTOMAC as she made her way to the same port via the same route, because the observed currents were not strong enough to have carried the principlal spill that far. Advection of the oil by the surface currents did, however, allow a large surface area to be exposed to the oil at one time or another. The exposed area 2 weeks after the spill was estimated at 500 sq mi based on oil locations

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4.3 Physical Observations

Shortly after the spill, the oil was reported to be in the form of small pancakes 10 to 25 cm in diameter and 0.5 cm thick, which were organized in windrows about 3 m wide presumably from wind-induced Langmuir circulation. Sheen, a visible but thin slick, was seen emanating from these pancakes, and major concentrations were easy to spot from the air. By August 19, 14 days after the spill, the oil was no longer noticeable from the air. Vessels at the site still reported some pancakes 1 to 13 cm in diameter on the surface, in streamers or rows several hundred meters long and about 70 m wide. Less than I percent of the surface in these windrows, however, was covered with oil. One windrow observed on August 20 was estimated to contain less than 350 gal in an area of 4,000 sq m. Eighty percent of the pancakes no longer were surrounded by sheen, and more than 95 percent of the area of the individual pancakes was submerged. Many pieces the size and shape of cornflakes were observed at the water surface and in the water column. On the previous day, a large number of subsurface flakes were also reported. By this time the surface oil had become spongy in texture, but it was not undergoing water-in-oil emulsification or "mousse" formation. Even after several days of weathering, less than 5 percent water was found in the surface oil after it had been heated to 80 C.

The spilled oil did not reach shore during the spill response. Icebergs in the vicinity of the spill were examined by the U.S. Coast Guard to see if oil was adhering to them. It was noted that the oil stayed away from the icebergs probably because they were actively melting.

Over the next 8 months, isolated reports of oil sightings and samples were received from biologists on expeditions (E. Born and T. Kristensen, personal communication to H. Petersen, 1978) and from local hunters. One oil sample (October 1) was confirmed as coming from the POTOMAC and some of the seal skins (Chapter 9) may have been contaminated by POTOMAC oil; whether this contamination occurred locally where captured or during their passage through Melville Bay is unknown. Oil clumps or tarballs were also reported to have been taken in seal nets north of Thule at Moriussaq (Figure 9-1) during the Autumn of 1977 and during April or May of 1978. A Greenlander hunting polar

bear in Melville Bay (southeast of Savigsivik) reported oil above and below the sea ice. This hunter noted that the oil was coming up through cracks in the ice.

With the exceptions noted, none of these reports were confirmed as coming from the POTOMAC spill by chemical analysis because the Greenlanders did not collect samples. However, for lack of another source, they may very likely have come from this spill. While the evidence (next section) strongly indicates that most of the oil sank, it is apparent that at least some of the oil remained in the sea surface and may have been advected to distant places over the next iew months.

4.4 Vertical Movement.

The initial specific gravity (s.g.) of the spilled oil was 0.976 which was a blend of 55 percent pitch with a s.g. of 1.054 and 45 percent cutter stock with a s.g. of 0.883. As the cutter stock lost its light fractions through evaporation, the s.g. of the remaining oil increased. A computation based on the percent n-alkanes remaining (54 percent) in a surface sample acquired on August 18 and the density of the original outter stock (0.883) indicated that, after 13 days of weathering, the s.g. had increased to 1.002. On this date small flakes of oil were observed beneath the sea surface. The water column in the area can be considered a two layer fluid system as seen in Figure 4-2 with the top layer being 10 to 20 m thick. The s.g. of the two layers were 1.023 and 1.027 respectively. The s.g. of the bulk weathered oil (1.002) indicates that it should still have been floating and indeed it was sampled from the surface. It is hypothesized that the skin of the oil pancakes was even more depleted in light fractions and, through an exfoliation process not fully understood, separated from the pancakes in flakes and sank because the s.g. was greater than 1.023. Calculations similiar to those mentioned above indicate that when 73 percent of the cutter stock had evaporated, the residue blend would have a s.g. of 1.023 and would start to sink. It cannot be assumed that the s.g. stopped increasing (because weathering stopped) as soon as the oil sank below the surface; chemical analusis of the one subsurface (bongo) sample (Chapter 5.2.2) indicated that weathering in fact increased through dissolution of the sparingly couple aromatic fractions. It is believed that a great amount of the weathered oil

(67 percent of the 107,000 gallons spilled) eventually sank to the bottom in the area where the spill was observed. Below 20 m, sinking whould have been accelerated by the greater compressibility of the oil compared with the water and by the nearly uniform density of the lower layer. Historical geostrophic current data indicate that the velocities are low (2 percent of the surface currents) in this deeper layer which actually consists of three water masses as noted earlier. Thus once the oil had sunk below 20 m, it would not tend to move horizontally during the several weeks that it would take co reach che bottom about 1000 m below. At a mean fall velocity of 1 cm/min, it would take less than 50 days for the oil to reach the bottom in most areas of Melville Bay.

4.5 Summary Of Oil Movement

The spilled oil was transported on the sea surface by variable winds and > slow circulation to the west or northwest. The variable winds probably caused little or no net movement while the slow circulation transported the oil a maximum distance of 40 nmi. The surface oil impacted approximately 500 sq mi of Melville Bay, and a small plume was left in the wake of the POTOMAC from continued light leakage while she proceeded to Thula. After sufficient evaporation of the cutter stock (about 33 percent of the total volume), it is expected that a great amount of the residue sank in the form of melville Lau. The water depth in the area of the spill was about 1,000 m and the detrital residue was scattered over a large area (~500 sq mi). It is expected that this petroleum detritus will remain indefinitely in the bottom sediments,

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5.0 WEATHERING OF SURFACE OIL

Both the Danish and the NOAA teams analyzed a time-series of surface oil ("tar") samples (Table 5-1), with the objectives of determining the degradation rate and the ultimate fate of the spilled bunker fuel, Bunker fuel is usually a very heavy material and in this case the fuel was comprised of a blend of 55 percent pitch (s.g. = 1.054) and 45 percent "cutter stock" (s.g. = 0.883). The pitch originates from the residuum of the refinery distillation process and would not be usable as ship fuel in its unblended form. Cutter stock is added to the pitch in order to reduce the viscosity of the blend sufficiently to allow it to be pumped, after heating, from the ship's fuel tanks to the burning orifices. Cutter stock can originate anywhere in the refining process and would normally be a distillate material, exhibiting complete volatilization over a discrete temperature range. In the case of the POTOMAC's spilled fuel, the cutter stock volatilzed completely over a temperature range of 154 C to 388 C, as shown in Figure 5-1. Because of its distillate nature, the cutter stock component of the Bunker fuel will evaporate, partially or entirely, on exposure to natural weathering processes at the sea surface. In measuring this process for the POTOMAC spill, both teams employed a combination of gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) in their efforts to address the following questions, among others:

1-How did the composition and density of the surface oil vary with time?

- 2-Did the low temperature and calm sea state produce slower evaporation than one would expect in temperate zones and rougher seas?
- 3-What was the "cutoff point" for the evaporative process in terms of relative vapor pressures or boiling points, e.g., did n-alkanes with boiling points of up to 250 C exhibit measurable evaporative losses? 300 C? 350 C?
- 4-Did dissolution of the low molecular weight aromatics occur at a measurable rate? Could it be distinguished from evaporation if losses
| Date 1977 | Time GMT | Station No. | Latitude N | Longitude W | Comments | |
|--------------|-------------|----------------|---------------|----------------|---------------------------------------|--|
| 7 Aug | | | Th | ule | From holed bunker - (not spilled oil) | |
| | | Retain | | | From Exxon Refinery Aruba, V.I. | |
| 10 Aug | | Wl | 75° 02' | 60° 50' | Taken by WESTWIND personnel | |
| 12 Aug | | W2 | 75° 06' | 61° 43' | Taken by WESTWIND personnel | |
| 13 Aug | 2330 | 5461 | 75° 10' | 61° 23' | Pancakes, 25 cm diameter | |
| 14 Aug | 2000 | 5462 | 75° 25' | 61° 44' | 0il slick with concentrated pancakes | |
| 15 Aug | 2300 | 5463 | 75° 13' | 61° 23' | Pancakes, 15 cm diameter | |
| 16 Aug | 1130 | 5464 | 75° 12' | 61° 30' | Pancakes, 15 cm diameter | |
| 17 Aug | 2100 | 5466 | 75° 20' | 61° 12' | | |
| 18 Aug | 0300 | 5467 | 75° 34' | 61° 09' | | |
| 18 Aug | 2100 | WW | 75° 18' | 61° 16' | Collected from skimmer | |
| 20 Aug | 0635 | WW-2 | 75° 17' | 61° 15' | Collected from Neuston Tow #2 | |
| 21 Aug | 1600 | 5475 | 74° 56' | 60° 12' | Taken in an area with 2 cm flakes | |
| 18 Sept | | | 75°? | 60° ? | Taken by local people in Melville Bay | |
| 1 Oct | | | 75°? | 60°? | Taken by local people in Melville Bay | |

Table 5-1. Surface oil samples POTOMAC oil spill 5 August 1977



Figure 5-1. Distillation curve for the cutter stock of the Bunker-C fuel spilled from the USNS POTOMAC.

were observed?

5-Did microbial degradation take place to any noticeable extent? Could microbial degradation have occurred at all in this relatively "pristine" environment?

6-Did the oil sink? Where did it go?

The USNS POTOMAC oil spill studies did provide answers to most of these questions. In some instances the answers were surprising, and in all instances the answers were welcome and provided field confirmation of one or another model of oil spill weathering processes. This chapter describes both the Danish and the NOAR approaches to these questions.

5.1 Analytical Procedures

The NOAA team entered into a contract with Energy Resources Company, Inc. (ERCO) of Cambridge, Mass., for the analyses of its POTOMAC spill samples. The principal investigator on the ERCO contract was P. Boehm, and the coauthor of ERCO's report to NOAA was D. Feist. Greenland Fisheries Investigations had arranged with the Danish Water Quality Institute and the University of Gothenburg, Sweden, for the analyses of their oil samples.

ERCO used similar procedures in analyzing both the seawater extracts (Chapter 7) and the surface oil samples. The latter were analyzed by silica gel/alumina column chromatography, glass capillary gas chromatography, mass spectrometry, spectrofluorometry, and determination of asphaltene content. The silica gel/alumina column chromatography procedure was the same for both the surface oil and the seawater extract samples, except that 1.0 g of copper metal powder was layered on top of the columns used for the surface oil samples to remove elemental sulfur from the oil. The silica gel (7.5 g) /alumina (2.5 g) column was then eluted with 18 ml of hexane and 25 ml of benzene to yield saturated (f1) and unsaturated (f2) fractions of each oil and water sample. The fractions were evaporated by rotary evaporation and an aliquot was subsequently weighed on a Cahn electrobalance.

The column chromatography fractions were then characterized by glass capillary gas chromatography using a Hewlett Packard Model 5840A gas chromatograph equipped with a flame ionization detector and interfaced to a PDP-10 computer. Samples were analyzed on a 15 m SE-30 column, with temperature programed from 50 to 260 C at 3 C/min. Retention indexes (RI) of individual components of each fraction were calculated by comparing observed retention times with the retention times of n-alkanes in a standard mixture.

The Danish Water Quality Institute (Hansen, et al., 1978) employed both SCOT (Support Coated Open Tubular) and packed columns on a Hewlett Packard Model 5830A and 5840A gas chromatographs, respectively.

The SCOT column was 56 m long, packed with OV-101, and was temperature programed from 85 C to 275 C at 4 C/min. None of the surface oil samples analyzed by Danish researchers were fractionated prior to injection into the gas chromatograph.

Selected spilled oil aromatic fractions (f2) were analyzed by ERCO by GC/MS using a Hewlett Packard 5700A chromatograph interfaced to a 5980A mass spectrometer with an electron ionization source and a 5934A data system. The gas chromatograph was equipped with a 15 m SE-30 glass capillary column and was temperature programmed from 80 C to 250 C at 4 C/min. Mass chromatograms were reconstructed from mass fragments characteristic of particular compounds, and peaks were electronically in:egrated to yield absolute concentrations.

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Unfractionated surface slick and selected f2 column chromatography fractions also were characterized by ERCO using spectrofluorometry with a Farrand MK-1 spectrofluorometer equipped with corrected emission and excitation modules. Two types of spectra were obtained. Emission spectra from 280 to 480 nm, with excitation of the sample at 254 nm, were used for "matching" with the Bunker fuel carried by the POTOMAC (Jademac, 1977). Synchronous scans, from 250 to 500 nm emission wavelength and 225 to 475 nm excitation wavelength, were used to examine compositional changes in the fluorescent compounds of the oil (Wakeham, 1977). Sample concentrations used for the fluorescence spectra ranged from 3.1 mg/ml for synchronous scans to 20.0 mg/ml for emission scans.

The analytical procedures used by ERCO for the surface oil samples are shown in Figure 5-2.

Asphaltenes were determined by ERCO using ASTM Standard Method D893-69, except that hexane was substituted for pentane. One gram subsamples of oil were repetitively dissolved in 10 ml of hexane and centrifuged at a relative centrifugal force of 600 to 700 g's. Approximately 10 washes were required to completely remove the hexane-soluble components of the oil. The residual "asphaltene" was dried at 110 C and its final weight was expressed as a percentage of the initial weight of the oil.

The Gothenburg University (Ahnoff and Eklund, 1979) analyzed oil samples and surface water samples suspected of containing oil particles or films. Fluorescence spectra were recorded using an Aminco-Bowman SPF Spectrofluorometer. For the qualitative comparison of different samples, intensities at three wavelength combinations were measured, 230/340 nm, 270/360 nm, and 310/400 nm, respectively. The Bunker-C fuel and one surface oil sample were further investigated by mass fragmentography, employing glass capillary gas chromatography combined with a computerized mass spectrometer



Figure 5-2. Analytical scheme for the surface oil sample, used by ERCO for the NOAA sample.

(Varian Mat 112 - Spectrosystem 100 MS). Mass fragmentography was used to determine the concentrations of selected aromatic hydrocarbons. Due to the high sensitivity of the mass spectrometer when used in the nonscanning mode, the same technique could be used to analyze subsurface water samples. Technical details are contained in Chapter 7.2.1.2, as well as an example of a mass fragmentogram (Figure 7-7).

5.2 Results

5.2.1 The Reference Sample

A sample of the Bunker-C fuel carried by the USNS POTOMAC was supplied by EXXON from the originating refinery. Both groups used the ENGON sample as a standard. From this sample two fractions were prepared by ERCO; an fl containing the saturated hydrocarbons (alkanes) and an f2 containing naphthenoaromatic and aromatic hydrocarbons. These were analyzed by glass capillary gas chromatography. The chromatograms, shown in Figures 5-3 and 5-4, indicate that the fi fraction is dominated by a series of normal and branched alkanes from n-C11 to n-C30, with a maximum abundance at n-C16 and by a significant proportion of unresolved components with similiar boiling range and maximum detector response. The observed n-alkane composition is quite similiar to an analysis of Bunker-C oil published by Clark and Brown (1977).

The f2 fraction is dominated by an unreceived complex mixture (UCM) with only small relative proportions of resolved components. The major resolved components as determined by GC/MS are methyl- and dimethyl-naphthalenes, phenanthrene, and methyl and dimethyl phenanthranes.

A sample of the Bunker fuel from the damaged tank was collected by the Danish laison officer at Thule shortly after the POTOMAC arrived in port. Details of exactly how and where the sample was obtained within the tank are not clear. This "Thule sample" was analyzed by the Water Quality Institute and found NOT to compare with either the EXXON sample or the samples collected from the sea surface of Melville Bay. The difference in composition between the "Thule" and other oil samples may be due to weathering of the oil which remained in the tank during the transit from the spill site, which is unlikely, or, more probably, the oil sampled from the tank was a residue from a previous fuel carried in the tank which had coated the tank sides.



Figure 5-3.. Gas chromatogram of fl (saturate) fraction of the spilled fuel.



Figure 5-4. Gas chromatogram of f2 (aromatic) fraction of the spilled fuel.

5.2.2 Gas Chromatography of the Surface Oil Samples

The glass capillary gas chromatograms of the spilled oil samples are quite similiar, except for some variability in the relative abundance of the more volitle and soluble components. The abundance of the n-alkanes in the fi fraction for each spilled oil sample was normalized to that of n-C20, allowing one to compare relative changes in the chemical composition of the spilled oil



n-ALKANE CARBON NUMBER

Figure 5-5. Relative peak abundance of n-alkanes for spilled oil samples analyzed by ERCO.



Figure 5-6. Relative peak abundance of n-alkanes for spilled oil samples analyzed by Water Quality Institute.

samples over time under the assumption that the concentration of n-C20 was constant. Since the primary short term weathering mechanisms, evaporation and dissolution, preferentially deplete lower molecular weight compounds, normalization to a relatively high molecular weight compound is reasonable. A graphic representation of the n-alkane relative peak abundances for selected samples is given in Figures 5-5 (ERCO) and 5-6 (Water Quality Institute). The scatter of the points for n-alkanes less than n-C18 is much greater than for those components above n-C18 and shows a trend of depletion of lower molecular weight compounds as function of time. The observed depletion of the lower molecular weight n-alkanes with time is the result of selective evaporation and dissolution of the lower weight alkanes with vapor pressures greater (boiling points less) than that for n-C17. The cold surface temperature (3 to 4 C), light winds (1 to 3 m/s), and the relatively thick (ca. 6 mm) form of the pancakes should tend to slow evaporation rates relative to warm water spills, thus suggesting losses of only the lightest compounds. This was not the case, however, as Figures 5-5 and 5-6 indicate. In fact, n-alkanes with boiling points of up to 300 C (n-C17; boiling point = 303 C) showed measurable losses after 2 weeks of weathering (Figure 5-7).

The small amounts of resolved components in the gas chromatograms of the f2 fractions of the spilled oil samples made ERCO's quantification of individual components difficult by GC/MS, and mass chromatograms were reconstructed to quantify individual compounds. Absolute concentrations were calculated by normalization to an internal standard.

