

## Hydrocarbon Biogeochemical Setting of the Baffin Island Oil Spill Experimental Sites. I. Sediments

WALTER J. CRETNEY,<sup>1</sup> DAVID R. GREEN,<sup>2</sup> BRIAN R. FOWLER,<sup>2</sup> BLAIR HUMPHREY,<sup>2</sup>  
DAVID L. FIEST<sup>3,4</sup> and PAUL D. BOEHM<sup>3,5</sup>

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**ABSTRACT.** A baseline for petroleum residues in the sediments of the Cape Hatt region of Baffin Island in arctic Canada was obtained in anticipation of controlled oil releases of the Baffin Island Oil Spill (BIOS) Project. In subtidal sediments, the existing background of petroleum residues has an upper limit in the low to sub  $\mu\text{g}\cdot\text{g}^{-1}$  concentration range. Petroleum was one of a variety of sources identified, including plant paraffin waxes and combustion products. Beach sediment hydrocarbons were quantitatively and qualitatively similar to those of subtidal sediments. The hydrocarbon baseline in sediments of the BIOS study area was found to be as low as might be found anywhere on earth and therefore ideally suited to the BIOS study.

**Key words:** BIOS, arctic marine Canada, hydrocarbon baseline, sediments

**RÉSUMÉ.** On a obtenu un niveau de référence pour les résidus de pétrole dans les sédiments de la région du cap Hatt de l'île Baffin dans l'Arctique canadien, en prévision des déversements de pétrole faits sous contrôle pour le projet BIOS (projet de déversement de pétrole à l'île Baffin). Les résidus de pétrole présents dans les sédiments sous la marée ont une concentration de fond maximum allant d'une fraction de  $\mu\text{g}\cdot\text{g}^{-1}$  à quelques  $\mu\text{g}\cdot\text{g}^{-1}$ . Le pétrole était l'une des sources identifiées, parmi lesquelles se trouvaient aussi des paraffines et des produits de combustion industriels. Les hydrocarbures des sédiments de la plage étaient semblables quantitativement et qualitativement à ceux des sédiments sous la marée. On a trouvé que le niveau de référence des hydrocarbures dans les sédiments de la zone d'étude du projet BIOS présentait des concentrations qui sont parmi les plus faibles qu'on puisse trouver dans le monde, et convenait donc parfaitement à l'étude du projet BIOS.

**Mots clés:** BIOS, Arctique marin canadien, niveau de référence d'hydrocarbures, sédiments

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### INTRODUCTION

#### *Study Perspective and Goal*

This paper is one of a series in a special issue of *Arctic* that describes the Baffin Island Oil Spill (BIOS) Project. The BIOS Project had two objectives. The first was to compare the fate and effects of oil released on the surface of the sea in the arctic nearshore and allowed to beach with those of a similar volume of oil mixed with dispersant and released under the surface nearby. The second was to test experimentally methods for cleaning oil on arctic beaches.

The experimental area selected for the BIOS Project was Cape Hatt on northern Baffin Island (Fig. 1). It was chosen as representative of a high proportion of arctic coastlines. In the area was a series of bays along Ragged Channel on the western side of the Cape Hatt peninsula suitable for controlled oil releases. In Z-Lagoon, on the northeastern side of the peninsula, a further series of bays provided a suitable site for the beach-cleaning experiments. Sergy and Blackall (1987) give a general description of the project and the area. Buckley *et al.* (1987), Sempels (1987), and Dickins (1987) describe the oceanography, geomorphology and sedimentology, and ice conditions respectively and offer detailed information about the characteristics of each bay. Snow *et al.* (1987) provide a general description of the marine biology.

The present paper is part I of a group of three that provides a detailed account of the hydrocarbon biogeochemistry of the area before the experimental oil releases took place. Part II (Cretney *et al.*, (1987a) focuses on the water and part III (Cretney *et al.*, 1987b) on the biota. These three papers also critically review the analytical methods used in the chemical studies and assess the reliability of the data obtained. Dickins *et al.*, (1987) describe

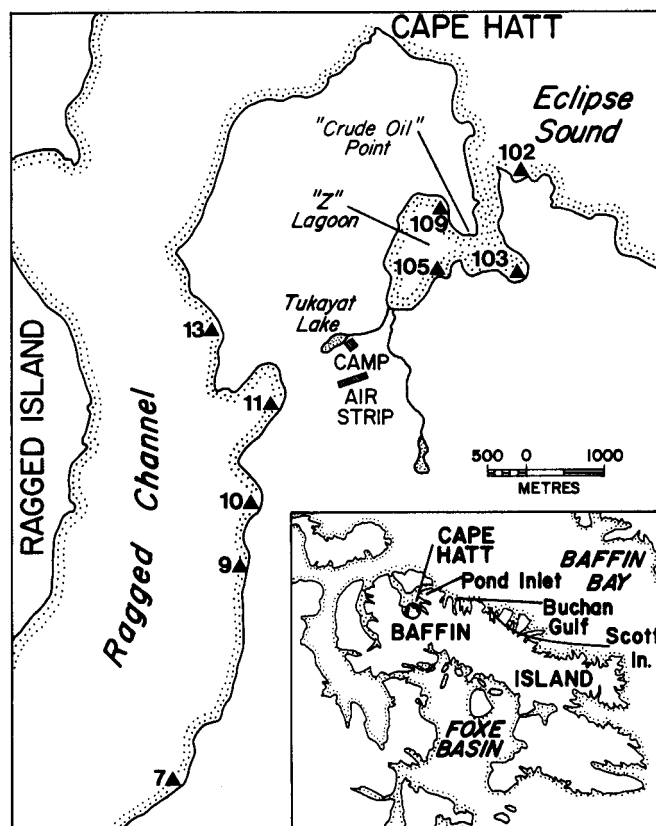


FIG. 1. BIOS site at Cape Hatt, Baffin Island. Experimental bays referred to in this report are numbered.

<sup>1</sup>Institute of Ocean Sciences, Patricia Bay, Department of Fisheries and Oceans, P.O. Box 6000, Sidney, British Columbia, Canada V8L 4B2

<sup>2</sup>Seakem Oceanography Limited, 2045 Mills Road, Sidney, British Columbia, Canada V8L 3S1

<sup>3</sup>ERCO Incorporated, 185 Alewife Brook Parkway, Cambridge, Massachusetts 02138, U.S.A.

<sup>4</sup>Present address: Hewlett-Packard Co., 1775 Minute Man Road, Andover, Massachusetts 01810, U.S.A.

<sup>5</sup>Present address: Battelle Ocean Sciences, 397 Washington Street, Duxbury, Maine 02332, U.S.A.

the actual oil releases. Humphrey *et al.* (1987a,b) deal with the fate of oil in the water column and biota after these occurred. Boehm *et al.* (1987) describe the fate of oil in sediments. These authors used the analytical methods described in this paper.

A prerequisite to fate and effect studies of controlled marine oil releases is a data base of pre-existing environmental hydrocarbons. Establishing this data base, which is generally unavailable in the case of studies initiated in response to accidental marine oil spills, was a priority of the BIOS Project. Furthermore, obtaining some rapid estimates of the general hydrocarbon burden in the area to aid in the experimental plan was deemed a necessity. Because establishing a data base for comparison with the petroleum hydrocarbon levels following the deliberate oil releases was the primary objective, a broad mix of methods was used. In many instances concentrations were measured near the detection limits of the method; because establishing a data base was the primary objective, some interesting findings were not followed up. While the contents of this paper form a complete unit, the reader should consider them in the context of those of its companion papers in this issue of *Arctic*.

#### *Geographical Setting — Global Context*

The BIOS Project study areas (Fig. 1) are remote from centres of industrialization and population. The hydrocarbons found in the environment of areas remote from population centres are generally very low in abundance and have a composition that reflects both local and remote sources (Peake *et al.*, 1972a,b; Wong *et al.*, 1976; Laflamme and Hites, 1978, 1979; Wakeham *et al.*, 1979; Mackie *et al.*, 1978; Platt and Mackie, 1979; Shaw and Baker, 1978; Shaw *et al.*, 1979; Stich and Dunn, 1980; Tan and Heit, 1981; Sporstøl *et al.*, 1983). With regard to the arctic region, evidence has accumulated in recent years of the transportation over thousands of kilometres of significant quantities of airborne pollutants to the Arctic from the lower latitudes (Kerr, 1981; Radke *et al.*, 1984; Oehme and Ottar, 1984).