Five aromatic isomeric groups of compounds, methyl naphthalenes (M/E 142), dimethyl naphthalenes (M/E 192), phenanthrenes (M/E 178), methyl phenanthrenes (M/E 192), and dimethyl phenanthrenes (M/E 206) were quantified in the Bunker-C fuel and in the spilled oil samples collected on August 17 and 19. The results are shown in Figures 5-8, 5-9, and 5-10 and in Table 5-2. The August 18 surface sample (Figure 5-8) is depleted in methyl naphthalenes and dimethyl naphthalenes, as one would expect from the known relatively high vapor pressure and solubility of these compounds. Absolute concentrations of phenanthrenes and methyl phenanthrenes in the oil slick samples appeared to increase slightly with time. The evaporation and dissolution losses of the lower boiling compounds probably accounts for the apparent increase in the methyl phenanthrenes.

1 5-10





Figure 5-7. Selected gas chromatograms from surface oil samples analyzed by Water Quality Institute.

| M/E | Compound group | Concentrations (µg/mg oil) * | | | | | |
|------|------------------------|------------------------------|--------------------------------------|--------------------------------------|--|--|--|
| м/ E | Compound Broup | Reference fuel (01-32) | August 18 slick sample (01-23) | August 19 bongo sample (01-30) | | | |
| 142 | Methyl naphthalenes | 1.7 | 0.5 | 0.0 | | | |
| 156 | Dimethyl naphthalcnes | 6.1 | 3.2 | 0.9 | | | |
| 178 | Phenanthrenes | 1.7 | 1.7 | 1.7 | | | |
| 192 | Methyl phenanthrenes | 3.3 | 3.8 | 3.8 | | | |
| 206 | Dimethyl phenanthrenes | 3.5 | 5.6 | 4.9 | | | |

Table 5-2. Concentrations of naphthalenes and phenanthrenes in selected oil samples analyzed by ERCO.

* Concentrations reflect the sum of all isomers of the compound group.



Figure 5-8. GC/MS total ionization current for the Bunker-C fuel, f2 (aromatic) fraction. Labels refer to alkyl-napthalencs (N) and phenanthrenes (P).



Figure 5-9. GC/MS total ionization current for the August 18 surface sample, f? (aromatic) fraction.



Figure 5-10. GC/MS total ionization current for the August 19 subsurface sample, f2 (aromatic) fraction.

The bongo net sample of oil (Figure 5-10), collected on August 18 during a biological tow, shows similiar but more extensive loss of the methyl and dimethyl phenanthrenes. The n-alkane ratios from the f1 fraction gas chromatogram for this sample are similiar to those of the August 18 surface sample. Thus, the more extensive loss of the substituted naphthalenes in this sample is not explained by evaporation alone. Boehm and Feist suggest that, once broken into smaller particles and dispersed into the water column, the spilled oil weathered more rapidly than surface oil, primarily due to dissolution of the aromatic compounds.



Figure 5-11. Ratio of n-C17/pristane for the surface oil samples. (*) sample from October 1 --56 days after the spill.

Because microbial degradation of oil results in a depletion of n-alkanes relative to branched alkanes (Zobell, 1969), the ratios of n-C17/pristane and n-C18/phytane can be used to monitor biochemical degradation processes (Blumer and Secs, 1972). The n-C17/pristane ratio for the spilled oil samples shows statistically significant fluctuations but does not show a consistent trend with time. The Danish SCOT column data show the same consistency over almost 2 months. Both sets of data are shown in Figure 5-11. If biochemical degradation of the opilled oil was extensive, the n-C17/pristane ratio would show a significant decrease with time. The absence of microbial degradation of the oil over several weeks after the spill is consistent with slow initial microbial activity b.cause of the low water temperature and also because of the small surface area/volume ratio of the oil pancakes. Both of these factors inhibit large-scale microbial degradation. It is difficult to say how long the October 1 sample was actually exposed to a potentially degrading environment, as we do not know the precise circumstances of its collection. Suffice it to say, though, that no microbial degradation took place for the first 2 weeks after the spill, and it is probable that none took place for the initial 4 to 8 weeks. Further discussion of microbial biodegradation is contained in Chapter 6.



Vigure J-12. Synchronus fluorescence scan of POTOMAC fuel by ERCO.

| Sample | Concentration | Relative peak height * | | | | | |
|---------------|---------------|------------------------|----------------------------|---------------------|--|--|--|
| | (µg/ml) | 307-nm (2-ring) | 365-nm (3- and 4- ring) | 405-nm (>5-ring) | | | |
| Bunker C fuel | 2 8 | 102 | 100 | 83 | | | |
| 10 August | 3.9 | 98 | 100 | 83 | | | |
| 12 August | 3.3 | 102 | 100 | 82 | | | |
| 15 August | 3.2 | 107 | 100 | 78 | | | |
| 18 August | 3.5 | 105 | 100 | 77 | | | |
| 20 August | 3.4 | 114 | 100 | 76 | | | |

Table 5-3. Concentrations of two-, three-, four-, and five-ring aromatic compounds in selected spilled oil samples

* The analysis was done by measuring peak height maxima on a synchronous fluorescence scan from 250- to 500-nm emission with excitation at a wave-length 25 nm shorter.



Figure 5-13. Relationship between peak height and Bunker-C fuch concentration for synchronous fluorescence scans.

5.2.3 Spectrofluorometry, NOAA Samples

Unfractionated spilled oil samples were dissolved in cyclohexane (2 to 20 ug/ml) and characterized by emission and sunchronous fluorescence scans by ERCO as described earlier. As the spilled oil weathered, the emission scans showed a slight enhancement of the concentration of aromatics fluorescing at wavelengths shorter than the maximum emission and a diminuation of those fluorescing at longer wavelengths. This trend is consistent with weathering patterns observed by U.S. Coast Guard investigators in oils with an emisson maximum between 240 nm and 400 nm (Eastwood, 1977). The sunchronous scans (Figure 5-12) are considerably more detailed quantitatively thus providing more chemical information than single wavelength emission scans. One can theoretically discriminate between one-, two-, three-, four-, and five-ring aromatic compounds based on discrete fluorescence bands for each compound type (Lloud, 1971), Sunchronous fluorescence bands are 280 to 290 nm for benzenes, 310 to 330 nm for naphthalenes, 340 to 380 nm for three- and four-ring compounds, and >405 nm for five-ring compounds. The relation between peak height and the Bunker-C oil concentration is linear for the peaks corresponding to two-, three-, four-, and five-ring aromatic compounds over a concentration range of 0 to 4.0 µg/ml of oil (Figure 5-13).

The relative concentrations of three- and four-ring compounds and five-ring compounds appeared to decrease about 10 and 20 percent faster, respectively, than two-ring compounds over a period of 2 weeks (Table 5-3), a result which appears anomalous. This trend contradicts the observations by GC/MS (Table 5-2) and University of Gothenburg rivorescence analyses (Table 5-4) that two-ring aromatics (naphthalenes) decrease at a greater rate than three-, four-, and five-ring aromatics. In light of the observation that no biological degradation took place during the same time period (Figure 5-11), these synchronous scan fluorescence results cannot be explained away as being due to the formation and dissolution of polar-substituted three-, four-, and five-ring aromatics. Hence the quantitative aspects of synchronous scan fluorescence analyses must be considered suspect.

5.2.4 Spectrofluorometry and Mass Fragmentography of Danish Samples

Oil samples and surface water samples, found to contain oil in amounts indicating the presence of particles or films, were characterized by spectrofluorometry and mass fragmentography. Fluorescence intensities at the three wavelength combinations, 230/340 mn, 270/360 nm, and 310/400 nm, were compared with the reference oil. Complete agreement would yield relative intensities of 1.0, 1.0, and 1.0 respectively. The results are shown in Table 5-4.

| Sample | Re | lative intensition | es* |
|---------------|---------|--------------------|---------|
| | 230/340 | 270/360 | 310/400 |
| Bunker C fuel | 1.0 | 1.0 | 1.0 |
| 10 August | 0.92 | 0.99 | 1.0 |
| 13 August | 0.87 | 0.96 | 1.0 |
| 14 August | 0.75 | 0.99 | 1.0 |
| 18 August | 0.83 | 1.0 | 0.99 |
| 20 August** | 0.74 | 1.0 | 0.96 |

Table 5-4. Characterization by spectrofluorometry of surface samples analyzed by the University of Gothenburg.

* Intensities are given relative to the Bunker C fuel and are normalized so that the highest value of the three is set to unity.

** See also Figure 5-14.

A typical set of spectra is shown in Figure 5-14. While intensities at the longer wavelengths stayed almost constant during the 15 days of weathering, a gradual decrease down to about 0.75 relative intensity is seen at the shortest wavelength combination of 230/240 nm. This is interpreted as a loss of the low molecular weight components and is in accord with the more specific mass fragmentographic analyses carried out on the reference fuel and one surface oil sample collected on August 10. Ten aromatic isomeric groups of compounds were quantitated. The concentrations found in the two analyzed samples are listed in Table 5-5. A comparison of these two samples is shown graphically in Figure 5-15. It is seen that, while the concentrations of dimethyl naphthalenes (M/E 156) and lower compounds have decreased, the concentrations of all other groups lie very near those in the Bunker-C fuel.



Figure 5-14. Excitation and emission spectra of a surface oil sample collected at Station 5473 on August 20 generated by University of Gothenburg. Intensities at 230/340 nm, 270/360 nm and 310/400 nm were used for qualitative comparison of the different samples.

A good fit between a spill sample and a reference oil can be taken as a strong indication of the origin of the spilled oil as has been shown by Grahl-Nielsen (1976) in connection with another spill incident.

| Table 5-5. | Concentrations of naphthalenes, phenanthrenes, and |
|------------|--|
| | dibenzothiophenes in two oil samples analyzed by the |
| | University of Gothenburg. |

| | | Concentrations (µg/mg oil) | | | | |
|-----|----------------------------|----------------------------|-----------------------------|--|--|--|
| M/E | Total ** | Reference fuel | August 10 slick sample * | | | |
| 128 | Naphthalene | 0.44 | 0.085 | | | |
| 142 | Methyl naphthalenes | 0.90 | 0.20 | | | |
| 156 | Dimethyl naphthalenes | 2.90 | 0.90 | | | |
| 170 | Trimethyl naphthalenes | 1.30 | 1.25 | | | |
| 178 | Phenanthrene | 0.28 | 0.25 | | | |
| 184 | Methyl phenanthrenes | 0.51 | 0.48 | | | |
| 192 | Dimethyl phenanthrenes | 0.80 | 0.80 | | | |
| 198 | Dibenzothiophene | 0.20 | 0.21 | | | |
| 206 | Methyl dibenzothiophenes | 0.55 | 0.50 | | | |
| 212 | Dimethyl dibenzothiophenes | 0.65 | 0.60 | | | |
| | Total ** | 8.09 | 5.19 | | | |
| | % | 0.81 | 0.52 | | | |

* Concentrations are not corrected for a few percent of water present in this sample

** Naphthalene excluded

5.2.5 Asphaltenes

Asphaltenes were measured gravimetrically as the hexane-insoluble fraction of the oil by ERCO. In contrast to shipboard estimates of asphaltenes made by the SOR Team, the laboratory data show no consistent changes over time. A slight decrease in the percentage of asphaltenes from 15 to 13.9 percent after 7 days followed by a gradual increase to 15.5 percent after 16 days were noted (Figure 5-15). No major changes in the asphaltene content are suggested by the data. Asphaltenes would not be expected to separate out by gravity settling since their density is approximately 1.0 and their surface activity tends to keep them dispersed in the oil (Milgram, 1977).



Figure 5-15. Comparison of concentrations of selected aromatic hydrocarbons in the surface oil sample collected August 10 with the POTOMAC Bunker-C fuel. Horizontal axis is molecular weight. Vertical axis is the ratio of the sample to the Bunker-C fuel in percent.



Figure 5-16. Change in asphaltene content of surface oil samples as a function of time.

5.3 Summary Fo, Weathering Of Surface Oil

Gas chromatography, mass spectrometry, and spectrofluorometry have been used to fingerprint and to investigate chemical changes in the spilled oil samples. Both gas chromatography and spectrofluorometry confirmed that all of the samples consisted of oil carried by the POTOMAC.

The primary weathering mechanisms for the first 2 weeks are evaporation and dissolution. N-alkanes with boiling points less than that of n-C17, and substituted naphthalenes, are depleted by 50 to 100 percent after 15 days of weathering. Dissolution may play a significant role in weathering once the oil is dispersed in the water column; a subsurface sample collected from a bongo net contained significantly smaller amounts of methyl and dimethyl naphthalenes than did a surface slick sample collected at aproximately the same time that contained similar amounts of n-alkanes with boiling points similar to those of the alkyl naphthalenes.

The synchronous scan fluorescence data on the NOAA samples failed to corroberate the GC/MS and single wavelength fluorescence data and hence the quantitative aspects of this analysis method must be considered suspect.

Microbial degradation of the oil appears to proceed slowly, if at all, since the n-C17/pristane ratio varied only slightly with time. There seems to have been no significant change in the asphaltene content of the oil samples 15 days after the spill. Asphaltenes did not appear to have been preferentially settling from the spilled oil. The tar flakes observed to be settling in the water column may have been "sloughing off" of the highly weathered "skin" that is known to form at the air-oil interface of thick lenses of oil (pancakes).

6.0 MICROBIOLOGICAL STUDIES

Sterile water samples were collected by the Danish team and sent to the Water Quality Institute where microbiological studies were undertaken to determine the presence of oil degrading microorganisms at the spill site and their effect on the spilled Bunker-C fuel. Three studies were completed. The first was to determine which microorganisms were present in the area and whether their abundance was increased by the spilled oil. The second study was to determine the rate of degradation of oil by the natural culture found at the site while the third was to study the rate of degradation for each component of the natural culture.

6.1 Counting And Identification Of Microorganisms

Surface water samples collected in the spill area on August 14 and 21 were used as the basis of this study. The sampling procedure is described in Chapter 3. While it was realized that the lag time for growth of cil degrading microorganisms would not be completed during the 1-week interval, an attempt was made to determine whether or not the natural populations were enhanced by the spilled oil. Five different counting techniques were used to measure the abundance of microorganisms and several tests were performed on each sample to isolate and identify the oil degrading microorganisms.

6.1.1 Analytical Procedures

6.1.1.1 Total Count on Agar Plates

Total counts were measured by culturing the water samples on marine agar (Difco Bacto marine agar 2216). The composition of this substrate is given in the Appendix. Sterile physiological sodium chloride solution (9 g NaCl disolved in 1 l of water) was used for the preparations of the dilutions of the seawater samples. I mi of the diluted samples was transferred to sterile petri dishes; then liquid marine agar, cooled to 45 C, was added to each dish and incubated for 7 days at 20 C.

6.1.1.2 Yeast and Fungi on Agar Plates

Counts of yeast and fungi were performed using marine agar as the substrate. Bacteria were inhibited by the addition of Streptomycine and Tetracycline (both at equal concentrations of 50 ug/ml) and the pH was adjusted to 5.0. The substrate and incubation were identical to that used for the Total Count described above.

6.1.1.3 Oil Degrading Bacteria on Agar Plates

Counts of oil degrading bacteria were measured on Colwell's MPN-medium solidified by the addition of 1.5 percent agar. Colwell's medium was modified by reduction of the amount of MgSO4,7H2O to avoid precipitation of phosphate. The composition of the actual substrate used is contained in the Appendix. Shell Vitrea oil 27 was used as the single carbon source for these cultures (0.5 percent on a volumetric basis). Shell Vitrea oil 27 is free from detergents and has a composition of 70 percent alkanes, 24 percent cycloalkanes, and 6 percent aromatics. A special technique as described by Baruah et al. (1967) was used to insure that the oil was homogeneously incorporated into the substrate. This technique called for dissolving 5 g of the oil in 15 ml of ethyl ether and then carefully mixing with 5 g of silica (Cab-O-Sil) in a morter. The ether was then evaporated in a rotary evaporator and the remaining powder (silica and oil) was easily distributed homogeneously on the substrate. Fungizone (at the rate of 10 µg/ml) was added to suppress ueast and fungi growth. Base agar (without the oil) was produced and used as control. Both oiled and unoiled plates were incubated at 20 C and counted after 14 and 28 days.

6.1.1.4 Oil Degrading Yeast and Fungi on Agar Plates

Counts of oil degrading yeast and fungi were made using the same substrate as for bacteria described above except that streptomycine and tetracycline (50 µg/ml each) were added to inhibit the bacteria and the pH was adjusted to 5.0. As with the bacteria counts, Shell Vitrea oil 27 was added as the single source (0.5 percent by volume) and incubation was at 20 C. Counts were made after 14 and 28 days.

6.1.1.5 Oil Degrading Microorganisms by Most Probable Numbers Counts of Oil degrading microorganisms by Most Probable Numbers (MPN method) were made using two mediums. The two mediums are described by Bunch and Harland (1976) and Mills, Brezil, and Colwell (1978) and are contained in the Appendix. The amount of MgSO4, H2O in Colwell's medium was reduced as mentioned earlier. Portions of these mediums (5 ml) were distributed into screw cap tubes. After sterilization, 50 ul of oil (Shell Vitrea oil 27) or paraffins were added to each tube. The substrates were tested by the following petroleum degrading microorganisms: Nocardia, Pseudomonas, Arthrobacter, Streptomyces, Graphilum, Pentamyces, and Candida. Both were found to be suitable for MPN investigations. Of the two, the Colwell medium was preferred. In all the MPN investigations, triplicate tubes were placed in a rotary shaker at 100 rpm during incubation at 15 C. The tubes were read weekly for six weeks.

6.1.2 Identification of Isolated Oil Degrading Bacteria

Qualitative examinations of the isolated bacteria were carried out for identification using the following tests: Haemolysis, pigmentation, cytochrome oxydase, catalase, tween 20, tween 80, gelatine, O/F test, Simmon's citrate, motility (S.I.M.), indole (S.I.M.), H2S (S.I.M.), 1 percent tryptone, 1 percent tryptone with 4 percent NaCl, 1 percent tryptone with 7 percent NaCl, V.P. broth, arginine, lysine, urea, nitrate, arabinose, cellobiose, lactose, sucrose, glycerol, starch, xylose, chitin, veal infusion broth with 1 percent NaCl at 5 C, 10 C, 15 C, and 30 C, antibiotica test (ptevidine), and gram staining. All the reactions were read daily over a period of 1 to 7 days. Unless stated above, all the incubation temperatures were at 20 C.

6.1.3 Results

The results from the microbiological examinations are presented in Table 6-1 for all five counting methods. In all cases and for all samples the observed counts are small. The concentrations of oil degrading microorganisms estimated by the MPN method are less than 1500 per liter, which corresponds to less than 1 percent of the total count.

As indicated by the values from Station 5474, the total count as well as the numbers of oil degrading bacteria do not appear to be a function of depth.

| | | | | | | Salahan and a | |
|---------|----------|-------------------------------|----------------|--|--|--|---------------------------------------|
| Station | Depth | Date of collec- tion | Total count | Number of oil degrading micro- organisms | Number of oil degrading bacteria on agar | Number of oil degrading yeast and fungi on | Numbe bacte on b aga plat |
| | | | | (MPN-method) | plates | agar plates | _ |
| no. | <u>n</u> | day/mo. | per ml | per liter | per liter | per liter | per 1 |
| 5462 | 0.0 | 14/8 | 50 | < 300 | < 5 < 5 | < 5 | < |
| 5462 | 0.0 | 14/8 | 2 | < 300 | < 5 | < 5 | < |
| 5466 | * | 17/8 | 560 | 700 | 85 | ** | |
| 5468 | 0.1 | 18/8 | 5 | < 300 | 30 | < 5 | |
| 5474 | 0.0 | 21/8 | 4 | < 300 | < 5 | < 5 | < |
| 5474 | 0.2 | 21/8 | 2200 | < 300 | < 5 | < 5 | |
| 5474 | 1 | 21/8 | 370 | 700 | 10 | < 5 | |
| 5474 | 3 | 21/8 | 3700 | < 300 | 5 | < 5 | |
| 5474 | 5 | 21/8 | 240 | < 300 | < 5 | 10 | < |
| 5474 | 10 | 21/8 | 10 | 1500 | < 5 | 5 | |
| 5474 | 30 | 21/8 | 2300 | 1500 | 205 | 15 | 3 |
| 5475 | 0.0 | 21/8 | 14 | 400 | 30 | ** | |
| | | | | | | | |

Table 6-1. Results of enumerations from microbiological examinations of water samples.

* Water surface with visible layer of oil

** No examination

The number of oil degrading bacteria on oiled agar plates was the same order of magnitude as the number of bacteria on the unoiled plates. This result corresponds to other studies conducted on water samples collected fro Greenland waters and indicates that the MPN method must be preferred to the

· agar plate method.

An increase in either the total count or the number was not found in the samples taken on August 21 relative to the values from the samples taken on August 14. This indicated that the spilled oil was probably not significantly biodegraded. This result confirms the findings from the gas chromatography performed on the surface oil samples (Chapter 5.2.2).

The results of the identification tests for all the bacteria isolated are presented in Table 6-2. Tentative identification of the isolated strains are as follows:

1-Strain 800 seems to be the genus Pseudomonas.

- 2-Strains 801, and 8012 seem to be <u>Entero bactericae</u>, but are untypical in the catalase test.
- 3-Strains 802, 803, and 804 seem to be the genus <u>Corunebacterium</u> according to tentative investigations performed by Dr. R.R. Colwell. The reactions indicate that these strains all could be indentified as the species <u>Corunebacterium Pseudodiphtheriae</u>.
 4-Strain 812 does not seem to fit into any known taxonomical group.

5-Strain 812a could not be placed in a taxonomical group based on the tests conducted.

It should be emphasized that none of the isolated strains could be identified as either fish or human pathogenic bacteria.

6.2 Degradation Rates By Natural Cultures Of Microorganisms

Three experiments were performed to determine the rate of degradation of oil by the natural cultures of microorganisms found in the Melville Bay area. The experiments were started on August 27, 1977 using seawater sampled sterilely at Station 5475 collected on August 21 and a surface oil sample collected on August 10. The first experiment was intended to determine the rate of oil degradation using the samples as collected. The second was a control experiment measuring the change of the oil in the absence of microbiological activity (control). The third experiment was to determine the rate of degradation of the samples with the addition of nutrients.

6.2.1 Procedures

For all the experiments, 50 ml of the water sample was mixed with 0.250 g of oil in a conical flask. To prevent biological activity for the second experiment, 0.25 percent formaldehyde, by volume, was added. For the third experiment 1 g/l of K2HPO4 and 2 g/l NH4NO3 were added as nutrients. Multiple

| | Strain No. | | | | | | | | |
|--|------------|-----------|-----------------|-----------------------|------------|------------|-----------|------------|--|
| Tests | 800 | 8001 | 8012 | 802 | 803 | 804 | 812 | 812a | |
| Haemolysis | + | | 1. 1 . 1 | | | + | - | - | |
| Pigmentation | | - | - | 840 | - | ** | | - | |
| Cytochrome oxydase | + | + | - | - | - | | - | (+) | |
| Catalase | -1- | - | ** | - | + | + | - | + | |
| Tween 20 | + | - | + | + | + | + | - | + | |
| Tween 80 | + | - | + | + | + | + | - | + | |
| Gelatine | + | | | ~ | - | *** | | - | |
| O/F test | 0 x | F | F | gl- | gl- | g1- | g1- | g1- | |
| Simmon's citrate | - | - | | - | - | | + | + | |
| Motility (SIM) | er. | - | - | · | - | - | - | - | |
| Indol (SIM) | - | | ~ | - | | | - | - | |
| H ₂ S (SIM) | ~ | - | - | | - | - | - | - | |
| 1% tryptone | + | + | + | + | + | + | - | + | |
| 1% tryptone + 4% NACL | (+) | (+) | + | + | + | + | + | + | |
| 1% tryptone + 7% NACL | (+) | (+) | (+) | (+) | (+) | (+) | + | (+) | |
| V.P. | - | Q.4 | - | M | M | М | М | - | |
| Arginine | - | | - | 6.0 | 474 | - | - | - | |
| Lysine | - | | ~ | - | | - | - | - | |
| Urea | + | + | + | + | + | + | ents | - | |
| N0 ³ | М | + | 4 | + | + | + | М | + | |
| Arabinose | M | - | - | М | M | М | M | М | |
| Cellobiose | М | ~ | ~ | М | М | М | M | М | |
| Lactose | М | (+) | + | М | М | М | М | М | |
| Sucrose | M | - | - | М | М | M | М | М | |
| Glycerol | - | ~ | - | ~ | - | + | 6449 | | |
| Starch | М | ~ | | М | М | М | М | М | |
| Xylose | ~ | - | ~ | - | <i>6</i> - | - | - | - | |
| Chitin | - | ~ | ~ | | <u>en</u> | - | - | - | |
| Veal infusion broth + 1% NACL at 5°C | (+) | - | - | (+) | (+) | + | - | (+) | |
| Veal infusion broth + 1% NACL at 10°C | ÷ | (+) | (+) | (+) | (+) | (+) | (+) | - | |
| Veal infusion broth + 1% NACL at 15°C | + | (+) | (+) | (+) | (+) | (+) | + | (+) | |
| Veal infusion broth + 1% NACL at 30°C | + | + | + | + | + | + | + | + | |
| Antibiotica test (Pteredine) | - | - | + | + | + | + | + | (+) | |
| Gram | g- rod | g- rod | g- rod | g † rod | gr+ rod | gr+ rod | g- rod | gr+ rod | |

Table 6-2. Biochemical examinations of strains isolated from substrates using oil as the single carbon source. All reactions read within 7 days.

M = test not carried out

gl = glucose negative

Ox = oxidative degradation F = fermentative (+) = weak reaction

flasks were prepared for each experiment: these were maintained at 15 C and carefully shaken (100 rpm) for the B-week duration of the experiment. At weekly intervals chemical and microbiological examinations were performed on one of the flasks for each experiment.

For the chemical examinations, the total mixture of oil and water from one flask was extracted three times with CCl4. The combined extract was diluted to 25 ml with CCl4. A few microliters were then injected into a gas chromotographic column. The gas chromotography was performed using a SCOT column as described in Chapter 7.2.1.2.

The microbiological examination were performed by the MPN method as described in Chapter 6.1.1.

6.2.2 Results

The results from the gas chromatographic analyses on the SCOT column are presented in Table 6-3. The relative amounts of n-C17/pristane and n-C18/phytane were determined and are shown in these tables. As previously mentioned, the n-alkanes such as C17 and C18 are degraded faster than pristane and phytane and thus their ratios can be used as indicators of biodegradation. Some of the chromatograms are included as Figures 6-1 to 6-3.

| Table 6-3. | Relative amounts | of n-C ₁₇ /pristane a | nd n-C ₁₈ /phytane |
|------------|------------------|----------------------------------|-------------------------------|
| | determined by GC | analyses of natural | cultures. |

| Date | Incubation | Experiment I (1) | | Experime | ent II (2) | Experiment III (3) | | |
|---------|------------------|------------------|------|----------------------|------------|----------------------|----------------------|--|
| 1977 | time (weeks) | | | C ₁₇ /Pri | | C ₁₇ /Pri | C ₁₈ /Phy | |
| Sept 14 | 2 ¹ 2 | 1.45 | 1.78 | 1.27 | 1.77 | 0.62 | 0.85 | |
| Sept 21 | 312 | 1.28 | 2.12 | - | - | - | - | |
| Cn & 28 | 4 ¹ 2 | 1.33 | 1.85 | 1.39 | 1.80 | 0.41 | 0.49 | |
| Oct 5 | 512 | 1.39 | 1.72 | 6 — 6 | - | - | - | |
| Oct 12 | 0 ³ 2 | 1.45 | 1.74 | | | - | - | |
| Oct 26 | 812 | 1.29 | 1.67 | 1.36. | 1.76 | 0.14 | 0.29 | |

(1) = Water and oil

(?) = Water, oil, and formaldehyde (control)

(3) = Water, oil, and nutrients



Figure 6-1. Gas chromatograms of oil degraded by natural cultures.

From Table 6-3 it is seen that the n-C17/pristane and n-C18/phytane ratios do not indicate degradation of the oil for the first two experiments where oil and water and then oil, water, and formaldehyde were cultured. In contrast, the third experiment with oil, water, and nutrients show a remarkable degradation of the oil after 2.5 weeks. The oil degradation continued during the incubation period.

The results of the microbiological examination are presented in Table 6-4. These results also indicate a much faster propagation of the oil degrading microorganisms in the experiments with the added nutrients. The



Figure 6-2. Gas chromatograms from the second oil degradation experiment (control).

first experiment indicates that the propagation of oil degrading microorganisms without added nutrients is a very slow process. The propagation rates in the Melville Bay area where the spill occurred would have been even slower as the ambient temperature there was about 4 C rather than the 15 C used in the experiments. ÷



Figure 6-3. Gas chromatograms from the third oil degradation experiment which had nutrients added.

•

| Incubation | Experim | ent I ⁽¹⁾ | Experim | ent II ⁽²⁾ | Experiment III (3 | |
|-----------------|---------------------|----------------------|---------------------|-----------------------|---------------------|---------------------|
| time (weeks) | A | В | A | В | A | В |
| 1 | 15,800 | - | - | - | 14,800 | _ |
| 2 | 720,000 | 300 | - | < 300 | 4.5×10^{6} | 460,000 |
| 3 | 4.1x10 ⁶ | 900 | 120,000 | 3,900 | 17.x10 ⁶ | 2.1x10 ⁶ |
| 4 | 19.x10 ⁶ | 110,000 | 1.2x10 ⁶ | 24,000 | 21.x10 ⁶ | 2.4x10 ⁶ |
| 6 | 22.x10 ⁶ | 460,000 | 6.3x10 ⁶ | 46,000 | 24.x10 ⁶ | 24.x10 ⁶ |
| 8 | 25.x10 ⁶ | 9.3x10 ⁶ | 8.8x10 ⁶ | 210,000 | 26.x10 ⁶ | 1.1×10^{9} |

Table 6-4. Growth of natural seawater cultures as a function of time.

A = Total count per ml

B = Oil degrading microorganisms per liter (MPN method)

(1) = Water and oil

(2) = Water, oil, and formaldehyde (control)

(3) = Water, oil, and nutrients

6.3 Degradation Of Oil By Isolated Monocultures

6.3.1 Procedure

All the oil degrading strains isolated from the natural cultures (Table 6-2) were tested for the ability to degrade the following mixtures of hydrocarbons:

1-Mixture of cyclopentane, cyclohexane, and cycloheptane (cycloalkanes) 2-Mixture of benzene, naphthalene, and phenanthrene (aromatics) 3-Paraffins (alkanes)

4-Shell Vitrea oil 27 (alkanes, cycloalkanes, and aromatics)

These investigations were carried out in screwcap tubes. The Colwell medium with reduced MgSO4,7H2O content was used as the medium with a 1 percent hydrocarbon concentration (50 µl hydrocarbon with 5 ml of medium in each tube). The tubes were placed in a rotary shaker (100 rpm) during the incubations at 5, 10, and 15 C. The reactions were followed weekly for 6 weeks.

| Bacterial | 5°C | | | 1 | 10°C | | 1 | 15°C | | |
|--------------------------------------|----------|---------|--------|---------|---------|-----------------|---------------------|---------------|--------|--|
| strain | 2 | 3 | 6 | 2 | 3 | 6 | 2 | 3 | 6 | |
| | ALKANI | 79 | | | | | | | | |
| 800 | - | - | - | _ | - | _ | | х | х | |
| 801 | - | - | _ | | - | | | - | - | |
| 801 8012 802 | _ | | | | _ | | | - | - | |
| 8022 | _ | - | x | | x | x | x | x | x | |
| 803 | | | - | | - - | - | X* | x | x | |
| 804 | | _ | - | | _ | _ | X* | X | x | |
| 812 | _ | х | х | _ | х | x | | X | X | |
| 812a | _ | - | - - | 1 2 | A - | - | - | - - | - | |
| 0128 | | | | - | - | | - | - | | |
| 35 J. G. | CYCLOA | ALKANES | | | | | | | | |
| 800 | - | - | | - | - | S. 7 | | | | |
| 8011 | 777.) | - | - | - | - | | 2.00 | - | | |
| 8012 | - | 200 | - | - | - | | 30 77 80 | - | - | |
| 802 | - | 1077 | - | - | - | $(1-1)^{2}$ | 1. 1 | - | - | |
| 803 | ~ | - | | | - | + | 2 2 | - | - | |
| 804 | - | - | - | - | - | + | 8 77 8 | | - | |
| 812 | ~ | - | - | | - | | 3. - 3 | . | - | |
| 812a | - | | - | - | ~ | - | - | - | - | |
| | AROMAT | TICS | | | | | | | | |
| 800 | <u> </u> | - | - | - | <u></u> | - | | - | - | |
| 8011 | - | - | - | - | - | - | - | _ | - | |
| 8012 | - | - | - | - | - | - | - | - | - | |
| 802 | - | - | - | - | - | - | - | - | - | |
| 803 | - | — | - | - | - | - | - | - | - | |
| 804 | | - | - | - | - | - | - | - | - | |
| 812 | - | - | - | - | | - | - | | - | |
| 812a | - | - | - | - | - | - | | - | - | |
| | र प्रस्य | VITTOEA | OTT 27 | ATVANES | | OALKANES | L ADOM | ATTCS) | | |
| 800 | SAELL | VIIREA | - | ALKANES | - | X | - AROPH | X | х | |
| 801 ₁ | - | - | - | _ | _ | + | x | x | x | |
| 801 ₁ 801 ₂ | _ | - | 2 | 1 2 | | - | | ~ - | + | |
| 8012 | - | | | _ | _ | x | X* | x | x | |
| 802 | | | - | - | - | | X* | x | x | |
| 803 | | | _ | | - | - | X | x | x | |
| 804 | | | - | | x | x | | л - | x | |
| 812 812a | | | - | 1 2 | л - | - | _ | - | - - | |
| 0124 | - | | 177 | | 570 C | 050 | - | 055 | | |

Table 6-5. Growth of isolated oil degrading strains in various petroleum hydrocarbon mixtures as functions of time and temperature. Times are in weeks.

- = no growth

+ = doubtful growth

X = visual growth

X* = visual growth after 1 week

6.3.2 Results

Results of the studies on monocultures are presented in Table 6-5 for each hydrocarbon mixture.

Strains 802, 803, and 804 appear to be very active oil degrading strains, especially in the biodegradation of paraffins and Shell Vitrea oil 27. After only I week at 15 C, these strains grow in mediums with oil as single carbon source.

Only two strains, 802 and 812, degraded oil (paraffins) at 5 C after 6 weeks.

In most cases the lag phase at low temperatures seems to be more than 6 weeks for the monocultures and depends on the species and composition of oil. However, in the natural environment the lag phase could be quite different from that determined from the monocultures in the laboratory, because the toxic constituents normally produced could be removed from the oil/water interface at the sea.

6.4 Summary Of Biodegradation Studies

The number of microorganisms found in Melville Bay water was small, and oil degrading microorganisms constituted less than 1 percent of the total amount. Eight different microbial strains were isolated in the water samples using oil as the only carbon source. No increase in total number of the oil degrading microorganisms was found in samples collected 16 days after spill as compared with samples collected 8 days after the spill.

All the microbiological examinations show that in situ biodegradation would have been very slow. The results from the degradation studies with seawater and oil show that, unless nutrients are added, oil degradation is a very slow process. The gas chromatographic analyses did not indicate oil degradation during an 8 week period, and the microbiological analyses showed a slow propagation of oil degrading microorganisms during the same period. This seems to indicate a lag period of more than 8 weeks and, consequently, a slow degradation process. The addition of nutrients to the oil and water increased the oil degradation strongly. Both the gas chromatography and the microbiological analyses show that, after 1 to 2 weeks, a high oil degrading activity was already present. In this case, the lag period was found to be less than 2 weeks.

The results from monoculture experiments showed that only two strains, 802 and 812, would degrade paraffins at 5 C after 6 weeks incubation.

7.0 ACCOMMODATION OF OIL INTO THE WATER COLUMN

Subsurface water samples were collected after the POTOMAC spill to determine the amount and composition of oil accommodated into the water column. These water samples were collected by both the Danish and NOAA teams, the former using a brown bottle in a stainless steel frame that was opened via a messenger puncturing a Teflon seal, and the latter using a General Oceanics Inc. "Sterile Bag" sampler. Analyses of the samples were carried out using UV-fluorescence spectrometry (UV), gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS), by Ahnoff and Eklund (1978) for the Danish samples and by ERCO (Boehm and Feist, 1978) for the NOAA samples.