#### *Geographical Setting — Local Context*

The nearest permanent human settlement to the study area and therefore a potential local source of hydrocarbons is the Inuit village of Pond Inlet, which is about 85 km away. Land and sea activities associated with hunting and fishing thus occur in the study area. Large vessels may occasionally visit the protected waters of Ragged Channel.

Activities associated with the BIOS Project itself increased the potential for oil contamination. Oil for the experiment was stored well inland from the experimental sites, and the BIOS experimenters were cognizant of the need to minimize careless environmental oiling. Only spot oil contamination, perhaps in association with vessel refuelling, seemed possible in view of the low level of human activity in the study area.

The potential for local, natural terrestrial inputs of hydrocarbons in the region appears to be low because of the paucity of vegetation and the short growing season. The sparse vegetation mostly consists of scattered pockets of mosses, lichens and a few vascular plants in the prevailing rocky landscape.

Of particular concern to the experimental plan was the possibility of more than trace concentrations of pre-existing petroleum hydrocarbons in the study area from local oil seep activity. Natural petroleum seepage has contaminated sediments and resulted in surface oil slicks in Buchan Gulf and Scott Inlet

on the northeast coast of Baffin Island (Maclean *et al.*, 1981; Levy and Ehrhardt, 1981). The fate of the oil from the experimental release would be difficult to follow given a high background of petroleum hydrocarbons. In addition, the effects of the oil would be less likely to be discernible in an oil-adapted population than in an oil-free one.

## METHODS

### *Sampling and Analytical Strategy*

Survey sampling (Green, 1981) was done in the 1980 field period as one aspect of the overall pre-oil release assessment of the study area. During this period samples of water, beach and subtidal sediments and marine organisms were collected from various embayments under consideration for the oil release experiments. Sampling for hydrocarbon analyses was done in conjunction with various other studies. Chemists versed in sampling for hydrocarbons were part of the sampling team. Where they could not actually collect the samples themselves, they established procedures for obtaining uncontaminated samples and recorded instances where contamination was suspect because of unsuitable handling procedures.

The locations at which samples of sediment as well as water and marine organisms were collected in 1980 differed from those in subsequent years as refinements were made in the overall BIOS Project design. In 1980, for example, the beach and subtidal sediment samples were collected from locations along the geomorphological transects (Fig. 2). In 1981, the subtidal sediments were collected at specific sites associated with the biological transects (Fig. 3). In 1980, the organism samples were taken in the vicinity of the biological transects but outside the plots established for the experiment. Samples were collected at a water depth of up to 20 m wherever organisms of a particular species seemed abundant.

The mix of analytical procedures was chosen to answer a number of questions about the pre-existing hydrocarbons at the experimental sites. Of most importance, it was necessary to quickly determine total hydrocarbon concentrations in sediment, water and biota in the area. As noted above, too high a background of petroleum hydrocarbons might seriously compromise the goals of the experiment and lead to consideration of alternative sites. There was also a desire to determine the environmental presence or absence of select constituents of the Lagomedio crude oil that had the potential of being "markers" of the oil, i.e., constituents whose presence could be taken as proof of the presence of Lagomedio crude oil. Finally, there was a desire to learn what possible sources contributed hydrocarbons in the study area. If, as hoped, the sites were found to be relatively pristine, then the mixture of hydrocarbons present in samples might reflect diverse sources such as terrestrial plants, marine organisms and industrial soot.

The analytical strategy adopted involved a hierarchy of methods. Quantification was achieved by relatively inexpensive methods involving infrared (IR) or ultraviolet-fluorescence (UV/F) spectrometry. A subset of previously analyzed samples was analyzed by capillary gas chromatography with flame ionization detection (GC/FID), and in turn a subset of these by capillary gas chromatography/mass spectrometry (GC/MS). This strategy was adhered to for the duration of the experiment. The basic analytical strategy was not followed, however, in the case of the samples from 1980. For these samples, more emphasis was



used polycarbonate tubes to scrape off surface samples as close to a specified depth of 2 cm as possible within the 2-3 m and 6-7 m water depth intervals. The scrapings were deposited underwater in Whirlpac bags, which were sealed immediately for transfer to the surface. As soon after collection as possible, the sediment samples were subsampled for hydrocarbon analysis into precleaned aluminum cans. The subsamples were immediately frozen and kept frozen through storage and transportation until analysis. Because there was possible trace contamination from the Whirlpac bags, the samples were analyzed only by IR for total hydrocarbons and extractable organics.

In August 1981 subtidal sediment samples were collected from Bays 7, 9, 10 and 11 prior to the experimental oil releases. At this time, the sampling was not done on the geomorphological transects, but rather within the tissue plots (Fig. 3) established for the biological component of the study (Snow *et al.*, 1987). All the collections were done by divers who swam along the contour lines established for the biological transects at 3 and 7 m water depths to a point corresponding to the centre of each tissue plot and then at right angles a distance that would bring them to the centre of the plot. A sediment sample was collected at an arbitrary location at or near the centre chosen for convenience in sampling. When replicate sampling was required, the same location was arbitrarily resampled.

The sediment samples were collected into precleaned wide mouth jars (240 ml) that had been transported to the bottom with threaded lids in place in a holder capable of holding several jars at a time. The container consisted of a PVC tube sealed at each end with a polyethylene bag for transport through the water surface. A diver removed the lid of a jar underwater, scraped a 2 cm deep layer of sediment into the jar, replaced the lid and returned the jar to the jar holder. Jars were returned in the original sequence to the surface vessel for labelling. Sealing for storage was done by screwing the lid down over a precleaned FEP Teflon sheet (51  $\mu\text{m}$ ). The sediment samples were frozen as soon as possible.

**Beach Sediment Sampling:** On 22 August 1980 beach sediment samples were collected for hydrocarbon analyses on three geomorphological transects in each of Bays 9, 10 and 11 at the high and low tide lines. On the same date and prior to the application of oil, a set of samples was collected from the upper, middle and lower portions of adjacent pairs of plots intended for the shoreline experiments (Owens and Robson, 1987) in Bays 102 and 103. Also, samples were collected at "crude oil" point and across from that point north of Bay 103. Samples (200 g) of surface material were transferred with a trowel into solvent rinsed aluminum cans or glass jars and then frozen.

**Sediment Floc Sampling:** Bays 11, 10, 9 and 7 were sampled for the mobile flocculent material lying on the sediments on 12, 14, 16 and 17 August 1981 respectively. The collections were made by divers using a sampler designed for the purpose (Fig. 4). The basic elements of the sampler were an inverted polyethylene funnel (20 cm diameter) with a line of holes drilled along the perimeter of the large end, a 1 m length of tygon tubing (19.1 mm o.d., 12.7 mm i.d., Type R3603), a submersible pump (Little Giant, model 4E 34R), a metal diverter valve (Kitz, two-way ball valve) and a 142 mm stainless steel filter holder (Millipore, model YY 2214230). The floc was collected on a glass fibre filter (Whatman GF/C or Gelman Type AE) by a diver using the following sequence of steps: The pump was primed with ambient water away from the bottom sediments with the diverter valve directing the flow of water to bypass the filter. The