7.1 Sampling Procedures

7.1.1 The Danish Samples

The Danish water samples were acquired with a noncommercial sampler. This device was actually constructed and supplied by M. Ahnoff and G. Eklund of the Department of Analytical Chemistry, University of Gothenburg, Sweden (Ahnoff et al., 1974). The sampler consisted of a 1-liter, wide-neck brown bottle held in a stainless steel frame. The bottle was sealed with a Teflon sheet placed under the screwcap. After lowering the sampler to the desired depth, a messenger was used to operate a mechanism which punched a hole in the Teflon sheet through a hole in the screwcap. The sampler was retrieved without reclosing the opening. Prior to the cruise, all sampling bottles were washed with tap water, distilled acetone, and purified n-hexane until the hexane showed no traces of contamination using uv-spectrofluorometry. During the cruise in Melville Bay, bottles were rinsed with purified n-hexane between samplings, but there was no opportunity to control the bottles. Throughout the sampling program, duplicate samples were taken on separate lowerings for separate analysis.

The samples were extracted in the sampling bottle by adding 10 ml of n-hexane and a magnetic stirring bar, stirring for 45 minutes, and then transferring 2 to 4 ml of the organic phase to test tubes sealed with Teflon lined screwcaps. All the test tubes had been quality controlled by
spectroflurometry prior to use. Sample extracts acquired from Station 5471 and subsequent stations were stored in glass vials supplied by NOAA. These samples were used for analyses by UV-spectrofluorometry only.

7.1.2 The NOAA Samples

The NOAA team used a commercial sampler made by General Oceanics, Inc. of Miami Florida. This sampler, called a "Sterile Bag Sampler", consists of a pair of hinged metal plates that, when triggered by a messenger, open a sterile polyethylene bag. The bags are used only once and, after being opened at depth, are resealed after filling. When filled and resealed, the bags contain between 0.8 and 2 liters of water, averaging about 1.5 liters.

Each water sample was taken as a "double replicate", in that each depth was sampled twice (on separate lowerings) and two 500 ml aliquots were taken from each bag. Each aliquot was extracted in a separatory funnel with 10 ml of UV-spectroquality hexane. No filtration of the samples was attempted before extraction.

The extracts were stored in prerinsed glass vials sealed with aluminum foil and screwcaps. Considerable difficulty was experienced because of the closures on the NOAA samples. For those samples which were not sealed tightly, the extract suffered from either spillage or evaporation causing the loss of some samples. Other vials which had been sealed too tightly suffered from contamination when the aluminum foil tore and allowed the solvent to extract the waxes in the normal cap liner. Because of the difficulties experienced, the NOAA team recommends that no substitutes for Teflon cap liners be used for any extract containers in the future.

Subsequent laboratory experiments (Boehm and Feist, 1978a) indicated that the polyethylene bags adsorb oil from the water sample and leach plastisizers into the sample. Indications are that the bags are inappropriate for water samples with oil concentrations less than 100 ppb or when the sample is held in the bag for much more than 15 minutes.

7.2 Analytical Methods

The water samples collected in Melville Bay were analyzed by UV-spectrofluorometry (UV), gas chromatography (GC), and gas chromatography mass spectrometry (GC/MS).

7.2.1 Danish Samples

According to Ahnoff and Eklund (1979), the reasons for choosing the UV technique for determination of petroleum hydrocarbons are that 1) the sensitivity is sufficient for measuring very low concentrations, down to "natural" background levels and 2) the technique is fast so that all samples can be analyzed within a few days after their arrival at the laboratory.

GC/MS, using a glass capillary column, was employed for the following reasons: 1) the high selectivity of the technique permits an unambiguous determination of single petroleum hydrocarbons; 2) the instrumental sesitivity is sufficient to measure concentrations down to "natural" background levels; and 3) compounds to be measured can be selected. By measuring aromatic hydrocarbons, high selectivity can be obtained relative to biogenic hydrocarbons found naturally in water.

The procedures had been designed to be as simple as possible to obtain low contamination of the samples. For example, the number of transfers of the sample between different vials was kept at a minimum, to minimize exposure to surfaces and atmospheres that could cause contamination. Glassware and solvents were checked before use by UV-specrofluorometric measurements on blanks.

7.2.1.1 UV-Spectrofluorometry

Oil fluoresces when exposed to UP-light. Fluorescence is the emission of light by previously excited electrons. Fluorescence in petroleum is dominated by aromatic molecules and is extremely complex because of the oil's complexity.

A complete characterization of an oil by spectrofluorometry would include registration of fluorescence intensities at a large number of excitation/emission-wavelength combinations and calculation of a three dimensional map of corrected fluorescence intensities. Such a procedure yields more information than is necessary when the object is to screen levels

of oil in a large number of samples. It is time-consuming, requires special equipment, and cannot be employed on samples containing oil in trace amounts.

On the other hand, a procedure consisting of measuring the fluorescence intensity at a single excitation/emission combination reduces the information level significantly and makes quantitative evaluation difficult.

A procedure which employs more than one excitation/emission combination is rapid and gives appreciably more information than a single point measurement. Measurements at 230/340, 270/360, and 310/400 nanometers (nm) were employed by the Swedish chemists. The qualitative information obtained from this procedure can be used to evaluate each measurement for quantitative determinations. The combination of measurements should indicate whether the fluorescence characteristics of the sample appear reasonable or if contamination has occurred.

Intensities at the different wavelength combinations were compared with corresponding intensities of a standard solution made from the reference oil. A blank correction was made for the contamination found in the solvent used for extraction.

7.2.1.2 Gas Chromatography/Mass Spectrometry

In this technique, glass-capillary gas chromatography is used to separate volatile petroleum hydrocarbons which are then selectively detected with a mass spectrometer. The technique is similiar to that described by Grahl-Nielson (1976) although he employed a quadrupole instrument.

Masses to be monitored were those of naphthalenes, phenanthrenes, and dibenzothiophenes. These aromatic hydrocarbons have low enough molecular weights to be soluble in seawater but sufficiently high molecular weights so as not to readily evaporate. These compounds are known to be biologically active, as they are easily absorbed by living organisms where they exhibit toxic and other detrimental effects. Two milliliter aliquots of hexane extracts of water samples were concentrated to about 50 µl under a stream of purified nitrogen. Five nanograms of 1-bromonaphthalene were added to each extract to serve as an internal standard. The background levels of the selected aromatic hydrocarbons in the n-hexane used for extraction were determined from a 10 ml sample concentrated to 50 µl (Table 7-1).

| Compound | nanogram per liter | | | |
|------------------------------|--------------------|--|--|--|
| Naphthalene | 1.3 | | | |
| Methyl naphthalenes | 1.0 | | | |
| Dimethyl naphthalenes | 0.30 | | | |
| Trimethyl naphthalenes | 0.15 | | | |
| Phenanthrene | 0.21 | | | |
| Methyl phenanthrenes | 0.24 | | | |
| Dimethyl phenanthrenes | 0.20 | | | |
| Dibenzotiophene | 0.05 | | | |
| Methyl dibenzotiophenes | 0.06 | | | |
| Dimethyl dibenzotiophenes | <0.03 | | | |
| Total (naphthalene excluded) | 2.3 | | | |

Table 7-1.--Background concentrations in Danish water samples due to trace impurities in the solvent used for extraction.

A combination of a Carlo Erba Fractovap 2101 gas chromatograph and a Varian MAT 112 mass spectrometer along with a Spectrosystem 100 MS was used. The gas chromatograph was equipped with a splitless injector. The extracts were analyzed on a 40-m by 0.33-mm (inside-diameter) OV-101 glass capillary column. The following conditions were chosen: injector block at 250 C, the oven temperature programmed from 100 C to 240 C at 4.5 degrees/minute after an initial isothermal period of 5 min at 25 C, and the carrier gas (He) at a flow rate of 2 ml/min at ambient temperature. Two microliters of the concentrated extracts were injected without stream splitting with a splitless period of 60 s.

The amount of the selected aromatic hydrocarbons was quantitated relative to a standard mixture containing 0.1 ppm naphthalene, phenanthrene, dibenzothiophene, and i-bromonaphthalene. For the quantitation of the alkylated naphthalenes, phenanthrenes, and dibenzothiophenes, the total ion current per mole was assumed to be the same for these compounds as for their nonalkylated homologues. From mass spectral data on pure substances, it was known how large a fraction of the total ion current was made up by the measured fragment ion. Thus the amount of each selected aromatic hydrocarbon was calculated. The sum total of selected aromatics was also calculated. An equivalent amount of reference oil was estimated by multiplying these values by a factor obtained from measurements on reference oil samples. This factor expresses the ratio between total weight and weight of the selected aromatics in the reference oil. It must be pointed out that, while the values for the selected aromatics are true values, the equivalent amount of reference oil is a theoretical value that may produce deviations between the total amount of petroleum hydrocarbons reported and the amount actually present in the water samples.

The precision in mass spectrometric determination of the selected aromatic hydrocarbons was determined by injecting the sample from each station five times and calculating relative standard deviations of the measured amounts. The precision is highly dependent on the magnitude of the ion current from the measured ionic species. Since the ion current from the more branched aromatics is distributed between several peaks, the magnitude of ion current is lower and hence the precision is poorer. The relative standard deviation is 1 to 5 percent for naphthalene, methylnaphthalene, and phenanthrene; 8 to 12 percent for dimethylnaphthalene, trimethylnaphthalene, methylphenanthrene, dimethylphenanthrene, and dibenzothiophene; and 20 percent for dimethyldibenzothiophene.

The detectability of aromatics in seawater by mass spectrometry is limited by the background levels in the extraction solvent and by contamination from glassware. The detection limit is low, about 0.1 picogram injected or 5 picograms per liter of seawater for a single compound. The overall contamination of samples during sampling and processing could not be precisely determined. The lowest values of the sum of the selected aromatics was about 20 ng/l. They are probably close to the detection limit set by the procedure used.

7.2.2 NOAA Samples

ERCO (Boehm and Fiest, 1978) performed the analyses on the NOAA water samples using procedures similiar to those for the surface oil samples. The details of these procedures are contained in Chapter 5.1 and will not be repeated here. In summary, the hexane extracts of seawater were dried over sodium sulfate, weighed, and selectively characterized by silica gel/alumina

column chromatography, glass capillary gas chromatography, and UV spectrofluorescence. A block diagram of the procedure is presented as Figure 7-1.

7.3 Results

7.3.1 The Danish Analyses

7.3.1.1 Quantitative UV-Spectrofluorometry

The spilled oil contained high amounts of heavy aromatic hydrocarbons giving rise to fluorescence at long wavelengths. Its fluorescence characteristics differed significantly from those of lighter oils such as diesel and lubricating oils, and also from the pattern found in apparently unpolluted water. Therefore, fluorescence patterns having characteristics similiar to the spilled oil could be found in many samples, even though the concentrations were quite low. The fluorescence patterns of the contaminated samples, including those samples with the highest concentrations, deviated significantly from that of the spilled oil. Dissolution and weathering processes produce a different composition of the petroleum hydrocarbons in the water column within a few days of the spille.

Since fluorescence at long wavelengths (310/400 nm) was considered typical for the spilled oil, it was used as an indication that the petroleum hydrocarbons originated with the spilled oil. Samples which contained petroleum hydrocarbons in amounts above the baseline level, but did not show the characteristics typical of the reference oil, were considered not to contain oil spilled from the POTOMAC. In at least one sample, the fluorescence spectrum was similiar to the spectrum of the cooling water from the ADOLF JENSEN.

Of the 76 subsurface samples that were taken, three were lost and five were considered as contaminated. These eight samples that were not analyzed are listed in Table 7-2. For the corresponding sampling points, results from quantitative spectrofluorometric (UP) measurements are based on single samples. For the other 30 sampling points, duplicate samples were analyzed.



Figure 7-1 Analytical scheme for hexane extracts of seawater used by ERCO for NOAA samples.

| Station | Depth | Code | Cause |
|---------|-------|------|-------|
| 5460 | 10 m | 1 | a |
| 5461 | 5 m | 8 | a |
| 5466 | l m | 16 | а |
| 5468 | 5 m | 29 | а |
| 5470 | 1 m | 39 | Ъ |
| 5470 | 20 m | 45 | с |
| 5471 | 20 m | 52 | а |
| 5477 | 5 m | 71 | Ъ |

Table 7-2. List of samples for which results are not reported.

a; Strong indication of contamination of sample. Comparatively high levels of oil with fluorescence characteristics strongly deviating from those of the spilled oil.

b; Screwcap on sample vial was not sufficiently tightened.

c ; Not delivered

As a rough test for similiarity to the spilled oil, a value of at least 0.5 for the following relative fluorescence intensity (r) was required:

r = c310/400 c270/360.

Here, c310/410 and c270/360 are fluorescence intensities at the indicated wavelengths expressed in reference oil equivalents of μ g/l. The results of these tests are shown in Table 7-3. Quantification was made with the reference oil from EXXON's Aruba refinery as the standard. All values are mean values from the duplicate samples, except for the sampling points listed in Table 7-2. The results, corrected for interference from the solvent, are shown in Table 7-4 expressed as equivalent concentraions of the reference oil in μ g/l.

Some profiles of concentration of petroleum hydrocarbons as a function of depth are contained as Figure 7-2. Fluorescence spectra of different types of water samples are shown in Figure 7-3 (contaminated by Bunker-C fuel), Figure 7-4 (contaminated by cooling water from the ADOLF JENSEN), and Figure 7-5 (apparently uncontaminated water).

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| Station | Depth (m) | micro meas | Spectral similarity to reference oil | | |
|---------|--------------|---------------|--|---------|-------------|
| | | 230/340 | 270/360 | 310/400 | |
| 5460 | 1 | 0.91 | 0.53 | 0.27 | + |
| 5400 | 10 | 0.22 | 0.14 | 0.049 | 6. . |
| 5461 | 1 | 4.9 | 3.5 | 2.5 | + |
| | 5 | 0.74 | 0.57 | 0.41 | + |
| | 10 | 0.53 | 0.40 | 0.29 | + |
| | 20 | 0.56 | 0.32 | 0.13 | |
| 5462 | 1 | 1.0 | 0.50 | 0.30 | + |
| 5466 | 1 | 1.5 | 0.90 | 0.48 | + |
| | 5 | 0.54 | 0.36 | 0.35 | + + + |
| | 10 | 0.48 | 0.32 | 0.19 | + |
| | 20 | 0.32 | 0.21 | 0.082 | |
| 5467 | 1 | 0.41 | 0.22 | 0.081 | |
| 5468 | 1 | 0.48 | 0.23 | 0.11 | + |
| | 5 | 0,59 | 0.40 | 0.20 | + |
| 5469 | 1 | 0.28 | 0.16 | 0.038 | |
| | 5 | 0.36 | 0.26 | 0.13 | + |
| | 10 | 0.28 | 0.20 | 0.11 | |
| | 20 | 0.28 | 0.18 | 0.065 | + |
| 5470 | 1 | 0.31 | 0.14 | 0.043 | |
| | 5 | 0.20 | 0.12 | 0.032 | |
| | 10 | 0.24 | 0.11 | 0.032 | |
| | 20 | 0.29 | 0.12 | 0.028 | |
| 5471 | 1 | 0.24 | 0.15 | 0.041 | |
| | 5 | 0.74 | 0.34 | 0.11 | |
| | 10 | 1.0 | 0.49 | 0.25 | + |
| | 20 | 0.23 | 0.12 | 0.026 | |
| 5473 | 1 | 0.47 | 0.27 | 0.13 | + |
| | 5 | 0.91 | 0.64 | 0.43 | + |
| | 10 | 0.56 | 0.24 | 0.10 | |
| | 20 | 0.53 | 0.25 | 0.11 | |
| | 30 | 0.37 | 0.25 | 0.12 | |
| 5474 | 1 | 0.87 | 0.32 | 0.11 | |
| 5476 | 1 | 1.7 | 0.77 | 0.19 | |
| 5477 | 1 | 1.3 | 0.73 | 0.28 | |
| | 5 | 0.47 | 0.27 | 0.072 | |
| | 10 | 0.63 | 0.28 | 0.083 | |
| | 20 | 0.63 | 0.19 | 0.079 | |

Table 7-3. Petroleum hydrocarbons in subsurface water samples, quantitated as the amount of reference oil that gives rise to the same fluorescence intensity at chosen wavelength combination

| Bottle | Used at stations | | microg | rams per liter |
|------------------|------------------|---------|---------|----------------|
| | 9 | 230/340 | 270/360 | 310/400 (nm) |
| I | 5460 - 5468 | 0.27 | 0.052 | 0.031 |
| II | 5469 - 5473 | 0.30 | 0.056 | 0.033 |
| III ^a | 5474 - 5477 | 0.75 | 0.19 | 0.047 |

Table 7-4. Amounts of interfering substances in solvents used for extraction, quantitated as micrograms of oil per liter of water sample.

^a American hexane

The relative difference between duplicate samples, calculated as (c1 – c2) / 0.5(c1 + c2), ranged between 2 and 103 percent. The median value was 40 percent and the arithmetic mean difference was 55 percent. The concentrations found at different sampling points ranged from $0.03-0.04 \mu g/l$ at Station 5470 to 2.5 $\mu g/l$ at Station 5461 at 1 m depth. Thus significant differences could be seen between different stations and between different depths, although the precision was relatively poor. The deviation between duplicates is due partly to the fact that recently polluted water is not homogenous; thus, the duplicate samples do not necessarily contain equal amounts of oil.

Judging from the fluorescence characteristics of the subsurface water samples, none of them contained oil which was identical in composition to the POTOMAC oil. Therefore, there will be a systematic error when the spilled oil is used as a reference for quantitative evaluation. This is not unique for the fluorescence technique but is a general problem when oil is to be analyzed at the 1 ppb level. Each technique which can be employed at this concentration level suffers from the drawback that it does not have equal sensitivity for all components of the oil. The UV-fluorescence technique is sensitive to aromatic hydrocarbons in oil and has the property of generally being more sensitive to larger molecules. Therefore, if the composition of the oil in the sample is shifted towards the lighter part of the reference oil, the total concentration can be underestimated. This can be partly overcome by choosing excitation and emission wavelengths that are typical of the lower aromatics, e.g., the naphthalenes and phenanthrenes.





Figure 7-2. Concentrations of petroleum hydrocarbons at four stations as a function of depth. Concentrations by UV-Spectrofluorometry. Values from duplicate samples are indicated. Spectral wavelengths: excitation 310 nm, emission 400 nm.



Figure 7-3. Fluorescence spectra of an extract of subsurface water collected on August 13 at Station 5461, 1 m depth. Left: excitation spectrum from fixed emission wavelength. Right: emission spectra from different excitation wavelengths (see also Table 7-10.).