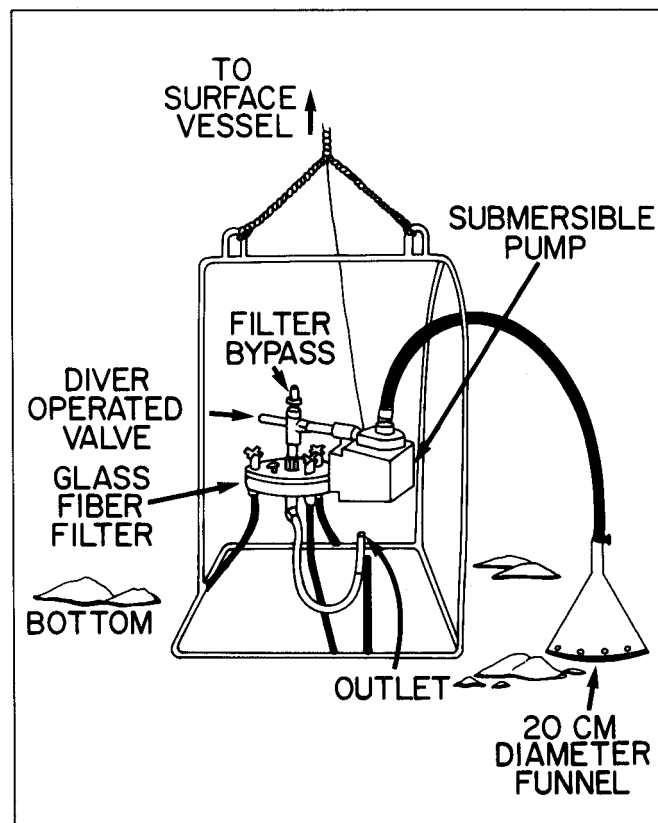


FIG. 4. Sampler used for collecting recently sedimented flocculent material from the surface of subtidal sediments.

sampler was then brought to the bottom and the inverted funnel was placed on the sediment surface. Rotation of the diverter valve into the sampling position caused water to be drawn primarily through the perimeter holes in the funnel. The surface floc that was entrained by the turbulent flow into the funnel was trapped on the glass fibre filter. By holding the inverted funnel to the sediment surface for 30 s in each of four nearby locations, the diver collected surface floc from a total area of slightly more than 0.1 m<sup>2</sup>. The diverter valve was rotated to different locations and while the apparatus was being transported to the sea surface for exchange of filters. The glass fibre filter was folded, placed in an aluminum foil envelope and frozen.

#### Laboratory Methods

Sediment samples were analyzed by a variety of methods, which are summarized in Figure 5. Only selected samples were analyzed by several methods in accordance with the hierarchical analytical strategy. Moreover, the analyses for azaarenes and pentacyclic triterpenes were not repeated for samples collected after the 1980 field season.

Quantification of hydrocarbon-containing isolates and fractions was achieved primarily by gravimetric, IR and UV/F analysis. The presence of the PAH perylene was tentatively identified in some samples by UV/F analysis, although the method was mainly used for non-specified quantification only. GC/FID analysis, though providing quantitative information, was mainly used to provide qualitative compositional information from which possible sources of some hydrocarbons could

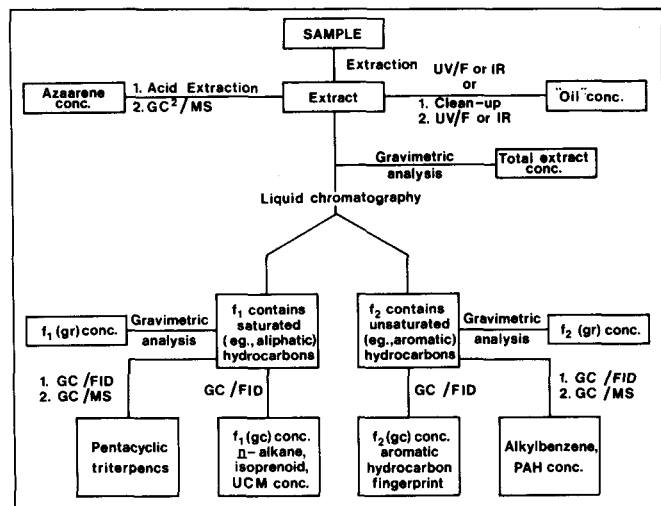


FIG. 5. General isolation, separation and measurement scheme used in the analysis of sediment, water and organism samples.

be inferred. The GC/MS analysis also provided both quantitative and qualitative information. It was used primarily to identify and quantify PAHs, their nitrogen-containing analogues the azaarenes and pentacyclic triterpenes in samples. From the GC/MS evidence, inferences could be made regarding the possible genesis of hydrocarbons such as combustion-derived (pyrogenic), petroleum-oil constituent (petrogenic) or recently biosynthesized (biogenic).

**Extraction of Hydrocarbons from Subtidal and Beach Sediments for IR Analysis:** About 60 g of wet sediment was allowed to air dry and then was weighed and extracted by 5 min agitation in an ultrasonic bath with each of three 40 ml portions of Freon 113. The solvent was recovered after each extraction by filtration. The combined extract was concentrated to a known volume by rotoevaporation and addition of Freon 113.

**Extraction of Hydrocarbons from Subtidal and Beach Sediments for UV/F Analyses** (Brown *et al.*, 1979; Boehm *et al.*, 1982): Wet sediment (ca. 10 g) was weighed into a 50 ml glass centrifuge tube having a Teflon closure. The sediment was dewatered by extracting it with three 15 ml portions of methanol. The sediment was then extracted with four 20 ml portions of dichloromethane:methanol (9:1) by agitating the solvent-sediment mixture each time on an orbital shaker for 10 min. The solvent extracts were combined in a 250 ml separatory funnel containing water (Millipore RO, 50 ml) and acidified to pH 2 with hydrochloric acid. The dichloromethane layer was drawn off and the aqueous layer was extracted with three 15 ml portions of dichloromethane. After the extracts had been combined and reduced in volume (ca. 1 ml) by rotoevaporation, the dichloromethane was displaced as solvent with hexane for UV/F analysis.

**Extraction of Hydrocarbons from Subtidal and Beach Sediments for GC/FID and GC/MS** (Brown *et al.*, 1979; Boehm *et al.*, 1982): Wet sediment (ca. 100 g) was weighed into a 250 ml Teflon jar and dewatered by extracting it with three 75 ml portions of methanol. Two internal standards, androstane and o-terphenyl (5 µg each), were added to the sediment, and the sediment was extracted with three 100 ml portions of dichloromethane:methanol (9:1). Each extraction was accomplished by shaking the mixture on a platform shaker for a

minimum of 4 h. In a separatory funnel (1 l), the combined extracts together with 100 ml of water (Millipore RO) were acidified to pH 2 with hydrochloric acid. After the dichloromethane layer had been drawn off, the aqueous layer was extracted with three 50 ml portions of dichloromethane. The combined dichloromethane extracts were reduced in volume (to ca. 1 ml), and the dichloromethane was displaced with methanol.

After being sealed with a Teflon cap in a 50 ml glass tube containing 10 ml of methanol and 4 ml of 10N aqueous potassium hydroxide, the extract was heated at 80°C for 4 h. The mixture was cooled and then extracted with three 15 ml portions of hexane. The combined extracts were dried over anhydrous sodium sulfate and reduced in volume to about 1 ml by rotoevaporation. Aliquots were evaporated on preweighed balance pans and the residues weighed using an electrobalance.

**Extraction of Azaarenes from Beach Sediments for GC/MS:** The procedures for the extraction of sediments for the UV/F analyses was followed. The hexane solution obtained was further extracted with aqueous 3N hydrochloric acid. The acid extract was washed with hexane, made basic with 6N KOH (to pH 11) and back extracted with dichloromethane. The dichloromethane extract was dried over anhydrous sodium sulphate and concentrated for injection into the GC/MS.

**Extraction of Hydrocarbons from Sediment Surface Floc:** The glass fibre filters containing the floc were cut into small pieces and placed into 250 ml Teflon jars together with 3 µg each of two internal standards (androstane and o-terphenyl) and 100 ml of a mixture of dichloromethane and methanol (9:1). The jars were shaken for 4 h on an orbital shaker, after which time the solvent was decanted off. The extraction procedure was twice repeated with fresh solvent. The three extracts were combined, dried over anhydrous sodium sulfate and reduced in volume to <1 ml by rotary evaporation. The extraction solvent was then displaced with hexane. Aliquots of a known volume of the hexane solution were evaporated on a disposable balance pan and the residual weight determined by difference using an electrobalance (0.1 µg sensitivity).

**Liquid Chromatography of Hydrocarbon Extracts from Beach and Subtidal Sediments:** Polar non-hydrocarbon materials in the Freon 113 extracts obtained from sediments for infrared analysis were removed using Florisil chromatography. Mini-columns consisting of 5% deactivated Florisil (0.7 g) in disposable Pasteur pipettes were charged with the extract, which had been concentrated to about 200 µg and eluted with two bed volumes (1.8 ml) of Freon 113.

Sediment extracts designated for UV/F analysis were cleaned up by alumina column chromatography in a procedure based on that of Goerlitz and Law (1974). An extract in hexane was transferred to the top of a chromatography column (9 mm i.d.) consisting of 7.5% water-deactivated alumina (6.5 g) that had been slurry packed in hexane and washed with an additional 30 ml of hexane. Elution with hexane (25 ml) provided a fraction containing saturated, unsaturated and aromatic hydrocarbons but devoid of more polar fluorescent compounds. After the hexane fraction had been concentrated by rotoevaporation, the hexane was displaced with cyclohexane for the UV/F analysis.

Extracts of sediment samples selected for GC/FID or GC/MS analyses as well as UV/F analysis were separated by silica gel/alumina chromatography. The chromatography column consisted of 100% activated silica gel (11 g), 5% water deactivated alumina (1 g) and activated copper (1 g), which had been wet-packed one upon another in dichloromethane and flushed

with a 30 ml portion of dichloromethane and hexane. Elution of the column with hexane (18 ml) and hexane:dichloromethane (21 ml, 1:1) provided fractions  $f_1$  and  $f_2$  containing mainly saturated and unsaturated (aromatic) hydrocarbons respectively. Aliquots were withdrawn from  $f_1$  and  $f_2$  for gravimetric analysis in the usual manner. Method precisions of 33% for fraction  $f_1$ , 31% for  $f_2$  and 9% ( $f_1 + f_2$ ) were determined as the pooled percentage relative standard deviations for duplicate determinations on two different sediment samples.

**Liquid Chromatography of Hydrocarbon Extracts from Sediment Floc:** The extracts in hexane were fractionated on silica gel/alumina columns as described for the beach and subtidal sediment samples.

**IR Analysis of Hydrocarbon Extracts from Subtidal and Beach Sediments:** The intensity of the 2930  $\text{cm}^{-1}$  peak was measured as above. The same peak was remeasured following column chromatography (see above) to remove polar (non-hydrocarbon) materials.

**UV/Vis Analysis of Hydrocarbon Extracts:** The technique used at the ERCO laboratory was based on those of Wakeham (1977) and Gordon and Keiser (1974). The fluorescence emission intensity of the sample extract diluted with cyclohexane to be within the linear range was recorded using a Farrand Mark I spectrofluorometer in the synchronous scanning mode over the range 250–500 nm with a wavelength differential of 25 nm. The intensity of emission at 350 nm (or the nearest spectral maximum), which corresponded to the peak maximum present in the reference sample of Lagomedio crude oil, was used to determine the concentration of fluorescent compounds in the sample. The concentration was expressed as "equivalents" of Lagomedio crude oil, that is, the concentration of Lagomedio crude oil that would give the same emission intensity at the measurement wavelengths as the fluorescent compounds in a given sediment extract. A method precision of 20% was determined as the pooled relative standard deviation for duplicate determinations on two different sediment samples.

**GC/FID Analysis of Hydrocarbon Containing Fractions:** At ERCO, each fraction ( $f_1$  or  $f_2$ ) was analyzed by fused silica capillary gas chromatography using a Hewlett Packard 5840 or 5880 gas chromatograph equipped with a splitless injector port and a flame ionization detector. Wall coated open tubular (WCOT) columns (0.25 mm i.d.  $\times$  30 m length, J&W Scientific) coated with SE 30 or SE 52 stationary phases were used with helium carrier gas to analyze the  $f_1$  and  $f_2$  fractions respectively. The column ovens were programmed from 40 to 290°C at 3  $^\circ\text{C}\cdot\text{min}^{-1}$ . Compounds were identified by comparing retention indexes of peaks in a standard mixture that was analyzed daily. Concentrations of individual components of  $f_1$  and  $f_2$  were determined from comparison of the integrated peak areas with those of appropriate internal standards (androstane for  $f_1$  and o-terphenyl for  $f_2$ ) following relative response correction. The area of the unresolved complex mixture (UCM) in each fraction was measured using a planimeter. The planimeter areas were converted to electronic integrator area units and summed with the integrator areas of the resolved peaks to provide total areas. The total areas were used to calculate  $f_1$  and  $f_2$  concentrations using androstane and o-terphenyl respectively as the internal quantification standards. Method precision of 8% and 20% for  $f_1$  and  $f_2$  respectively were determined as the pooled relative standard deviation for duplicate determinations on two sediment samples.

**GC/MS Analysis of Hydrocarbon Containing Fractions:** At

ERCO, selected sample fractions were analyzed by GC/MS qualitatively or semi-quantitatively for pentacyclic triterpanes (hopanes) and azaarenes in 1980 samples and quantitatively for polycyclic aromatic hydrocarbons (PAHs) and the dibenzothiophenes in 1980 and 1981 prerelease samples. A Finnegan 4530 gas chromatograph mass spectrometer with Inco data system, which was equipped with a splitless injector and an SE 52 and fused silica capillary column (0.25 mm i.d., 30 m length, J&W Scientific) threaded up to the ion source, was operated in the sequential scanning mode at 70 eV. The oven was programmed from 40 to 290°C at 10  $^\circ\text{C}\cdot\text{min}^{-1}$ . Helium was used as the carrier gas. The system was calibrated daily using perfluorotributylamine (FC43), decafluorotriphenylphosphene (DFTPP) and an aromatic hydrocarbon mixture. o-Terphenyl was used as the internal quantification standard for aromatic hydrocarbons and the dibenzothiophenes. Response factors relative to o-terphenyl were determined for authentic samples of the quantified aromatics or were estimated by interpolation and extrapolation.

Selected ion searches by the data system were used to locate aromatic hydrocarbons (molecular ions), heteroaromatic compounds (molecular ions) and pentacyclic triterpenes ( $m/z$  191). Verification of identity was accomplished by comparison of mass spectra and retention times of determinands with those of authentic samples when available or by comparison with the disc base EPA/NIH library.

**Lead-210 Geochronology:** Three of the cores collected in June 1980 were sectioned for  $^{210}\text{Pb}$  dating. The core sections were analyzed under subcontract by Controls for Environmental Pollution, Inc., Santa Fe, New Mexico. The "bismuth ingrow" technique was used (Koide *et al.*, 1972). The sediment was heated at 400°C for several hours to remove much of the organic carbon and then leached with 6N HCl. The leachate was evaporated to dryness. The residue was dissolved in 1.5N HCl, from which hydrated silica gel was precipitated on warming and removed by centrifugation. A  $^{210}\text{Pb}$ -free lead nitrate solution was added as carrier and the mixture passed through an anion exchange column. After the column was washed with 1.5N HCl, the lead was eluted with distilled water and precipitated at pH 2 with the addition of a saturated solution of sodium sulfate. The radiometric assay of the dried precipitate utilized the growth of the  $^{210}\text{Bi}$  daughter ( $E_{\beta_{\text{max}}}$  1.2 MeV) from the  $^{210}\text{Pb}$  decay ( $E_{\beta_{\text{max}}} = 0.023$  MeV).

#### Quality Control and Assurance (QC/QA)

Energy Resources Co. Inc. (ERCO) maintained a QC/QA program designed to meet standards required by protocols of the U.S. Environmental Protection Agency. The program included routine quality control methods such as use of periodic calibrations, replicate check samples, split samples and spiked samples, as well as frequent sampling and method blanks. Methods were validated prior to use using spiked blanks and naturally contaminated samples. Quality assurance was also obtained through participation in intercalibrations, such as the NOAA-OCSEAP Duwamish River sediment (MacLeod *et al.*, 1982) exercises, in which aromatic and aliphatic hydrocarbon concentrations reported by ERCO were well within accuracy limits set by NOAA and NBS.