A simple recovery test was made to check the efficiency of the Danish extraction procedure. Tap water was added to a sampling bottle, adjusted to a salinity of 30 g/l, and 10 µg of the reference oil dissolved in 10 µl of dichloromethane was added. The water was stirred for 30 min, extracted with hexane, and analyzed using the normal procedure for the water samples. The recovery was close to 100 percent as is seen in Table 7-5. However, Ahnoff and Eklund's experience (1979) from real seawater samples that have been extracted in two consecutive steps indicated that extraction is not 100 percent but somewhere between 80 and 100 percent and that the extraction efficiency is affected by the particulate load of the water.

7.3.1.2 UV Comparison of the Danish and NOAA Sampling Methods At Station 5471, water samples were taken using both the Danish and NOAA procedures. Two of the NOAA samples which had been extracted by the NOAA team were analyzed by Ahnoff and Eklund. A comparison of these two samples with the Danish samples taken at the same depths at this station is presented in Table 7-6. Spectra of these samples are shown in Figure 7-6. The fact that the emission spectra look the same, independent of the excitation wavelength



Figure 7-4. Fluorescence spectra obtained from a surface water sample, station 5474, that contained waste cooling water from the ADOLF JENSEN. (for explanation see Figure 7-3.)

is atypical of oil and suggests the presence of only one or a few similiar fluorescing compounds, possibly naphthalenes.

7.3.1.3 Mass Spectrometric (MS) Analysis

Table 7-7 lists the surface oil and water column samples that were analyzed using the MS method in Sweden. The concentrations of different aromatic hydrocarbons found in these water samples as determined by MS analysis are given in Table 7-8. According to UV analyses, three of these contained less than i µg/l total petroleum hydrocarbon concentration as noted in this latter table. These samples contained aromatic hydrocarbons in amounts barely above the practical detection limit of the MS method. This limit was not set by instrument sensitivity, but rather by the amount of contamination introduced into the samples during the analytical procedure. Contamination interfered more strongly with the MS than with the UV analyses.



Figure 7-5. Fluorescence spectra obtained from a surface water sample, Station 5469, collected well to the north of the spill area. The vertical scale is more expanded than in Figures 7-3 and 7-4.

| Table 7-5. | Recovery of Melville reference oil from synthetic seawater | |
|------------|--|--|
| | using hexane as extractant. | |

| Excitation/emission wavelength (nm) | 230/340 | 270//360 | 310/400 |
|--|---------|----------|---------|
| Recovery (%) | 96.1 | 98.7 | 96.9 |

| Station | Depth | Method | mi | crogram per | liter |
|---------|--------|--------|---------|-------------|--------------|
| | | | 230/340 | 270/360 | 310/400 (nm) |
| 5471/1 | 0-0.5m | NOAA | 6.2 | 2.1 | 0.20 |
| | Om | GU | 0.59 | 0.31 | 0.20 |
| 5471/2 | 0-0.5m | NOAA | 10 | 2.8 | 0.40 |
| | Om | GU | 0.24 | 0.15 | 0.042 |

| Table 7-6. | Comparison between | samples | taken | by | NOAA | and | Gothenburg | Uni- |
|------------|---------------------|---------|-------|----|------|-----|------------|------|
| | versity sampling me | thods. | | | | | | |

The sample at 1 m depth from Station 5461, which contained a few µg/l of petroleum hydrocarbons, showed 50 ng/l of selected aromatic hydrocarbons (Table 7-8). Mass fragmentograms are shown in Figure 7-7. In Figure 7-8, the concentrations of different aromatic hydrocarbons are compared with the concentrations found in the surface oil sample collected on August 10. It can be seen in this figure that, for each type of aromatic hydrocarbon, the relative concentrations decrease with increasing molecular weight. This is in accord with the lower solubility of the higher weight compounds. For the naphthalenes, evaporation of the lightest naphthalenes from the oil can also contribute to the differences seen in Figure 7-8.

7.3.1.4 Comparison of MS and UV Results

The selected aromatic hydrocarbons make up approximately 1 percent of the total weight of the original POTOMAC fuel which was spilled (Table 5-5). Assuming that the same relation between the selected aromatics and the total amounts of petroleum hydrocarbons exists in the water samples (obviously this is not true), values of total petroleum hydrocarbon concentrations can be calculated. Table 7-9 presents such concentrations for the sample at 1 m from Station 5461.

Obviously, these values must be maxima since the selected aromatic hydrocarbons belong to the most water soluble components of the oil and thus would be expected to be present in high relative concentrations. The UV analysis shows lower relative concentrations. Compared with the MS technique, the UV method measures a broader spectrum of aromatic hydrocarbons. Higher wavelengths are more selective for the heavy aromatic components, and they



Figure 7-6. Fluorescence spectra obtained from a water sample collected in a polyethylene bag by NOAA at Station 5471 just below the surface.

also yield lower concentrations. Values from measurements at 310/400 nm can be regarded as minimum concentrations. Consequently, it can be concluded that there is good agreement between the MS and the UV determinations on at least this sample.

7.3.2 The NOAA analyses

The NOAA hexane extracts were analyzed by ERCO, and a complete report of their findings is contained in Boehn and Feist (1978) from which the following material was extracted.

Table 7-7. Samples analyzed by mass fragmentography.

"Thule oil" acquired from tank of the POTOMAC. 1 2 Reference oil Bunker-C retain acquired from EXXON refinery at Aruba where POTOMAC last loaded with fuel Surface oil sample collected on August 10, 1977. 3 4 Station 5460 1 m code=4 5 Station 5461 1 m code=5 6 Station 5461 5 m code=7 7 Station 5469 5 m code=33

Table 7-8. Concentrations of naphthalenes, phenanthrenes, and dibenzothiophenes in subsurface water samples.

| Compound | 5460 (1m) | 5461 (1m) | 5461 (5m) | 6569 (5m) |
|------------------------------|------------|----------------|------------|------------|
| | | nanogram j | per liter | |
| Naphthalene | 4.3 | 5.7 | 5.5 | 6.6 |
| Methyl naphthalenes | 3.2 | 7.2 | 1.8 | 3.4 |
| Dimethyl naphthalenes | 0.9 | 12 | 1.5 | 3.3 |
| Trimethyl naphthalenes | <2.0 | 8.4 | 1.8 | 4.2 |
| Phenanthrene | 5.8 | 5.5 | 1.1 | 1.5 |
| Methyl phenanthrenes | 2.3 | 5.3 | 0.9 | 0.6 |
| Dimethyl phenanthrenes | 0.7 | 4.4 | <0.1 | <0.1 |
| Dibenzothiophene | 0.6 | 1.9 | 0.2 | 0.3 |
| Methyl dibenzothiophenes | 0.2 | 2.7 | 0.4 | 0.7 |
| Dimethyl dibenzothiophenes | <0.1 | 2.5 | 0.5 | 0.9 |
| Total (naphthalene excluded) | 14 | 50 | 10 | 15 |
| | Spectroflu | orimetric anal | ysis | <u></u> |
| 230nm/340nm 270nm/360nm | 930 560 | 4900 3200 | 740 570 | 500 350 |

1900

240

310nm/400nm

410

180



Figure 7-7. Mass fragmentogram reconstructed from a water sample collected at Station 5461 at 1 m depth.



Figure 7-8. Comparison of concentrations of naphthalenes, phenanthrenes, and dibenziothiophenes in the subsurface water sample from Station 5461 at 1 m depth with the surface oil sample collected on August 10. Vertical axis is the concentration in the water sample divided by the concentration in the surface sample. Concentrations of the water sample have been corrected for background effects by subtracting out the mean concentrations found in three other water samples (see Table 7-8). Horizontal axis is molecular weight.

Fifty-six hexane extracts were characterized by total extractables (Table 7-10), after which 36 extracts were characterized by either GC or GC-MS depending upon the concentration levels. The goals of the analyses were 1) to characterize the chemical fractionation of the oil incorporated into the water column and 2) to estimate the quantity of oil incorporated into the water column. These goals were achieved only partly, because several of the , extracts prepared in the field were either contaminated or evaporated because of faulty closures.

7.3.2.1 Gas Chromatography

Where column chromatography preceded gas chromatography, two fractions of the hexane extract were analyzed: an f1 fraction containing saturated hydrocarbons and an f2 fraction containing naphthenoaromatic and aromatic hydrocarbons. In the case of samples containing smaller concentrations of total extractables,

| | microgram per liter (ppb) |
|--|---------------------------|
| Sum of selected aromatic hydrocarbons | 0.050 |
| Total concentration of petroleum hydrocarbons assuming that selected aromatics constitute 0.81% of total | 6.2 |
| Fluorescence intensities in reference oil equivalents | |
| Excitation/emission (nm) 230/340 270/360 310/400 | 4.9 3.1 1.9 |

Table 7-9. Comparison between mass fragmentographic and spectrofluorimetric analysis on a subsurface water sample (Station 5461 at 1m)

only the unfractionated (f0) extract was analyzed. The samples were grouped into three broad classes as shown in Table 7-11.

Three water extracts, samples 1, 2, and 3, collected 12 days after the spill at Stations 5466 and 5467 contained high concentrations of total extractables (>1500 µg/500ml). Their GC spectra contained a trimodal distribution of high molecular weight unresolved components in the f1 fraction (Figure 7-9) and a characteristic distribution of resolved components with a relative index (RI) between 1400 and 1700 in the f2 fraction (Figure 7-10). The gas chromatograms of these three samples were remarkably similiar to each other but not to the spectra from the POTOMAC oil (Figures 5-3 and 5-4). This indicates that the oil in these samples came from a source other than the POTOMAC.

Fifteen other samples were characterized by varying concentrations (generally 100 to 500 μ g) of a suite of n-alkanes from RI 2100 to 3100, with the maximum at 2500 in the f1 fraction (Figure 7-11) and also by a bimodal unresolved complex mixture (UCM) in the f2 fraction (Figure 7-12). These GC patterns are atypical of Bunker-C fuel but match a hexane extract of a clean sample vial cap (Figure 7-13). The contamination of samples in this group from the wax coating on the vial caps precluded measurement of oil in these

| Lab. | Vial | Total | fl | f2 | | GC | | |
|----------------|----------------------|----------------------|-------------------|-------|----------------|----------------|-------|--|
| I.D. | I.D. | extractables (µg) | (_µ g) | (µg) | f ₁ | f ₂ | Total | |
| 08-81 | MCB H-1 | 138 | 87.5 | 277.9 | x | х | | |
| 08-105 | 1 | 22,500 | 7280 | 8112 | х | х | | |
| 08-106 | 2 3 | 15,380 | 5175 | 7315 | х | х | | |
| 08-107 | 3 | 16,120 | 3465 | 5210 | х | х | | |
| 08-99 | 4a | 759 | 318.4 | 163 | х | x | | |
| 08-97 | 6a | 114 | | | | | | |
| 08-98 | 5 | 16 | 23.5 | 25 | X | x | | |
| 08-96 | 7ъ | 202 | 32.0 | 64 | X | L | | |
| 08-95 | 8ъ | 46 | | | | | | |
| 08-94 | 9 | 23 | | | | | | |
| 08-93 | 10 | 33 | | | | | Х | |
| 08-92 | 11 | 874 | 201 | 227.9 | х | х | | |
| 08-85 | 12 | 548 | 145.4 | 106.1 | х | х | | |
| 08-86 | 13 | 112 | | | | | х | |
| 08-87 | 14 | 435 | 34.4 | 24.6 | х | X | | |
| 08-88 | 15 | 284 | 26 | 52 | x | х | | |
| 08-89 | 16 | 88 55 | | | | | v | |
| 08-66 08-67 | 5469-фа 5469-фЪ | 108 | | | | | х | |
| 08-77 | | 100 | | | | | v | |
| 56-77 | 5470- _φ A | 100 | | | | | X | |
| 08-76 | 5470- _∲ B | 35 | | | | | | |
| 08-75 | 5470-1a | 224 | 115 | 79 | х | х | | |
| 08-72 | 5470-1Ъ | 0 | | | | | | |
| 08-65 | H-la | 0 | | | | | | |
| 08-64 | H-1b | 35 | | | | | х | |
| 08-63 | H-2a | 249 | 81 | 74 | x | X | | |
| 08-62 | Н-2Ъ | 286 | | | | | х | |
| 08-61 | 1~la | 1700 | 665 | 560 | х | х | | |
| 08-60 | 1-1b | 204 | | | | | X | |
| 08-115 | 1-2a | 63 | | | | | х | |
| 08-114 | 1-2b | 20 | | | | | х | |
| 08-68 | 5-1a | 63 | | | | | Х | |
| 08-69 | 5-1b | 83 | | | | | | |
| 08-70 | 5-2a | 41 | | | | | х | |
| 08-71 | 5-2Ъ | 78 | | | | | | |

Table 7-10. Seawater extract analyses, NOAA

7-23

| Lab. | Vial | Total | fl | f2 | GC | | |
|-----------------|----------------------|----------|-------|----------------|--------|--------|-------------|
| I.D. I.D. | extractables (µg) | (µg) | (µg) | f ₁ | f 2 | Total | |
| 08-113 | 10-1a | 17 | | | | | 1000 |
| 08-112 | 10-16 | 29.4 | | | | | х |
| 08-84 | 10-2a | 67 | 162.0 | 100 / | | | |
| 08-83 08-111 | 10-2b 20-2a | 418 5 | 163.2 | 189.4 | x | x | |
| 00-111 | 20-28 | 5 | | | | | |
| 08-110 | 20-2ъ | 6.4 | | | | | х |
| 08-109 | 20-4a | 23 | | | | | X X X |
| 08-108 | 20-4ь | 40 | | | | | х |
| 08-100 | 30-la | 0 | | | | | |
| 08-101 | 30-1Ъ | 19 | | | | | X |
| 08-102 | 30-2a | 0 | | | | | |
| 08-103 | 30-2ъ | 35 | | | | | х |
| 08-79 | 10-¢a | 12 | | | | | |
| 08-78 | 10-фЪ | 153 | | | | | х |
| 08-74 | 11- <i>q</i> a | 51 | | | | | |
| 08-73 | 11- 4 b | 98 | | | | | X |
| 08-90 | 11-10A | 108 | | (<u>4</u> | | | x x |
| 08-91 | 11-10B | 185 | | | | | x |
| 08-82 | Fisher 765498 | 118 | 72 | 60.9 | х | х | |
| 08-80 | MCB Blank | 254 | 149 | 108.6 | х | X X | |

Table 7-10. Seawater extract analyses (continued)

L = Lost

X = GC'ed

samples. Three of the four procedural blanks were similiarly contaminated, and the fourth contained small amounts of hydrocarbons (<5 μ g) confirming the contamination.

The 14 remaining samples were not contaminated by the vial caps but contained only minor amounts (<10 µg/500ml) of a few resolved components in the unfractionated sample (Figure 7-14). The small number of resolved components, usually one or two, argues against gross contamination by the POTOMAC oil and suggests a biogenic origin of these components. In no case was major contamination of the water column with POTOMAC oil observed. Selective dissolution should result in a series of substituted naphthalenes, and gross incorporation of oil into the water column should result in an fi

| Sample I.D. | Date (August) | Station No. | Depth (m) | Group |
|----------------|------------------|----------------|--------------|---------|
| 1 | 17 | 5466 | 1 | T |
| 1 2 | 18 | 5467 | 0 | Т |
| 3 | 18 | 5467 | 0 | T |
| 4a | 18 | 5468 | 1 | C C |
| 5 | 18 | Blank | | C |
| 7Ъ | 18 | 5468 | 0 | LL |
| 10 | 18 | 5468 | 1 | LL |
| 11 | 18 | 5468 | 1 | LL |
| 12 | 18 | 5468 | 1 | LL |
| 13 | 19 | 5469 | 0 | LL |
| 14 | 19 | 5469 | 0 | LL |
| 15 | 19 | 5469 | 0 | LL |
| 0a | 19 | 5469 | 0 | |
| 0a | 19 | 5470 | 0 | 0000000 |
| H-la | 19 | 5470 | 1 | С |
| H-1b | 20 | 5471 | 0.2 | С |
| H-2a | 20 | 5471 | 0.2 | С |
| H-2b | 20 | 5471 | 0.2 | С |
| 1-1a | 20 | 5473 | 1 | С |
| 1-1b | 20 | 5473 | 1 | С |
| 1-2a | 20 | 5473 | 1 | LL |
| 5-1a | 20 | 5473 | 5 | LL |
| 10-1b | 20 | 5473 | 10 | LL |
| 10-2b | 20 | 5473 | 10 | С |
| 20-2b | 20 | 5473 | 20 | LL |
| 20-4b | 20 | 5473 | 20 | LL |
| 30-1b | 20 | 5473 | 30 | LL |
| 30-2b | 20 | 5473 | 30 | LL |
| 10-0Ъ | 21 | WW-10 | 10 | С |
| 11-0b | 21 | WW-11 | 0 | C . |
| 11-10a | 21 | WW-11 | 10 | С |
| 11-10b | 21 | WW-11 | 10 | С |

Table 7-11 Groupings of seawater samples NOAA

T = Trimodal unresolved envelope.

C = Cap liner contamination.

LL = Low level concentrations (< $10\mu g/500 ml$).

pattern similar to that for the whole oil (Figure 5-3). Neither of these patterns was observed in any of the NOAA water sample extracts analyzed by GC techniques.



Figure 7-9. Gas chromatogram of the fl (saturate) fraction from extract 2 showing the trimodal group. Analysis by ERCO.



Figure 7-10. Gas chromatogram of the f2 (aromatic) fraction from extract 2 (trimodal group). Analysis by ERCO.

7.3.2.2 UV-Fluorescence

Three f2 fractions of water extracts, incuding members of the trimodal alkane group, the cap blank group, and a shipboard blank, were analyzed by synchronous-scan spectrofluorometry and compared with an f2 fraction of the reference oil. No conclusions could be drawn from the results because of the similarity of peak shape and concentration of the two water sample extracts and the blank.



Figure 7-11. Gas chromatogram of the fl (saturate) fraction from extract 10-2b showing cap liner contamination. Analysis by ERCO.



Figure 7-12. Gas chromatogram of the f2 (aromatic) fraction from extract 10-2b showing cap liner contamination. Analysis by ERCO.



Figure 7-13. Gas chromatogram of a sample vial cap liner (unfractionated).





7.4 Summary Of Accommodation Into The Water Column

UV-spectrofluorometry, gas chromatography, and mass spectrometry were used to analyze the Danish and NOAA hexane extracts of water samples to investigate chemical changes of the spilled oil incorporated into the water column. Use of these techniques was hindered by contamination of some of the samples, both during collection and during storage. Some of the extracts showed gas chromatography patterns atypical of the oil spilled by the POTOMAC.