Seakem Oceanography Limited also had routine QC/QA methods in place for the analyses and sampling carried out by its personnel. Of particular importance were sample collection, handling and transportation protocols established in consulta-

tion with the scientific staff of ERCO and the Chemistry Technical Committee for the BIOS Project. These protocols, for example, extended to having a Seakem Oceanography scientific staff member accompany all samples air shipped from the BIOS site to ERCO and having an ERCO scientific staff member join the field unit in the summer of 1981, when the experimental oil releases were conducted.

Limits of detection were calculated as twice the standard deviation of the blanks unless otherwise noted. Precision was determined as relative standard deviations expressed as a percentage, because the standard deviations tended to be approximately proportional to means for the data reported here. All precisions are method precisions except when noted.

## RESULTS

**Lead-210 Geochronology:** As anticipated for the area, the three cores from Bays 9 and 13 and Z-Lagoon showed no evidence of an activity gradient in  $^{210}\text{Pb}$ . The method of obtaining and processing the core was not expected to retain any mobile surface material. The sectioning was too coarse to reveal any gradient from bioturbation or chemical mobilization.

**IR Analyses of Subtidal Sediments:** The results (Tables 1 and 2) of the infrared analyses, intended as an inexpensive, rapid survey tool, did demonstrate some statistically significant (95% confidence level) differences among sediment samples. The

TABLE 1. Concentration of extractable organics and hydrocarbons in subtidal sediment samples by IR spectrophotometry — May/June 1980 samples

Location	Sample	Collection date (1980)	Depth (cm)	Water (%)	Extractable organics ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>	Hydrocarbons ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>
Bay 9	CC-14	6 June	c.s. <sup>b</sup>	26.3	3.52	0.37
			0-3	24.3	4.48	0.65
	CC-15 <sup>c</sup>	6 June	9-11	30.6	2.44	n.d.
			17-19	27.7	2.59	0.41
CC-18	18 June	1-3	20.9	5.38	n.d.	
Bay 10	CC-8 <sup>d</sup>	30 May	1-3	28.7	4.79	1.66
			8-10	29.9	1.87	n.d.
			14-16	19.8	1.42	n.d.
	CGS-1	31 May	g.s. <sup>e</sup>	45.4	11.11	3.11
CGS-2	3 June	g.s.	72.5	11.43	1.35	
Bay 13	CC-1 <sup>f</sup>	25 May	3-7	27.2	3.04	0.50
			11-13	29.0	3.81	1.58
			16-18	27.6	1.69	0.68
	CC-2	25 May	1-3	13.7	1.66	n.d.
	CC-6	28 May	3-7	39.4	4.62	1.90
Z-Lagoon	CC-21 <sup>g</sup>	11 June	0-4	31.1	3.82	1.58
			10-14	41.3	1.69	0.37
			19-22	41.1	1.45	0.50
Bay 103	CGS-38	13 June	g.s.	44.1	5.58	1.72
Bay 105	CGS-12	11 June	g.s.	66.8	12.52	3.82
Bay 109	CGS-48	14 June	g.s.	52.5	6.92	1.18

<sup>a</sup>Lagomedio crude oil equivalents per dry unit weight of sediment.

<sup>b</sup>c.s. = core surface sample unspecified depth; other core samples have specified depth segments.

<sup>c</sup>Remains of sea cucumber lying on surface.

<sup>d</sup>Remains of decaying sea cucumber and rock fragments on top of core (0-1 cm).

<sup>e</sup>g.s. = grab sample surface subsample.

<sup>f</sup>Core was thick with dead and live clams.

<sup>g</sup>Decaying organic matter visible on surface of core.

n.d. = not detected; detection limit =  $0.30\ \mu\text{g}\cdot\text{g}^{-1}$ .

TABLE 2. Concentrations of extractable organics and hydrocarbons in subtidal sediment samples by IR spectrophotometry — September 1980 samples

Location	Site description	Water content (%)	Extractable organics ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>	Hydrocarbon ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>
Bay 9	2-3m depth, <sup>b</sup> shoreward of CC-14	26.2	35.9	2.0
	6-7m depth, 1/3 way from CC-14 to CC-15	23.3	7.1	0.6
	2-3m depth, shoreward of CC-12	23.2	23.0	n.d.
	6-7m depth, near CC-12	25.8	22.4	0.9
	2-3m depth, shoreward of CC-18	21.5	9.8	n.d.
	6-7m depth, near CC-18	30.0	22.7	1.5
Bay 10	2-3m depth, shoreward of CC-11	21.1	15.0	0.4
	6-7m depth, near CC-11	27.3	12.9	2.6
	2-3m depth, shoreward of CC-7	17.7	7.2	0.3
	6-7m depth, offshore side of CC-7	24.9	9.4	1.2
	2-3m depth, near CC-9	21.6	24.5	n.d.
	6-7m depth, 1/2 way from CC-9 to CC-10	23.8	7.3	0.6
Bay 11	2-3m depth, south dive profile	32.1	18.6	0.3
	6-7m depth, south dive profile	24.1	10.9	1.5
	6-7m depth, centre dive profile	32.5	14.4	1.4
	2-3m depth, north dive profile	22.4	26.7	n.d.
	6-7m depth, north dive profile	14.4	11.8	1.4

<sup>a</sup>Lagomedio crude oil equivalents per dry unit weight of sediments.

<sup>b</sup>The samples were collected by divers along the geomorphology transects that were used in the May/June sampling period at the estimated water depths recorded. The sampling sites roughly correspond to the 3 m and 7 m depths of the macrobiology benthic transects.

n.d. = not detected; detection limit =  $0.3\ \mu\text{g}\cdot\text{g}^{-1}$ .

surface and near surface (above 3-4 cm depth) sediment samples obtained as core segments and grab sample subsamples in May and June contained significantly less (two sample t-test) extractable organics than did the ones obtained as scrapings by divers in September. With the exclusion of core CC-1, for which the top 3 cm was not analyzed, the core samples (CC-8, CC-15 and CC-21) obtained in May and June and sectioned contained significantly more extractable organic material in the uppermost segment analyzed than was contained in the next lower two segments (two-tailed paired sample and two sample t-tests).

The results for hydrocarbons were much less definite. Indeed, there was not a significant difference in hydrocarbons in the surface sediments between the May/June and the September samplings. The differences between the hydrocarbon concentrations in the uppermost segments and the two next lower segments in the three cores (CC-8, CC-15 and CC-21) were not significant by the paired sample and two sample t-tests.

The results point to a depth gradient in extractable organics and perhaps one in hydrocarbons as well. The difference in extractable organic material between May/June and September 1980, though statistically significant, may be a sampling artifact because of the different sampling methods used and the apparent depth gradient. The September samples, however, all smelled

strongly of sulfide, indicating anoxia, whereas the May/June samples did not.

*UV/F Analysis of Subtidal Sediments and Surface Floc:* The UV/F analysis of selected subtidal sediment samples obtained in June 1980, like the infrared analyses, showed very low equivalent-oil concentrations approaching the detection limit of the method (Table 3). Similar results were found for the sediment samples

TABLE 3. Concentrations of hydrocarbons in subtidal sediment samples by UV/F spectrophotometry — 1980 samples

Bay	Sample	Depth (cm)	Concentration <sup>d</sup> ( $\mu\text{g}\cdot\text{g}^{-1}$ )
10	CC-10	0-2	0.8
	CC-11 <sup>a</sup>	0-2	n.d. <sup>d</sup>
13	CC-4 <sup>b</sup>	0-12	1.0
	CC-5	0-4	0.5
9	CC-12	0-2	n.d.
	CC-16 <sup>c</sup>	0-4	0.6
		10-15	2.2, 3.0
		28-33	1.3
	CC-17	0-2	7.5
105	CC-20	0-2	0.9, 0.7

<sup>a</sup>Sandy with kelp on surface.

<sup>b</sup>Large rock, live clam, rock fragments in top 12 cm excluded, sand analyzed.

<sup>c</sup>Live clams and rocks excluded from analysis.

<sup>d</sup>8% weathered Lagomedio crude oil equivalents measured at 356 nm per unit dry weight of sediment.

n.d. = not detected.

collected in 1981 for the surface floc (Table 4). Both the procedural blank and core cap extracts gave concentrations less than the detection limit. The perylene doublet (Wakeham, 1977) was observed in the synchronous scans of the extracts of many of the subtidal sediment samples. Perylene was confirmed in those extracts selected for GC/MS analysis (see below).

*GC/FID and Gravimetric Analysis of Subtidal Sediments:* GC/FID analysis revealed compositional details about the subtidal sediment hydrocarbons that existed prior to the experimental oil releases and, supplementary to the spectrometric and gravimetric analyses, provided quantitative data concerning individual and groups of hydrocarbons (Table 5). The gravimetric analysis of the  $f_1$  fractions (Table 5) gave gratifyingly comparable results (range: 0.8-7.6  $\mu\text{g}\cdot\text{g}^{-1}$ ) to those for the hydrocarbon fractions obtained by IR analysis (ranges: <0.3-3.8  $\mu\text{g}\cdot\text{g}^{-1}$  and <0.3-2.6  $\mu\text{g}\cdot\text{g}^{-1}$  for Tables 1 and 2 respectively). Given that the samples for GC/FID analysis were prepared using a more efficient extraction procedure than was used for the samples for the IR analysis, it was not surprising that the extractable organics obtained for the GC/FID analysis greatly exceeded in quantity those for IR analysis.

The high pristane:phytane ratios and CPI values (Table 5) determined for the subtidal sediment samples illustrated the dominance of biogenic hydrocarbons over any petrogenic hydrocarbons that might have been present. Gas chromatograms of the  $f_1$  fractions typically (Fig. 6) showed the dominant influence of terrigenous (high molecular weight *n*-alkanes) and marine (pristane and group near *n*-heneicosane) hydrocarbons (Cranwell, 1982; Requejo and Quinn, 1983). Notably absent in most of the

TABLE 4. Concentrations of hydrocarbons in subtidal sediment samples by UV/F spectrophotometry — 1981 samples

Stratum	Plot	Concentration <sup>a</sup> ( $\mu\text{g}\cdot\text{g}^{-1}$ , sediments; $\text{mg}\cdot\text{m}^{-2}$ , floc)							
		Bay 7 <sup>b</sup>		Bay 9		Bay 10		Bay 11	
		Sediment	Sediment	Floc	Sediment	Floc	Sediment	Floc	
10m <sup>c</sup>	N-macro	n.a. <sup>d</sup>	0.36	n.a.	0.75	n.a.	0.43	n.a.	
		0.53	0.37	n.a.	0.48	n.a.	0.38	n.a.	
		0.57	0.46	n.a.	0.19	n.a.	p.r. <sup>e</sup>	n.a.	
		n.a.	0.51	n.a.	0.54	n.a.	0.24	n.a.	
		0.16	0.28	n.a.	0.78	n.a.	0.70	n.a.	
	S-micro	0.43	0.31	n.a.	0.14	n.a.	p.r.	n.a.	
		0.34	0.37	n.a.	0.40	n.a.	0.41	n.a.	
		0.15, 0.79	0.29, 0.47	n.a.	0.19, 0.85	n.a.	0.20, 0.82	n.a.	
		0.62	0.14	0.03	0.38	0.18	0.63	0.19	
		0.50	0.06	n.a.	0.40	n.a.	0.22	n.a.	
7m <sup>f</sup>	1	n.a.	n.a.	0.04	n.a.	0.20	n.a.		
	2	n.a.	n.a.	n.a.	0.44	n.a.	0.50		
	3	0.27	0.36	n.a.	0.18	n.a.	0.99		
	4	0.57	0.37	n.a.	0.18	n.a.	0.99		
	5	0.47	0.18	0.035	0.33	0.19	0.51		
	Geometric mean:	0.26, 0.83	0.05, 0.73	0.01, 0.22	0.17, 0.64	0.10, 0.37	0.19, 1.4	n.a.	
	95% confidence interval:	0.22	0.31	0.05	0.64	0.11	0.12	0.05	
	6	0.20	0.32	n.a.	0.38	n.a.	0.19	n.a.	
	7	0.20	0.32	n.a.	0.38	n.a.	0.19	n.a.	
	8	n.a.	n.a.	0.02	n.a.	0.09	n.a.	0.12	
9	0.82	0.54	n.a.	0.23	n.a.	0.20	n.a.		
3m <sup>f</sup>	10	0.32	0.21	n.a.	0.77	n.a.	0.42	n.a.	
	Geometric mean:	0.33	0.33	0.032	0.46	0.10	0.21	0.08	
	95% confidence interval:	0.12, 0.91	0.18, 0.61	0.00, 11	0.19, 1.1	0.03, 0.36	0.10, 0.48	0.00, 20	

<sup>a</sup>8% weathered Lagomedio crude oil equivalent measured at emission wavelength of 356 nm per unit dry weight of sediment.

<sup>b</sup>No floc samples were analyzed.

<sup>c</sup>Sampled on 8, 14, 23 August; concentrations are listed in order of sampling for each plot.

<sup>d</sup>n.a. = not analyzed.

<sup>e</sup>p.r. = post-release, sample not included.

<sup>f</sup>Bays, 7, 9, 10, 11 were sampled on 17, 10, 14 and 12 August respectively at the 7 m and 3 m depth strata.

<sup>g</sup>n.d. = not detected; detection limit — 0.01  $\text{mg}\cdot\text{m}^{-2}$ .



TABLE 5. Hydrocarbon geochemical data for subtidal sediment samples by GC/FID — 1980 samples

Bay	Sample	Concentration ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>		Pristane: phytane Ratio	Fraction 1		Concentration ( $\mu\text{g}\cdot\text{g}^{-1}$ )		Fraction 2		Fraction 3 <sup>b</sup>	
		Extractable Organics <sup>b</sup>	CPI <sup>c</sup>		ng·g <sup>-1</sup>	Phytane <sup>d</sup>	Resolved <sup>d,e</sup>	Total <sup>b</sup>	Resolved <sup>d,e</sup>	Total <sup>b</sup>	Concentration ( $\mu\text{g}\cdot\text{g}^{-1}$ ) <sup>a</sup>	Total <sup>b</sup>
10	CC-10	660	10.8	7	2	0.3	0.4	2.0	0.8	175	121	
	CC-11	92	6.2	3	2	0.6	0.1	7.6	0.1	9.3	13.4	
13	CC-4	329	5.1	5	5	1	0.4	1.6	0.5	32.3	143	
	CC-5	155	6.1	6	6	1	0.7	6.0	0.7	11.4	42.5	
9	CC-12	301	7.2	>20	2	n.d. <sup>g</sup>	0.4	0.8	0.7	29.4	69.6	
	CC-16	228	10.0	8	8	1	0.4	2.0	0.4	31.2	43.2	
	(0-4cm)											
	CC-16	289, 341	6.1, 9.2	7, 14	7, 7	1.0, 0.5	0.7, 0.6	3.6, 2.0	1.1, 0.8	23.5, 40.6	73.3, 116	
	(10-15cm)											
	CC-16	333	5.8	15	15	1	0.7	1.6	0.7	18.8	94	
	(28-33cm)											
	CC-17	89	3.3	12	12	1	0.2	1.6	0.1	11.3	33	
105	CC-20	337, 323	5.3, 5.5	10, 9	10, 9	1, 1	0.6, 0.6	2.6, 1.9	1.1, 1.4	63.7, 47.4	107, 115	

<sup>a</sup>With respect to dry weight of sediment sample.

<sup>b</sup>Weight in extract or fraction thereof determined gravimetrically.

<sup>c</sup>CPI = carbon preference index =  $2[(n-C_{27}) + (n-C_{29})] / [(n-C_{26}) + 2(n-C_{28}) + (n-C_{30})]$ .

<sup>d</sup>Determined by GC/FID.

<sup>e</sup>Sum of all the resolved peaks in chromatogram.

<sup>f</sup>Sample was divided and duplicate subsamples analyzed by GC<sup>2</sup>/FID.