Most of the remaining samples contained small amounts of resolved components (<20 µg/ml).

UV-spectrofluorometry was used to screen the horizontal and vertical distribution of oil in Melville Bay. Petroleum hydrocarbons were found in the Danish samples at concentrations from 0.03 μ g/l up to above 2 μ g/l, using spectral wavelengths typical for quantification of the spilled oil. Using different wavelengths for quantitation, the maximum concentration found was between 2.5 and 4.9 μ g/l. The spilled oil could be traced by UV techiques down to about 0.1 μ g/l.

Depth profiles, taken 8 to 12 days after the spill occurred, showed maximum concentrations near the surface (1 m depth) and a repid decrease down to 10 to 20 m depth. Profiles taken 13 to 15 days after the spill showed maximum concentrations at 5 to 10 m depth corresponding to the bottom of the surface layer (Chapter 4.1).

The petroleum hydrocarbons in the water column contained higher relative amounts of the low-molecular-weight aromatic compounds than the reference oil and surface oil samples.

Mass spectrometric analysis was used on a small number of the Danish water sample extracts as a comparison with their UV-spectrofluorometric analysis. Good agreement was found between the two techniques.

While large-scale dispersion of the oil into the water column might have occurred during the 8 days before the first water samples were collected, no gross accommodation of the spilled oil into the water column was found in any of the water sample extracts analyzed.

8.0 BIOLOGICAL STUDIES ON PLANKTON AND FISH

Samples of zpoplankton and fish were collected in the vicinity of the spill as well as in reference areas to examine the impact of the oil (Tables 8-1 and 8-2).

The Danish samples were forwarded to the Water Quality Institute for hydrocarbon analysis, to Marin ID for analysis of the composition of species and identification, and to Greenland Fisheries Investigations (GF) for examination of contaminated plankton.

The 13 U.S. biological samples were forwarded to the Plankton Ecology Laboratory, National Marine Fisheries Service, Narragansett, R.I., for analysis of species composition, abundance, and contamination of plankton.

8.1 Sampling Procedure

8.1.1 Danish Sampling

Plankton samples were collected with a Stramin net (2 m diameter, mesh 500 threads/m hauled from 200 m to the surface at 1.5 kn over a period of about 30 min) and Hensen net (72 cm diameter, No 3 silk hauled vertically at 0.3 m/s from 50 m to the surface.) (Table 3-1.)

One plankton sample was collected with the Stramin net at the spill site (Station 5460) and two samples were collected in areas with oll pancakes on the surface; at Station 5461, the Stramin net broke the surface within the oiled area and at Station 5464, the Stramin net broke the surface outside of the oiled area after hauling inside the oiled area. Three samples were collected on a line north of the center of the oiled area (Stations 5469, 5470, and 5471). One sample was collected in an area with subsurface oil flakes (Station 5473) and one in a reference area (Station 5477). Samples were also collected with the Hensen net at Stations 5460, 5469, 5471, and 5477 (Figure 3-2).

The volume of the plankton samples from the Stramin net were measured immediately (Table 8-1) and the plankton were examined for oil contamination.

| | | | | | Time | Depth | Volume | Total | 0il Present | | |
|------------------|---------|---------|---------|------|------|--------|--------|--------|-------------|----------|--|
| Gear | Station | Post | ition | 1977 | GMT | m | wet ml | number | visible | analysis | |
| Stramin | 5460 | 74°53'N | 61°10'W | 8/13 | 1325 | 0-225 | 3000 | 143680 | no | yes | |
| 11 | 5461 | 75°10' | 61°23' | 8/14 | 0201 | 0-225 | 2000 | nm | pancakes | yes | |
| n. | 5464 | 75°12' | 61°30' | 8/16 | 1123 | 0-225 | 900 | 31826 | pancakes | nm | |
| 13 | 5469 | 75°44' | 61°35' | 8/19 | 1448 | 0-225 | 1300 | 132224 | no | no | |
| | 5470 | 75°35' | 61°24' | 8/19 | 1830 | 0-225 | 1300 | nm | no | ? | |
| 11 | 5471 | 75°26' | 61°10' | 8/20 | 0851 | 0-225 | 3000 | 150264 | no | ? | |
| u. | 5473 | 75°16' | 61°15' | 8/20 | 2137 | 0- 1 | 150 | nm | flakes | yes | |
| 1Î | 5477 | 74°21' | 58°37' | 8/21 | 0207 | 0-225 | 2000 | 57472 | no | no | |
| Hensen | 5460 | '75°53' | 61°10' | 8/13 | 1325 | 0-50 | nm | 15065* | 545 | | |
| 11 | 5469 | 75°44' | 61°35' | 8/19 | 1448 | 0-50 | nm | 5713* | | | |
| 11 | 5471 | 75°26' | 61°10' | 8/20 | 0851 | 0-50 | nm | 8367* | | | |
| " | 5477 | 74°21' | 58°37' | 8/21 | 0207 | 0-50 | nm | 13093* | | | |
| Pelagic trawl | 5465 | 75°10' | 60°38' | 8/17 | 1310 | ca 250 | nm | | | | |

Table 8-1. Summary of Danish biological stations including plankton volume.

nm = not measured

? = uncertain results

* = total number per m^2

| Gear | Station | Pos | ition | Date 1977 | Time GMT | Surface_area (m ²) | Wet volume (ml/1000m ²) | Filtered volume (m ³) | Wet volume (m1/100m ³) |
|-------------|---------|-----------|----------|--------------|-------------|-----------------------------------|-------------------------------------|-----------------------------------|---------------------------------------|
| Newston | 1 | 75°16.5'N | 61°20'W | 8/20 | 0540 | 550 | 50.7 | | |
| U | 2 | 75°17.5' | 61°15' | 8/20 | 0635 | 550 | 46.2 | | |
| | 3 | 75°18.5' | 61°12.5' | 8/20 | 0723 | 550 | 200.9 | | |
| rt. | 4 | 75°19.5' | 61°10.5' | 8/20 | 0748 | 550 | 34.2 | | |
| n | 5 | 75°20.5' | 61°14' | 8/20 | 0827 | 550 | 36.0 | | |
| ** | 6 | 75°22.5' | 61°04' | 8/20 | 0945 | 550 | 3.6 | | |
| | 7 | 75°18.5' | 61°19' | 8/20 | 1045 | 550 | 5.4 | | |
| | 8 | 75°18' | 61°17' | 8/20 | 1056 | 550 | 13.5 | | |
| | 9 | 75°26' | 61°52' | 8/21 | 0843 | 550 | 45.0 | | |
| | 10 | 75°47' | 65°50' | 8/21 | 1253 | 550 | 10.8 | | |
| " | 11 | 75°53' | 67°58' | 8/20 | 1600 | 550 | 8.1 | | |
| Bongo/0.333 | 3 1 | 75°15' | 61°15 | 8/19 | 1600 | | | 722 | 29.1 |
| Bongo/0.505 | 51. | " | tt | п | | | | п | 28.2 |
| Bongo/0.333 | 3 2 | 75°15' | 61°15' | 8/19 | 1700 | | | 964 | 47.4 |
| Bongo/0.50 | 5 2 | | | ш | " | | | 11 | 40.1 |

Table 8-2 Summary of U.S. biological stations including plankton volume.

Samples of the dominant groups (Copepods, Parathemisto, and Pteropods) were selected and kept frozen for hydrocarbon analysis. The remainder of each sample was preserved in 4 percent Formalin for identification, counting, and further examination for oil occurring as external smudges or ingested into the gut.

8.1.2 U.S. Sampling

Neuston samples were collected at 11 stations with a 0.5 by 1.0 m rectangular frame fitted with a 0.505 mm mesh net. Tows of 10 min duration were conducted at speeds of 3.3 km/hr, effectively sampling a surface area of 550 sq m. In addition, at Stations 1 and 2, stepped oblique tows were made with a 61 cm bongo sampler fitted with 0.505 and 0.333 mm mesh nets. At Station 1, a 45 min tow was conducted which sampled at 20, 15, and 10 m depth each for 15 min. At Station 2, the tow was for 1 hr and sampled 20, 15, 10, and 5 m depths each for 15 min. All samples were preserved in 10 percent Formalin. A summary of these tows is contained in Table 8-2.

8.2 Species Composition

8.2.1 The Danish Samples

The Stramin net samples were reduced to an aliquot of about 3000 specimens with a sample divider and identified to the lowest possible taxa. The Hensen net samples were totally counted and identified (Table 8-3). The fish larvae from all the samples were identified (Table 8-4).

The copepods were the dominant group in the plankton. <u>Calanus</u> <u>hyperboreus</u> was the dominant species in all the Stramin net samples accounting for 37 to 82 percent of the specimens. <u>Calanus glacialis</u> was the second most numerous species and occurred at all stations. At the reference station, <u>Metridia longa</u> was the dominant species, but only a few or no specimens were present at the other stations. In the Hensen net samples, the small copepod <u>Pseudocalanus minutus</u> was the dominant species, possibly because of the smaller mesh in this net. Because of the known daily vertical migration of plankton, natural variation present in the samples made comparison between samples collected at different times uncertain.

| Station number | 5460 | 5464 | 5469 | 5471 | 5477 | 5460 | 5469 | 5471 | 5477 |
|---------------------------------------|-----------|-------|-----------|---------|-------------|-------------|--------------------|------------|----------------------|
| Type of net and depth | S 200, | 225-0 | m, 30 m | in haul | | 0,45 | m ² Hen | sen, 5 | 0~0 m |
| Sarsia princeps | 64 | 8 | | 70 | | | | | |
| Leukartiara breviconia | 64 | | | | | | | | |
| Aglantha digitale | 5440 | 2040 | 4960 | 3238 | 128 | 61 | 63 | 54 | 67 |
| Clione limacina ad. | 704 | 72 | 1216 | 70 | | 5 | | 1 | |
| juv. | | | | | | 8 | 4 | 6 | 5 |
| Limacina helicina ad. | 704 | 24 | 2144 | 141 | 64 | 3 | 1 | | 3 |
| juv. | | | | | | 9 | 4 | 4 | 20 |
| Hiatella sp. juv. | | | | | | | | | 1 |
| Conchoecia sp. | | | | | | 1 | | | |
| Calanus hyperboreus 9 | 50880 | 3920 | 39360 | 66520 | 26880 | 120 | 19 | 86 | 36 |
| <u>n</u> n y | 54720 | 7600 | 42240 | 49984 | 44720 | 124 | 4 | 109 | 93 |
| IA | 9600 | 3040 | 20800 | 5280 | 10880 | 44 | 9 | 71 | 51 |
| " " III | 960 | | 320 | | 1280 | - | - | - | - |
| Calanus glacialis ? | 7680 | 1040 | 1280 | 5280 | 9600 | 96 | 3 | 27 | 28 |
| | 121111213 | 80 | 120203030 | 2200 | 121211-0121 | 1011112 | 27.9 | 0.0125 | 1212-025 |
| υ n Δ | 5120 | 2840 | 3200 | 6688 | 52480 | 376 | 21 | 103 | 354 |
| " . " IV | | | | | | 4 | 8 | 4 | 12 |
| Calanus finmarchicus 9 | | | | | 3200 | 60 | 6 | 18 | 50 |
| ה יי ער יי | | | | | | | 2.92 | 12020 | 3 |
| 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 | | | | | 640 | 192 | 14 | 49 | 114 |
| | | | | | | | 1 | | |
| Calanus copepodits IV | | | | | | 856 | 96 | 364 | 819 |
| Calanus nauplii | • | | | | | 192 | 312 | 196 | 30 |
| Pseudocalanua minutus | | | | | | 280 | 36 | 68 | 75 |
| | 9 | | | | | 568 | 390 | 444 | 845 |
| | 6 | | | | | 368 | 228 | 188 | 510 |
| " " II | V 7 | | | | | 2084 552 | 132 560 | 832 492 | 1170 265 |
| Pareuchaeta | 4 | | | | | 224 | 500 | 492 | 205 |
| glacialis 9 | ũ. | 152 | | 141 | 320 | | | | |
| " " Vg | | 88 | | 141 | 128 | | | | 1 |
| " " Va | | 1 | | 70 | 256 | | | 1 | 1 |
| " " IV9 | | 1 | | 10 | 2)0 | 1 | | 1 | |
| " " IVa | | | 320 | 70 | | | 2 | | |
| " " III | | 80 | 520 | 10 | | 1 | - | 2 | 2 |
| Metridia longa 9 | | 00 | 32 | 70 | 64000 | | 4 | 33 | 543 |
| " " V2 | | | 12 | 10 | 04000 | | 1 | 4 | 30 |
| " " V3 | | | | | 640 | | 2 | 5 | 30 |
| Oithona similis 9 | | | | | 040 | 112 | 44 | 80 | 10 |
| Microsetella norvegica | | | | | | | | | 6 |
| Harpacticida sp. | | | | | 640 | 4 | | | |
| Parathemisto libelluls | | 192 | 352 | 710 | 64 | 2 | 4 | 4 | 3 |
| Epicarida sp. | | | | | | - | | | 1 |
| Pandalus borealis juv. | | 66 | | | | | | | 5 |
| Ophiura sarsi | | | | | | | 16 | 16 | |
| Ophiocten sericeum | | | | | | | 5 | 4 | |
| Sagitta elegans | 256 | 2112 | 1280 | 1420 | 6144 | 3 | | 4 | 21 |
| Eukrohnia hamata | 6848 | 8280 | 14720 | 7040 | 5824 | 37 | 27 | 35 | 34 |
| Fritillaria borealis | | | | | | 4 | | 8 | 27 |
| Oikopleura vanhoeffeni | | | | | | 2 | 316 | 102 | 84 |
| | | | | | | | | | |
| Totel | 143680 | 31826 | 132224 | 150264 | 227888 | 6149 | 2332 | 3415 | 5344 |
| | | 21020 | | | | 0149 | | 7417 | 3344 |
| | | | | | 1 8 4 5 H | | 17101000000000 | | 10 10 10 10 10 10 10 |

Table 8-3. Results of zooplankton enumerations for Danish stations.

| Fish larvae | | | | Station | | | |
|-------------|------|-------|------|---------|------|------|------|
| | 5460 | 5461. | 5464 | 5469 | 5470 | 5471 | 5477 |
| Liparis sp. | 7 | ? | 16 | 6 | 1 | 7 | 2 |
| Boreogadus | | | | | | 1 | |

Table 8-4. Fish larvae collected at Danish stations.

The lack of available background data from the spill area make comparisons of numbers and species of zooplankton with the "normal" situation difficult, and conclusions about impact of the oil on the plankton community at the spill area cannot be firmly drawn. An investigation in 1928 (Jespersen, 1934) found <u>Calanus finmarchicus</u> and <u>Calanus hyperboreus</u> to be the predominant copepods in the upper water layers, but <u>Metridia longa</u> also appeared. Generally, the same species of copepods were found during the investigations of both 1928 and 1977.

Very few fish larvae were found in the Stramin net samples (Table 8-4). All of these were <u>Liparis</u> sp. except for a single <u>Boreogadus</u> <u>saida</u>. A 1-hr midwater trawl (Station 5465) resulted in only 11 adult <u>Boreogadus</u> <u>saida</u> being collected.

8.2.2 The U.S. Samples

Analysis of the U.S. samples was performed by R.Maurer and J.Kane at the Narragansett Laboratory of the National Marine Fisheries Service (Maurer and Kane, 1978). Plankton biomass was measured at each station by determining the displacement volume of each sample (Table 8-2). Volumes were recorded to the nearest milliliter following the method described by Anlstrom and Thralkill (1963).

When necessary, plankton samples were reduced to an aliquot of approximately 350 to 500 specimens using a modified Motoda box-type splitter. Zooplankters were identified to the lowest possible taxa, counted, and examined for oil contamination (Table 8-5).

| Station | | NOTION BONGO NOTION NOTION | | | | | | | | | | | | | |
|-----------------------------|------|----------------------------|-------|------|------|-----|----------|-----|------|-----|-----|----------|--------------|----------|------------|
| Spectes | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 . | 10 | 13 | 1(0.333) | 1(0.505) | 2(0.333) | 2(0,505) |
| alanus hyperboreus | 29 | 29 | • | 15 | 14 | 2 | 15 | 7 | 36 | 58 | 11 | 13252 | 14049 | 25908 | 21192 |
| alan <u>us</u> glacialis | 403 | 58 | 58 | 15 | 30 | 18 | 469 | 47 | 73 | 56 | 40 | 1906 | 2061 | 3056 | 6510 |
| alanus finmarchicus | 189 | 15 | 58 | - | 14 | 11 | 105 | 15 | 51 | 78 | 9 | 7490 | 399 | 10895 | 731 |
| seudocalanus minutus | - | - | • | - | | - | : | - | - | - | 44 | 8997 | 133 | 13685 | - |
| similis | - | - | • | • | - | • | - | - | - | | 7 | 709 | 44 | 531 | - |
| alanus sp. | - | • | - | - | - | ÷ | - | e | - | - | 98 | - | - | - | - |
| letridia longa | - | - | - | ÷ | - | - | - | 4 | - | ~ | - | - | - | - | |
| Parathemisto Tibellula | 4712 | 5236 | 21990 | 2843 | 4989 | 80 | 229 | 147 | 4632 | 22 | - | 355 | 244 | 266 | - |
| imacina helicina: | 115 | 116 | 58 | 175 | 58 | 105 | 149 | 196 | 80 | 11 | 133 | 89 | 44 | 8 | 1 |
| Clione limacina | 15 | - | | 7 | 29 | - | 5.0 | = | 44 | 5 | 2 | 266 | 111 | 266 | 199 |
| Conchoecia sp. | 15 | | - | 7 | - | - | - | 2 | - | - | - | 121 | 5 - 2 | 5415 | 3 2 |
| ukrohnia hamata | - | - | | - | - | - | 4 | - | - | 11 | - | - | - | - | 2.5 |
| <u>Sagitta</u> sp. | - | - | - | | - | - | | - | - | - | - | - | | 133 | 66 |
| omopteris sp. | - | | - | • | - | - | - | - | - | 7 | ×. | - | - | - | - |
| Polychaeta | | | - | - | - | - | - | - | 15 | - | - | | - | - | - |
| Siphonophora | | - | - | 73 | 73 | 7 | - | ÷ | - | - | - | 44 | - | 133 | - |
| Gymnosomata | - | 15 | 175 | - | - | - | - | 5 | 20 | - | 2 | - | - | - | - |
| Coelenterata | | | | - | - | • | - | • | - | - | - | - | - | - | 266 |
| lydromedusa | - | - | - | | - | • | 4 | - | 7 | R | - | - | | • | - |
| Total number | 5479 | 5469 | 22339 | 3135 | 5207 | 223 | 975 | 423 | 4938 | 248 | 346 | | | | |

Table 8-5 Results of zooplankton enumeration for U.S. stations

Large Calanoid copepods strongly dominated the plankton in the 0.505 mm mesh Bongo samples. <u>Calanus hyperboreus</u>, one of the largest known calanoids and one which occurs primarily in Arctic waters, accounted for approximately 77 percent of the total zooplankton numbers at Stations 1 and 2. <u>Calanus alacialis and Calanus finmarchicus</u>, smaller, morphologically similiar, and congeneric species, occurred at both stations but were not numerous enough to be considered dominant. It should be noted that <u>Parathemisto libeilula</u>, a hyperid amphipod, and smaller copepods were not ranked high in the 0.505 mm mesh bongo samples.

<u>C. huperboreus</u> also dominated the smaller mesh (0.333 mm) bongo samples (Table 8-5). The noticeable difference in species composition between the smaller and larger mesh samples was the increase in numbers of smaller species, <u>P. minutus</u> and <u>Oithona similis</u>, in the smaller mesh samples. <u>P. minutus</u> was ranked second in numerical importance for these samples.

Neuston samples taken in the vicinity of the spill (Stations 1 to 8) were dominated by <u>P. libellula</u>. In the control area (Stations 9, 10, and 11), <u>P. libellula</u> was also dominant.

The composition of communities in the neuston (surface) and bongo (water column) samples are compared in Figure 8-1. The two dominant species appear to be almost mutually exclusive. The neuston samples are strongly dominated by <u>P. Libellula (91 percent) while C. hyperboreus (76 percent) dominates the bongo samples. Calanus glacialis, C. finmarchicus, and Limacina helicina were of less importance in both biotopes.</u>

Sars (1390) reported that <u>P. (ibellula</u> is a good indicator of the Arctic water and occurs in large numbers at the surface. Populations are known to be composed primarily of juveniles, as the large adult individuals are seldom encountered. Similarly, in this survey the population was disproportionately juveniles. From 95 to 100 percent of <u>P. libellula</u> at any one station were juveniles. Hyperid amphipods are known to be extremely strong swimmers, capable of extensive vertical movement and <u>P. libellula</u> has been reported from the surface to 2,500 m. Examination of the diurnal occurrence of <u>P. libullela</u> in the neuston samples during this survey indicates that this species is from 100 to 1,000 times more abundant at the surface during the Arctic night and twilight periods.





If a slick was present, as at station 2, then the plankton movement into and out of contaminated waters would provide a pathway for hydrocarbon compounds to enter major plankton and fish communities in the water column. Amphipods, because of their numerical importance, are considered as a major food resource for fish species and the ringed seals. Whether or not there is a food chain magnification of hydrocarbon compounds as has been shown for other pollutants, e.g., pesticides and heavy metals, has yet to be determined. However, the potential for significant impact exists if these compounds are transferred to the more sensitive deepwater environments. Characteristically, these low productivity regions are inhibited by long-lived slow-growing species with low levels of fecundity; therefore, the carrying capacity for such pollutants in these environments would be expected to be minimal.

Fish larvae were virtually absent in the plankton during this survey. The only specimen collected was a radiated shanny. Stichaeus punctatus.
8.2.3 White Particles on the Sea Surface

Eleven days after the spill, small white particles were observed floating on the sea surface. Some of the particles could be identified as the remains of dead zooplankton (copepods). These white particles appeared to be globules of white fat or oil.

It is suspected that no relation exists between dead plankton and the spilled oil, as the white particles were observed both within oiled areas as well as in areas that the spilled oil did not reach. Furthermore, dead plankton have been reported in this area during 1928 as a natural phenomenon of the copepod <u>Metridia longa</u> (Jespersen, 1934). The most probable reason for the association of the dead plankton and the oil is that they were both concentrated by convergent processes such as Langmuir circulation. This explanation does not however preclude an adverse effect of oil on plankton which could conceivably contribute to plankton mortality.

8.3 Oil Contamination Of Zooplankton And Fish

8.3.1 Chemical Examinations

Ten samples of zooplankton and fish from Danish hauls were chemically examined for petroleum hydrocarbons by the Water Quality Institute (Hansen et al., 1978).

8.3.1.1 Analytical Procedure

In general, the procedure of Farrington and Tripp (1975) and Farrington and Mederias (1975) was applied for extraction and isolation of the hydrocarbons between n-C12 and n-C36. An amount of 2 to 20 g (wet weight) of biological material was used for each analysis. After homogenization in a blender, the sample was refluxed for a few hours with 40 g KOH per liter of 90 percent methanol. After cooling, the mixture was filtered with suction if solid materials were present. The residue was washed off the filter with a small volume of pentane. The saponification mixture, if filtration was necessary. was extracted three times with pentane. The extract was evaporated with a rotary evaporator until 1 to 2 ml remained.

Column chromatography of the extract was performed by using a column of equal amounts of alumina (Al2O3) packed on top of silica (SiO2). The alumina

and silica were activated overnight at 250 C and 150 C, respectively, and both were subsequently deactivated with 5 percent of water. The ratio of column material to nonsaponifiable lipid had to be 100:1 or more for the analysis to continue. The column was eluted with 1.5 column volumes of pentane + benzene (80 percent + 50 percent by volume). The eluate was evaporated to near dryness on a rotary evaporator and then redissolved in a small volume of CCl4. A few microliters were injected into the gas chromatographic column. A standard n-alkane mixture of known concentration was used to measure the detector response per unit weight of alkane. The internal standard used was n-C22. Gas chromatography was performed on a SCOT column as described in Chapter 5.1.

8.3.1.2 Results

The results from some of the gas chromatographic (GC) analyses on the SCOT column are shown in Figures 8-2 through 8-5. In all the chromatograms a few



Figure 8-2. Gas chromatogram of Boreomysis from station 5465.

very strong peaks dominated, showing the presence of biogenic hydrocarbons. One of these, pristane, has been found in all the samples.

Most of the samples also show the presence of a complex mixture of petroleum hydrocarbons. The amounts of petroleum hydrocarbons are low



Figure 8-3. Gas chromatogram of Themisto from station 5465.



Figure 8-4. Gas chromatogram of a Copepod from station 5470.



Figure 8-5. Gas chromatogram of a Copepod from station 5477. Reference station located 50 nmi southeast of the spill site.

compared with the amounts of the biogenic hydrocarbons. Petroleum hydrocarbons were found even in the reference sample from Station 5477 (Figure 8-5). Only two samples seemed to be uncontaminated with petroleum hydrocarbons.

8.3.1.3 Discussion

The copepod sample from Station 5477 was taken as a reference sample far from areas contaminated by the POTOMAC oil. The small amounts of petroleum hydrocarbons found by GC may indicate inadvertent contamination either during sampling or analysis. However, the analytical method could not distinguish between internal or external oil on the organisms. As a whole, the largest amounts of petroleum hydrocarbons were found in copepods, which have a rather high lipid content, and the lowest amounts were found in pterapods, which have low lipid content. This indicates that only part of the petroleum hydrocarbons found are related to contamination either during sampling or analysis.

No correlation was found between the water analysis performed by fluorescence and the zooplankton analyses performed by GC. This could be the result of the fact that the amounts of petroleum hydrocarbons found in the zooplankton are relatively low and dependent on other factors such as lipid content or the fact that the results indicate the possibility of contamination during either sampling or analysis as mentioned above.

Earlier investigations (Johansen et al 1977) in the area off West Greenland which studied invertebrates, fish, and sediments, showed no presence of petroleum hydrocarbons.

S.3.2 Physical Examinations

8.3.2.1 Procedure

The Danish plankton samples were examined under a dissecting microscope for the presence of oil. The contamination was classified as 1) external for oil adhering to the cuticle and adhesion to appendages or 2) internal for ingested oil. Specimens suspected to be contaminated in the gut with oil were cleared with lactic acid.

8.3.2.2 Results

The occurrence of contamination is shown in Table 8-6.

Station 5460: The sample was collected at the spill site where no oil was visible, but increased hydrocarbon levels were found in the water. The highest percent of oil ingestion was found at this station. The number of plankton with algae in their guts was also high.

Station 5461: The sample was collected in an area with oil pancakes on the surface and the plankton net retained both oil and plankton organisms. Many of the organisms had oil adhering to their exoskeletons, but it was impossible to determine whether or not the oil was present before they were caught in the net. It was remarkable that the mandibles were often contaminated. No oil was seen as ingested, and very few organisms had ingested algae.

Station 5464: The sample was taken in an area with oil pancakes on the sea surface; however an attempt was made to avoid oil contamination of the plankton net. Even so, contamination of the plankton after capture cannot be excluded. About 1 percent of the copepods were found contaminated with oil

Station Plankton Examined Contaminated Type of Contamination No. % No. External Ingested 5460 Copepoda 1739 62 4 5 57 N* N^{*} 5461 Copepoda 2005 0 5464 Copepoda 1044 11 1 9 2 Parathemisto 2 1 19 11 1 Chaetognatha 715 2 0.3 2 0 5473 Copepoda 355 1 0.3 1 N* Parathemisto 520 4 0.8 4

Table 8-6. Occurrence of oil contamination on dominant plankton groups.

N Many individuals were observed with external contamination. These were not counted because oil particles were also caught in the net and the contamination may have occurred after collection.

and two specimens were found with oil in their guts. Of the 19 Parathemisto in the sample, one was contaminated externally and another internally.

Stations 5469, 5470, and 5471: These Stations were acquired well to the north of the oiled area. No oil contamination in the gut or on cuticle was found. Many of the copepods had algae in their guts.

Station 5473: Both oil flakes and plankton were contained in the sample so the number of externally contaminated specimens was not determined.

No cil at all was found in the guts of pterapods and only two specimens of arrow worms were externally contaminated.

The oil particles found in the guts of the copepods were examined with a fluorescence microscope but no fluorescence was seen.

Oil was collected together with plankton in all of the NOAA samples. The alimentary tracts of individuals that appeared dark were removed, cleared, and examined to determine whether or not oil had been ingested. No oil was found in any of the alimentary tracts examined.

8.3.2.3 Discussion

The percentage of planktonic organisms affected by oil was small and thus there was probably no major effect on the plankton population. The percentage of individuals with oil in their guts was smaller than that found at the ARGO MERCHANT oil spill (Maurer, 1976). The sample collected at the spill site (Station 5460) was the only one with a high percentage of copepods having oil in their guts. Furthermore, the samples which had oil collected in the net did not show a high incidence of copepods with oil in their guts. The number of <u>Parathemisto libellula</u> was generally low except at station 5473 and the neuston stations; however, the percentage of individuals which had ingested oil was higher. This may be the result of differences in the size of the oil particles availible for consumption.

Parker (1969) found that copepods with small particles of a Bunker-C oil in their guts did not show signs of distress. However, larger oil particles might cause a blockage of the guts with fatal effects for the individual specimens. In cases of both internal and external contamination, the growth and reproduction of individuals, if not their very survival, may be affected. Exoskeleton contamination may inhibit sensitive chemo-receptive pores used for positioning during reproduction (Fleminger, 1973). Adhesion of oil to appendages could also interfere with the feeding currents and food handling. In addition, those individuals which were contaminated to the extent that they could not make quick escape responses would be more vulnerable to predation.

8.4 Summary

Two separate and distinct plankton communities were present in Melville Bay during the post-spill sampling period. The surface layer was strongly dominated by the hyperid amphipod <u>Parathemisto</u> <u>libellula</u>, while the water column plankton were dominated by the copepod <u>Calanus</u> hyperboreus.

White particles, which were determined to be the remains of dead copepods in some cases, were observed floating in long streamers in parts of Melville Bay after the spill. This phenomona appears to be natural and not related to the oil spill.

As evidenced by gas chromatography of selected zooplankton, low levels of petroleum hydrocarbons were found in most of the samples including that

collected at a reference station which should not have been impacted or exposed by oil from the USNS POTOMAC. This indicates that either the samples at the reference station were inadvertently contaminated by the gear used or were contaminated by the ADOLF JENSEN cooling water.

Visible oil contamination was observed on il percent of the Parathemisto at one station. Copepod contamination did not exceed 4 percent at any station. Ingested oil was the dominant contamination only at the spill site (Station 5460); at the other stations, external contamination predominated. The effects of this visible contamination, either internal or external, on the survival or reproductive behavior is not known. Since only a small portion of the total zooplankton population of Melville Bay was believed to be affected by the oil spilled from the USNS POTOMAC, there was probably no major effect on the zooplankton population from this spill.

9.0 MARINE MAMMALS AND SEABIRDS

9.1 Observations Of Marine Mammals

Marine mammals were observed from the ADOLF JENSEN by J. Christiansen of Marin ID. In the area north of Upernavik over the period from August 12 to 20, 43 ringed seals (Pusa hispida), 4 hooded seals (Cystophora cristata), 1 bearded seal (Erignathus barbatus), and 7 unidentified seals were observed. During two helicopter flights on August 16 covering most of Melville Bay, scientists from the ADOLF JENSEN observed only 2 seals. Of the 43 ringed seals, 32 were observed in association with winter ice and 25 of these 32 were observed before reaching the spill site while passing through a belt of pack ice. The remaining 7 were observed amongst and on rotten ice near Thoms Isle (75°43'N 60°35'W). The other seals were observed in open water, often near icebergs. In an oiled area, 4 seals were observed together near an iceberg, but nothing unusual was observed about their behavior. The sightings of most of the seals near sea ice rather than in open water was guite normal and agreed with investigations made in the area two years earlier. The small number of seals observed in the oiled area can be explained by the lack of ice in the area without recourse to an avoidance behavior of seals for oiled water. No deaths or abnormalities of seals were reported except for some instances of oil contamination on their skins.

9.2 Oil Contamination Of Sealskins

While no seals were captured during the spill response, a local hunter did report oiled sealskins about one month after the spill. In total, about 25 oiled skins were reported. The skins of 18 seals, all shot or captured in nets, were delivered to Denmark for analysis (Figure 9-1 and Table 9-1). Seven of the seals were heavily contaminated with oil on their backs with lesser amounts on their necks (seals 1, 2, 4, 8, 9, 11, and 13). Three seals had spots of oil on their backs or necks (seals 3, 6, and 10). On eight of the seals it was not possible to either see or smell oil (seals 5, 7, 12, 14, 15, 16, 17, and 18). Ten samples from oiled skins and four samples from seals

| Seal no. | Date | Location | Posit: | ion |
|-------------|------------|----------------------|---------|---------|
| 1 | 9/29/77 | Moriussaq | 76°48'N | 70°05'W |
| 2 | 9/15/77 | Kuvdlorssuaq | 74°34' | 57°20' |
| 3 | 11/23/77 | Tasiussaq | 73°20' | 56°05' |
| 4 | 1/26/78 | Godhaven (Parry Skær | 69°10' | 53°40' |
| 5 - 12 | Jan-Feb 78 | Upernavik area | 72°35' | 56° |
| 13 | April 78 | Niaqornarssuk | 68°15' | 52°50' |
| 4 - 18 | Mar-Apr 78 | Upernavik area | 72°35'' | 56° |

Table 9-1 Date and Location of Seal Catchings.

with no visible oil were analyzed by the Water Quality Institute to determine whether or not any oil originated from the USNS POTOMAC spill.

9.2.1 Analytical Procedure

The oil was mechanically isolated from the hair and the fat. For one sample (seal 1), the isolated oil was dissolved in a small volume of CCl4 and a few microliters were injected into a gas chromatographic column. For all other samples, a cleanup procedure was necessary to isolate the hydrocarbons from interfering components. The cleanup procedure was similar to that described in Chapter 8.3.1.1.

9.2.2 Results

Gas chromatograms were obtained on a SCOT column and a few examples are presented in Figures 9-2 to 9-7. It was not possible to detect petroleum hydrocarbons on seals 5, 7, 12, or 14 confirming the visual and olfactory examinations. Petroleum hydrocarbons were detected in the extracts made from seals 1, 2, 3, 4, 6, 8, 9, 10, and 11.

The compositions of the hydrocarbons from seals 1 and 2 (Figures 9-2 and 9-3) were similar to the composition of the hydrocarbons collected on the sea surface at the spill site. In these cases it seems probable that the contamination of these two seals originated from the POTOMAC spill.



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Figure 9-1. Capture locations of the analyzed seals. See Table 9-1.



Figure 9-2. Gas chromatogram from seal 1. Heavily oiled on back. Collected north of Thule, Greenland on September 29, 1977.



Figure 9-3. Gas chromatogram from seal 2. Heavily oiled on back. Collected east of the spill site on September 15, 1977.

The compositions of the hydrocarbons from seals 4 (Figure 9-4), 6, 9, 10 (Figure 9-5), and 13 (Figure 9-6) were different from the surface oil samples. The sharp peaks found in the surface oil samples (Figure 5-4) were lacking in the chromatograms from the seals. This difference may be due to biodegradation, and it should be considered that these petroleum hydrocarbons might have originated from the POTOMAC spill.

The missing peaks are also evident in the chromatogram from seal 3 (Figure 9-7). Furthermore, the composition of the hydrocarbons in samples



Figure 9-4. Gas chromatogram from seal 3. Spots of oil on neck. Collected southeast of the spill site on November 23, 1977.



Figure 9-5. Gas chromatogram from seal 4. Heavily oiled on back. Collected well south of spill site on January 26, 1978.



Figure 9-6. Gas chromatogram from seal 10. Spots of oil on neck. Collected southeast of the spill site in January 1978.



Figure 9-7. Gas chromatogram from seal 13. Heavily oiled on back. Collected well south of the spill site in April 1978.

from seal 3 showed more n-alkanes with carbon numbers above 20 than did the surface oil samples. Some n-alkanes with carbon numbers above 20 were also found in extracts from seals 8 and 11. The presence of these n-alkanes could be due to a contamination source other than the POTOMAC. It was not possible to determine if the other hydrocarbons on these seals came from the POTOMAC oil spill, because the analytical procedure was not definitive enough to distinguish between the seal contamination and the USNS POTOMAC slick samples.