<sup>g</sup>n.d. = not detected; detection limit =  $0.1\mu\text{g}\cdot\text{g}^{-1}$ .

<sup>h</sup>Eluted with methanol.

chromatograms was a prominent UCM. Its presence in chromatograms of a few samples might represent the residuum of petroleum inputs.

The gas chromatograms of the  $f_2$  fractions were typified (Fig. 6) by what were tentatively identified as olefinic hydrocarbons of biogenic origin. Program restraints prevented further characterization of these compounds. Neither a suite of resolved aromatic hydrocarbons nor a prominent UCM of aromatic hydrocarbons was indicated in any of the chromatograms.

*GC/MS Analysis of Subtidal Sediments:* As suggested by the low values obtained by UV/F analysis and the apparent lack of peaks attributable to aromatic hydrocarbons in the gas chromatograms, GC/MS analysis revealed only very low concentrations of aromatic compounds (Table 6). About equal

TABLE 6. Concentrations of aromatic compounds in subtidal sediment samples by GC/MS — 1980 samples

Bay	Concentration ( $\text{ng}\cdot\text{g}^{-1}$ ) <sup>a</sup>		
	9	10	13
Sample:	CC-16	CC-10	CC-5
Compound <sup>b</sup>			
Phenanthrene	1.6	1.4	1.6
Methylphenanthrenes	2.0	1.2	1.9
Fluoranthene	n.d.	n.d.	0.3
Pyrene	0.5	n.d.	0.4
Chrysene	n.d.	n.d.	0.6
Perylene	2.8	10.4	0.9

<sup>a</sup>Weight of aromatic compound per unit dry weight of sediment.

<sup>b</sup>Mass chromatograms for molecular ions corresponding to aromatic compounds were used for quantification. In general, the searches included alkyl homologues containing one to four carbon atoms of aromatic compounds containing one to five rings.

n.d. = not detected; detection limit =  $0.01\text{ng}\cdot\text{g}^{-1}$ . Only compounds that occurred at a concentration greater than the detection limit in at least one of the three samples are reported.

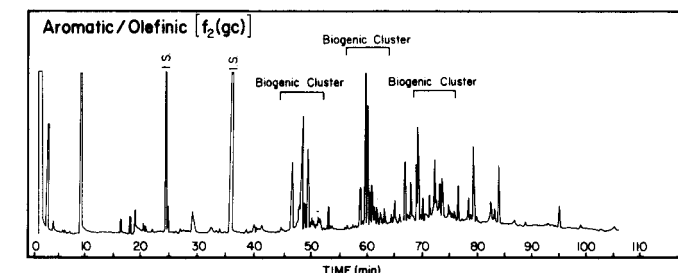
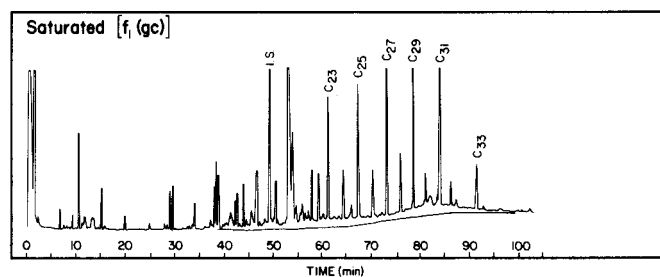


FIG. 6. Representative capillary gas chromatograms of liquid chromatography fractions  $f_1$  and  $f_2$  of subtidal sediment sample extracts.

concentrations of phenanthrenes were present in the three subtidal sediment samples analyzed. The parent and monomethyl phenanthrenes were nearly equal to each other in concentration, while the di- and trimethylphenanthrenes were more than an order of magnitude less concentrated at less than the detection limit of  $0.01\text{ng}\cdot\text{g}^{-1}$ . Curiously, in the three samples analyzed the methylphenanthrenes were identified as the 2- and 3-methyl isomers. If the other two common isomers, the 1- and 9-methylphenanthrenes, were present, it was in concentrations below the detection limit. In Lagomedio crude oil all four isomers were found to be present in about equal amounts.

The four-ring hydrocarbons fluoranthene, pyrene and chrysene were detected in the Bay 13 sample and pyrene was detected in the Bay 9 sample. The alkyl derivatives of these aromatic hydrocarbons were below the detection limit, however.

Perylene was prominent in all three sediment samples exam-

ined by GC/MS. The concentrations of this PAH, on the basis of the three samples, appeared to be positively correlated with the concentrations of extractable organics and total hydrocarbons. The phenanthrenes, by comparison, showed no such relationship.

Reconstructed ion chromatograms for the  $m/z$  191 fragment from the GC/MS analyses of the  $f_1$  fractions of the subtidal sediment samples from Bays 10 and 13 indicated the presence of low concentrations of pentacyclic triterpenes of the hopane series (Table 7). The detectable compounds all appeared to have the  $17\alpha$ ,  $21\beta$  configuration. Further, the ratios of the two diastereomers at position 22 were 1:1 for homohopane ( $C_{31}H_{54}$ ) and bishomohopane ( $C_{32}H_{56}$ ).

TABLE 7. Pentacyclic triterpanes in subtidal sediment samples by GC/MS

Bay: Sample: Compound <sup>a</sup>	10 CC-10	13 CC-5
$18\alpha(H)$ - 22,29,30-trisnorhopane	+ <sup>b</sup> (3) <sup>c</sup>	+(3)
$17\alpha(H)$ - 22,29,30-trisnorhopane	+(4)	+(5)
$17\alpha(H)$ - 30-norhopane	+(10)	+(9)
$17\alpha(H)$ - hopane	+(15)	+(11)
(22S)- $17\alpha(H)$ - homohopane	+(6)	+(4)
(22R)- $17\alpha(H)$ - homohopane	+(5)	+(3)
(22S)- $17\alpha(H)$ - bishomohopane	—	+(3)
(22R)- $17\alpha(H)$ - bishomohopane	—	+(2)

<sup>a</sup>Tentative identifications based on characteristic fragment ion  $m/z$  191, molecular ion and common known pentacyclic triterpanes found in sediments.

<sup>b</sup>+ presence of  $m/z$  191 and molecular ion corresponding to a pentacyclic triterpane; — absence of  $m/z$  191, molecular ion or both.

<sup>c</sup>Estimated concentrations in  $ng\ g^{-1}$  dry weight of sediment based on  $m/z$  191 fragment; brackets denote tentative nature of assignment and quantification.

**IR Analysis of Beach Sediments:** The concentrations of extractable organics (Table 8) in beach sediments by IR analysis were found to be generally about 10% of those determined for the subtidal sediments. A similar large difference in hydrocarbon concentrations was not observed. Given that there is uncertainty in the data, the concentrations of hydrocarbons determined by the IR method appeared to be about the same in beach and subtidal sediments.

**UV/F Analysis of Beach Sediments:** The UV/F analyses of the beach sediments gave results similar to those of the subtidal sediments. The concentrations (Table 8) in the beach sediments were about the same as those in the subtidal sediments. The perylene doublet was observed in the synchronous spectra of several of the beach sediments.