Histological examinations were conducted on the skin underneath the oiled areas on some backs of the seals. No damage was seen during these examinations. In controlled experiments with heavily ciled seals (Engelhardt, 1978), the only long term effect of oil contamination found was the appearence of cornea lesions. Although the seals were totally coated with oil during Engelhardt's experiment, they were completely clean after 6 days in an oil free environment. The persistent external contamination of seals from the West Coast of Greenland after the POTOMAC oil spill might be attributed to differences in the composition of the contaminating oils. All the oiled seals reported were either shot or caught in nets; however, it is not certain whether or not the oiled seals were more susceptible to capture.

9.3 Seabird Observations

Observations of seabirds were routinely conducted from the ADOLF JENSEN. Very few birds were observed in the oiled areas during the August study period. Apart from a few flocks of Little Auks (<u>Flotus alle</u>) and Kittiwakes (<u>Rissa tridactyla</u>), only solitary birds such as Gulls (<u>Larus sp.</u>), Guillemots (<u>Cepphus grylle</u>), and Fulmars (<u>Fulmarus glacialis</u>) were observed. Some of the birds were seen floating on the sea surface and observed to take off in areas where an oil film covered the surface; however, no smudged birds were observed and the birds in the oiled areas behaved identically to those in unoiled areas. Birds were not observed in direct contact with oil pancakes nor were any troubled or dead birds observed. Furthermore, observations from helicopters did not indicate any effect of the oil on the birds.

Except near birdcliffs, none of which were located in the vicinity of the spill, very few birds were observed either in the spill area or along the cruise track to the south. The stomach contents of a single Fulmar, shot in the spill vicinity, showed no signs of petroleum hydrocarbons with gas

chromatographic analysis. A young Gull with black legs and breast was reported on October 2, 1977 at Savigsivik (76° 02'N 65° 00'W) (~92 nmi to the northwest of the spill site). As the vicinity of the spill area is generally deserted, it is understandable that few oiled birds were reported.

The spill occurred in a location and season such that no harm to birds was observed. However, during another season or near birdcliffs, a spill of the same size as that of the POTOMAC might have caused extensive damage, especially when young birds might be leaving their nests.

10.0 IMPACT ASSESSMENT

10.1 Fate Of The Spilled Oil

On August 6, 1977, approximately 107,000 U.S. gallons (~380 tons) of Bunker-C fuel from the USNS POTOMAC was spilled into Melville Bay, Greenland after a fuel tank was "holed" by a small iceberg. This fuel was a blend of 55 percent pitch (specific gravity 1.054) and 45 percent cutter stock of No. 2 fuel (specific gravity 0.883) which initially remained on the sea surface because its specific gravity of 0.976 was less than that of the surface seawater, 1.024. The floating oil was advected to the north and west by the slow general circulation in the area. Highly variable light winds tended to disperse the oil over a large area. Based on various measurements, it is estimated that the oil was not advected more than 40 nmi from the spill site, with the initial direction being north then shifting to the west after one week. The traces of surface oil found in neuston tows during the return to Thule, Greenland of the USCG icebreaker WESTWIND are believed to have originated by continued light leakage from the holed fuel tank as the POTOMAC continued to its destination at Thule. The return path of the WESTWIND was identical to that of the POTOMAC so that these samples would have been taken where the probability of finding oil from continued leakage was highest. During the two weeks following the spill, the composition of the oil on the sea surface changed through evaporation such that, by August 20, almost all of the low boiling point fraction of the cutter stock, components up to n-C17 (boiling point 300 C), had disappeared. This evaporative loss amounted to about 33 percent of the total spill (35,000 gallons). It is estimated that a great part of the remaining oil (66 percent of the total) sank 1,000 m to the bottom over a large area (~500 sq mi) of Melville Bay, because of the increase in specific gravity of the oil remaining after evaporation. Sinking was confirmed by the visual observation of small flakes (1 cm diameter) within the water column after August 18. It is hypothesized that the flakes were originally the skin of oil lenses which, after depletion of the more volitile components, were sloughed off or exfoliated from the pancakes.

By August 20, only small amounts of oil were observed on the sea surface in the spill area. The oil was in the form of small pancakes (maximum diameter of 5 cm) which had lost almost all of the sheen which had surrounded them earlier. These pancakes were found in windrows several hundred meters long and a few tens of meters wide with a mean spacing of I or 2 meters between pancakes. The total volume of oil in each of these windrows (300 m by 30 m size) was estimated to be about 20 gallons. On August 21 windrows of oil were sighted at 74°55'N, 60°12'W from the ADOLF JENSEN. These were the most southerly observations of the oil. Some, if not all, of this oil may have remained on the surface until it blodegraded or moved out of Melville and Baffin Bays and into the North Atlantic Ocean. Scattered sightings of oil were received from the region over the 9 months following the spill. One sample collected on October 18, 1977, was analyzed by GC and appears to be identical to the POTOMAC oil. Since Melville Bay should have started freezing over by late September, six weeks after the spill, whatever oil remained on the surface would have been trapped into sea ice where it might have become highly visible. Also, the end of the shipping season arrived in early September, effectively removing the possibility of any subsequent sources of spilled oil. Thus it is reasonable to assume that any oil sighted during the next 9 months came from the one known large spill, that of the USNS POTOMAC.

Low concentrations of USNS POTOMAC oil were found in the water column with maximum reported concentrations being between 2.5 and 4.9 ppb. Oil was also found adhering to and injested by some zooplankton.

At the low water temperatures of 4 C, there was virtually no biodegradation of the oil over the duration of the major part of the spill (2 to 3 weeks) as indicated by microbiological studies and chemical analyses (n-C17 / pristine and n-C18 / phytane ratios).

Despite the high asphaltene content (15 percent), the spilled oil did not form a water-in-oil emulsion (mousse). This can probably be attributed to the small amount of mixing energy available (wave heights were typically less than 30 cm) and to the oil temperature being quite close to the pour point for the unweathered Bunker-C fuel.

In summary, the fate of the 107,000 gallons (380 tons) of spilled Bunker-C fuel was that 33 percent (~35,000 gallons) evaporated; the major part of the remaining ~71,000 gallons seems to have sunk in 1,000 meters of water

over a large area of Melville Bay and a small part remained on the surface as small pancakes (maximum diameter of 5 cm). A very samll amount of the oil was accommodated into the water column.

10.2 Impact Of The Spilled Oil On Biota

Melville Bay is not a highly bioproductive area in terms of fisheries, although it is important as a native sealing area. Analyses of plankton samples acquired during Danish trawls indicated that there was oil ingested by some copepods and amphipods. Four percent of the copepods at the spill site (station 5460) were found to be internally contaminated with oil, with lesser amounts observed at other stations. External contamination of plankton was also observed but, because the nets also collected oil, it was not possible to determine whether this contamination occurred before or after the plankters were caught. The actual impact of zooplankton contamination is unknown; however, the consensus of the concerned fisheries biologists is that there would be no lasting effect for two reasons: first, the total occurrence of the contamination was low, with only 4 of 15 stations reporting any occurrence of internal contamination and second, the contamination was observed only during two weeks of the more than 12 week ice-free period. As a worst-case estimate, a maximum of 0.2 percent of the total seasonal plankton might have been contaminated.

Floating white particles, some of which were identified as remains of zooplankton, were observed within windrows in the Melville Bay area. It is believed that these were a naturally occurring phenomona and not related to the spilled oil as they were also observed in nonoiled areas and had been reported in the historical literature.

There was oil contamination on the skins of some seals killed by native hunters after the spill incident. Some of this contamination may have come from the USNS POTOMAC. It is improbable that these instances of oil pollution had any effect on the health or activities of the seals.

Sea birds were rare in the vicinity of the oll spill, and no noticeable impact was observed on the few individuals studied.

10.3 Conclusions

The oil spilled from the USNS POTOMAC significantly contributed to the pollution of Melville Bay which normally has very low petroleum hydrocarbon levels in its surface waters. This incident probably had no lasting effect on the ecology of the region. It is estimated that the greatest part of the spilled oil sank to the bottom where it is expected to remain indefinitely.

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11.0 SIGNIFICANT SCIENTIFIC FINDINGS

During the course of the USNS POTOMAC spill response and the subsequent analysis, there were several findings which are worth isolating either because they were significant with regard to the behavior and fate of the spilled oil or were of interest for ecological reasons.

11.1 Observations On The Behavior And Fate Of The Spilled Oil

Significant rindirers were made concerning the sinking of the oil and the weathering rates in the Arctic environment.

11.1.1 Sinking of the Oil

In terms of the observed behavior of the fuel spilled from the USNS POTOMAC, the sinking of the oil was probably the most important. Eleven days after the spill, flakes of oil were observed within the water column. These flakes were from 5 to 10 mm on a side and about 1 mm thick, resembling soggy breakfast cereal flakes. Two possible mechanisms can be hypothesized for their origin. Either they were the residual of weathered lenses of once floating oil or they were pieces of the skin of oil lenses. Since the pitch component of the blended Bunker-C fuel was significantly denser than seawater, after 73 percent of the cutter stock (33 percent of the original blend) had evaporated, the density of the residual would be high enough to sink. The evidence points to exfoliation of the skin, rather than total weathering of small lenses, as being the origin of the subsurface flakes. This evidence is indicated by the small size of the subsurface flakes as well as the asphaltene analyses of the surface oil. Total weathering of lenses should have produced a size range of subsurface flakes which corresponded to the original lens sizes; however, only small subsurface flakes were observed. The asphaltene analyses are somewhat anomalous, but they do indicate a differential process as the origin of the flakes. It was observed that the asphaltene content of the floating oil remained constant during the first 15 days of weathering. During this same time period, the lighter fractions of the cutter stock were being preferentially removed, presumably by evaporation. To retain the constant levels of asphaltene in the remaining floating oil, the asphaltenes

would have to be removed at a rate proportional to the lighter fractions. Evaporative losses of the asphaltenes appear unreasonable because of their high molecular weight. However, the asphaltenes may have become enriched in the surface layers of the floating lenses by a mechanism such as crystallization or precipitation as the light fractions evaporated. Since the mobility of the hydrocarbons within the bulk oil is limiting for weathering processes (as opposed to the evaporation rate), it is reasonable to expect that the surface skin could be rapidly depleted in the lighter fractions and become significantly denser than the bulk oil of each lens. Given sufficient mechanical energy to peel the the skin from the lens, the skin should be dense enough to sink. The exfoliation process may have been augmented by the plate-like structure of the pitch which formed the larger component of the original blend. The exfoliation explanation for the origin of the flakes could have been confirmed if the apphaltane content of subsurface flakes had been measured; however, the one flake which was collected was too small for this type of analysis. A further caution is that actual instances of exfoliation in the field were not observed. But some mechanism must deplete the asphaltenes in the bull oil; and the exfoliation of weathered skin, which is enriched in apphallemes, is one which appears viable.

The significance of the sinking is that the causative process was not sedimentation but a process possibly more complex than simple evaporative weathering. If the hypothesized exfoliation of lens skin was the actual process, then a relatively new sinking process is brought to light which can potentially cause rapid breakup of oil lenses and (possibly) sinking. The exfoliation process should be investigated further.

11.1.2 Weathering Rates

Over the course of the eight days of field observations, it was noted that the sheen surrounding lenses of thick (ca. 6 mm) oil decreased in area to the point that, by the 14th day after the spill, the sheen was no longer visible. Chemical analyses of the oil remaining in the floating lenses indicated that almost all of the fractions which had GC retention times less than n-C12 were lost. Also, fractions between n-C12 and n-C17 were substantially depleted with losses decreasing as the carbon number got larger. These loss rates were surprising in light of the cold temperature (4 C), low wind speed (maximum of 4 m/s; average of 2 m/s), and the thickness of the

lenses. The loss of sheen at the same time that the lighter fractions vanished suggests that the sheen was composed predominately of these lighter fractions. Thus the generation of sheen serves to deplete the bulk oil (thick lenses) of the lighter fractions by physical fractionation. The increased surface area of the sheen, attributable to the lower surface tensions of the lighter fractions, would allow for increased evaporative losses.

The maximum concentration of petroleum hydrocarbons actually found within the water column appeared on August 13, the first day on which water samples were collected. It amounted from 2 to 6 μ g/l, depending on the method used for quantification.

11.2 Biological Findings

Biological findings included the potential for biodegradation of the spilled oil and further information on some aspects of the ecology of Melville Bay.

11.2.1 Biodegradation

Specific studies using both natural and isolated monocultures of microorganisms were conducted to investigate the potential for biodegradation of the spilled oil. From the collected water samples, eight microbiological strains were found which degraded oil. These represented less than 1 percent of the total organisms found. Of these eight, two were found to degrade paraffins (alkanes) at a temperature of 5 C. At these temperatures, no strains were found which would degrade cycloalkanes or aromatics. As expected at this low temperature of 5 C, the observed degradation rates were slow as evidenced by no increase in the total numbers of oil degrading microorganisms in water samples collected in the oiled area 8 days apart. The lag period for cultured growth appeared to be in excess of 8 weeks using Melville Bay seawater at 15 C temperature. However, the addition of nutrients (1 g/l of K2HPO4 and 2 g/l of NH4NO3) induced more rapid growth at 15 C. With the adde_ nutrients, the lag period was found to be less than 2 weeks.

11.2.2 Zooplankton

Zooplankton samples collected in Melville BAy were dominated by copepods (<u>Calanus hyperboreus</u> and <u>C. glacialis</u>) in trawls integrating the upper water column from 250 meters to the surface. These two species also dominated the Bongo tows taken between 5 and 20 meters deep, while an amphipod (<u>Parathemisto</u> l<u>ibellula</u>) dominated the surface neuston tows. Temporal spacing of the samples precluded more quantitative vertical zonation because of known migration habits. Ingested oil was found in up to 3 percent of the examined copepods at any one station and up to 5 percent of the amphipods.

At several locations within Melville Bay, white particles (opaque fat globules) were observed in windrows where they had been naturally concentrated. In some instances these white particles had remains of copepod tissue associated with them which identified their origin. It is felt that these kills were a natural phenomona and not related to the oil spill because they were found in areas which should not have been affected by any oil from the USNS POTOMAC.

11.2.3 Birds and Mammals

Birds and seals were not abundant in Melville Bay during the August field study period. A few flocks of Auks and Kittiwakes were observed as well as a few solitary Gulls and Fulmars. None were observed to be influenced by the oil. Fifty-five seals were observed, 43 of which were ringed seals. Twenty-five of the seals were spotted well south of the spill site. Only 4 seals were seen in the oiled area; however, no unusual behavior was observed. Starting in September, 5 weeks after the spill, the first of 29 reports of oiled sealskins surfaced. All of these reports came from native eskimo seal hunters. Eighteen of the 29 skins were delivered to Denmark for analyses. Ten of the 18 were surficially contaminated by petroleum hydrocarbons, while the remaining 8 were clean. Seven of the contaminated skins may have contained oil from the USNS POTOMAC. No damage to the skin underneath oiled hair was observed during histological examinations.

11.3 Conclusions

While the Bunker-C fuel spill by the USNS POTOMAC was an unfortunate accident, the incident did produce an opportunity to study the behavior and fate of oil spilled in the Arctic environment. Excellent cooperation among the operational and scientific personnel from the United States, Greenland, and Denmark allowed for a comprehensive study of this spill which not only led to a better understanding of the fate of oil in the cold marine environment but also its impact on Arctic marine ecology.

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13.0 APPENDIX

13.1 Marine Agar

| Bacto-peptone | 5. | g |
|---------------------|--------|----|
| Bacto-yeast extract | 1. | g |
| FeC13 | 0.1 | g |
| Nacl | 19.45 | g |
| Na2504 | 3.24 | g |
| MgCl2 | 8.8 | g |
| CaCl2 | 1.8 | g. |
| KCL | 0.55 | g |
| NaHCO3 | 0.16 | g |
| KBr | 0.08 | g |
| SrCl2 | 0.034 | g |
| H3B03 | 0.022 | g |
| Na25103 | 0.994 | g |
| NaF | 0.0024 | g |
| NH4N03 | 0.0016 | g |
| Na2HPO4 | 3.008 | g |
| Bacto-agar | 15. | g |

To rehydrate the medium, suspend 55.1 g in 1,000 ml of distilled water and heat to dissolve the medium completely. Sterilize in the autoclave for 15 min at 121 C. Adjust pH to 7.6.

13.2 Agar Substrate

| NACL | 24. | g |
|-------------|-----|---|
| Mg504, 7H20 | 0.5 | п |
| KCL | 0.7 | g |
| KH2P04 | 2.0 | g |
| N32HPO4 | 3.0 | g |
| NH4N03 | 1.0 | g |
| Agar | 15. | g |

To rehudrate the medium, suspend 46.2 g in 1,000 ml of distilled water and heat to boiling to dissolve the medium completely. Sterilize for 10 min at 115 C. Adjust pH to 7.1. After Colwell (Mills et al., 1978)

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13.3 Bunch Substrate (used for MPN method)

| Nacl | | 5.53 | g |
|-------------|---------|------|---|
| MgCl2,6H20 | | 2.54 | g |
| KCL | | 0.1 | g |
| CaC15,2H20 | €i | 0.37 | g |
| Tris buffer | (Sigma) | 7.69 | g |
| NH4N03 | | 1.0 | g |
| K2HPO4 | | 0.1 | g |

Add 1.0 ml chelated solution of metal salts (below). The compounds are dissolved in 1,000 ml distilled water. The pH is adjusted to 7.5. After Bunch and Harland, (1976).

Chelated solution of metal salts

| CoC12,6H20 | 0.004 | g |
|---------------|--------|---|
| CuS04, 5H20 | 0.004 | g |
| TeCl3.6H20 | 1.0 (| g |
| ZnS04, 7H20 | 0.3 | g |
| MnS04, H20 | 0.6 | ŗ |
| Na2MoO4, 2H2O | 0.15 0 | 3 |
| E.D.T.A. | 6.0 (| 3 |

These compounds are dissolved in 1.000 mL distilled water and the pH adjusted to 7.5.

13.4 Colwell Substrate (used for MPN method)

| NaCL | 24. g |
|-------------|-------|
| MgS04, 7H20 | 0.5 g |
| KCI | 0.7 g |
| кнаро4 | 2.0 g |
| Na2HPO4 | 3.0 g |
| NH4N03 | 1.0 g |
| | |

To rehydrate the medium, suspend 31.2 g in 1,000 ml distilled water and heat to boiling until the medium is dissolved completely. Sterilize for 10 min at 115 C. The pH is adjusted to 7.1. After Mills et al. (1978).

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