**GC/FID and Gravimetric Analyses of Beach Sediments:** Because the beach sediment samples were subsampled for analysis by IR and gravimetric methods, a comparison of the  $f_1$  gravimetric concentrations (Table 9) with the IR hydrocarbon concentrations (Table 8) using the Spearman rank correlation was possible. The correlation coefficient  $r_s$  ( $n = 20$ ) was only 0.23 ( $0.5 > p > 0.2$ ), however. The smallness of the coefficient and the lack of significance at the 95% confidence level ( $p < .05$ ) was hardly surprising, given the nature of the data. The concentration range was small and near to the detection limit. As stated earlier, the standard deviations were comparable to or greater than the means. As in the case of the subtidal sediments, nevertheless, the gravimetric and IR analyses did generally

TABLE 8. Concentration of extractable organics and hydrocarbons in beach sediment samples by IR and UV/F spectrophotometry — August 1980 samples

Location	Sample	Collection date (1980)	Water content (%)	Extractable organics ( $\mu g\ g^{-1}$ ) <sup>a</sup>	Hydrocarbons by IR ( $\mu g\ g^{-1}$ ) <sup>a</sup>	Hydrocarbons by UV/F ( $\mu g\ g^{-1}$ ) <sup>a</sup>
Bay 9	9-S-L <sup>b</sup>	22 Aug	7.4	0.69	0.37	0.1
	9-S-H		2.3	0.64	n.d.	0.2
	9-C-L		10.1	0.38	n.d.	0.6
	9-C-H		2.2	1.18	0.48	0.3
	9-N-L		7.0	1.00	1.00	0.2
	9-N-H		4.1	0.73	0.39	0.2
Bay 10	10-S-L	22 Aug	8.4	2.99	2.30	0.2
	10-S-H		13.4	0.33	n.d.	0.1
	10-C-L		11.9	1.26	0.60	0.6
	10-C-H		7.8	0.32	0.32	0.2
	10-N-L		12.0	0.60	0.42	0.6
	10-N-H		9.1	0.41	n.d.	0.3
Bay 11	11-S-L	22 Aug	13.7	0.69	0.29	0.3
	11-S-H		12.9	1.37	0.42	0.4
	11-C-L		5.5	0.67	n.d.	0.1
	11-C-H		14.1	0.89	0.89	0.1
	11-N-L		10.8	1.06	n.a.	0.1
	11-N-H		14.0	1.22	n.d.	n.d.
Crude oil point	T-1 (pre-spill)		n.a.	0.43	0.27	0.2
	T-2 (pre-spill) <sup>c</sup>		n.a.	2.47	1.77	n.a.
Bay 102	H-1 + H-2		n.a.	n.d.	n.d.	n.d.
Bay 103	L-1 + L-2		n.a.	1.29	0.48	0.3

<sup>a</sup>Lagomedio crude oil equivalents per dry weight of sediment.

<sup>b</sup>Code means: Bay 9—south transect—low tide mark; for other samples C and N are centre and north transects respectively and H refers to the high tide mark.

<sup>c</sup>H-1 + H-2 denotes a composite sample.

n.d. = not detected; detection limit =  $0.25\ \mu g\ g^{-1}$ (IR),  $0.1$  (UV/F).

n.a. = not analyzed.

agree as measures of the magnitude of hydrocarbons present in the beach sediments. Not unexpectedly, the  $f_2$  gravimetric concentrations did not show a significant correlation with the UV/F concentrations for the beach sediment samples:  $r_s$  ( $n = 21$ ) =  $-0.25$  ( $0.5 > p > 0.2$ ). The  $f_2$  fractions of the beach sediments tended to be dominated by putative biogenic hydrocarbons (Fig. 7).

The gas chromatograms (e.g., Fig. 7) of the  $f_1$  fractions from the beach sediment samples were very similar to those of the subtidal sediment samples. In the  $n$ -heneicosane ( $n-C_{21}$ ) to  $n$ -tritriacontane range ( $n-C_{33}$ ), the  $n$ -alkanes with an odd number of carbon atoms were more abundant than their even-numbered homologues. As in the subtidal sediment, pristane was much more abundant than phytane. Indeed, the pristane:phytane ratios for the beach sediment samples were generally higher than those for the subtidal sediment samples. Furthermore, whereas a few of the offshore sediment samples yielded chromatograms of the  $f_1$  fraction having a definite UCM, the chromatograms for the beach sediments were uniformly devoid of that feature.

**GC/MS Analysis of Beach Sediments:** Although there were only five beach sediments analyzed, a correlation between the results of the GC/MS analysis (Table 10) and those of the UV/F analyses (Table 8) was sought. A correlation coefficient  $r_s$  ( $n = 5$ ) of  $0.60$  ( $0.5 > p > 0.2$ ) was obtained by comparing the sum of the phenanthrene concentrations determined by GC/MS with the concentrations determined by UV/F spectrometry. By including the three subtidal sediments analyzed by GC/MS to raise the number of comparisons to eight, the Spearman rank correlation coefficient scarcely changed to  $0.61$  ( $0.2 > p$

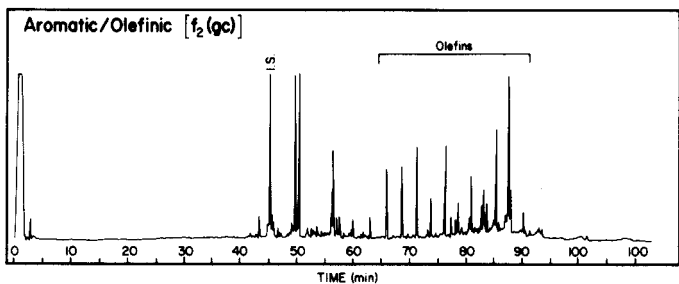
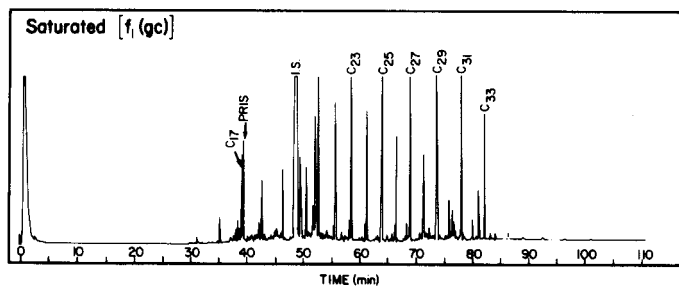
TABLE 9. Hydrocarbon geochemical data for beach sediment samples by GC/FID — 1980 samples

Location	Sample	Concentration <sup>a</sup> (μg·g <sup>-1</sup> )									
		Fraction 1					Fraction 2				
		Extractable organics <sup>b</sup>	CPI <sup>c</sup>	Pristane: phytane ratio	(ng·g <sup>-1</sup> )		(μg·g <sup>-1</sup> )		(μg·g <sup>-1</sup> )		
			Pristane <sup>d</sup>	Phytane <sup>d</sup>	Resolved <sup>d,e</sup>	Total	Resolved <sup>d,e</sup>	Total <sup>b</sup>			
Bay 9	9-S-L	2.0	n.d.	10	2	0.2	0.03	0.2	0.013	0.4	
	9-S-H	3.9	4.0	—	n.d.	n.d.	0.04	0.6	0.05	0.2	
	9-C-L	1.0	9.3	—	n.d.	n.d.	0.03	0.1	n.d.	0.1	
	9-C-H	4.5	2.8	—	1	n.d.	0.02	1.7	0.008	0.1	
	9-N-L	0.7	2.5	—	n.d.	n.d.	0.03	0.17	0.007	0.26	
	9-N-H	6.2	4.1	—	n.d.	n.d.	0.1	0.12	0.06	0.12	
Bay 10	10-S-L	13.9	5.5	17	5.0	0.3	0.08	3.1	0.1	1.2	
	10-S-H	14.8	2.3	—	1	n.d.	0.04	3.0	0.02	1.1	
	10-C-L	81.3	4.0	17	22	1.3	0.35	2.5	0.15	5.2	
	10-C-H	3.5	2.7	—	1	n.d.	0.04	0.3	0.05	0.2	
	10-N-L	65.8	3.5	17	17	1	0.28	10.6	0.11	3.0	
	10-N-H	1.3	4.2	25	5	0.2	0.05	0.2	0.02	0.3	
Bay 11	11-S-L	26.0	9.5	13	6.5	0.5	0.30	2.2	0.10	1.7	
	11-S-H	70.0	10.8	50	10	0.2	0.45	2.9	0.37	2.7	
	11-C-L	14.7	4.5	29	5.8	0.2	0.04	2.1	0.04	1.0	
	11-C-H	54.1	4.6	34	3.4	0.1	0.28	4.8	0.39	2.1	
	11-N-L	38.6	4.6	170	17	0.1	0.12	5.9	0.17	2.4	
	11-N-H	55.7	8.8	10	2	0.2	0.10	2.7	0.5	2.5	
Crude Oil Pt.	T-1	2.2	12.4	1500	75	0.05	0.5	0.6	0.17	0.3	
Bay 102	H-1+H-2	1.3	7.8	—	n.d.	n.d.	0.01	0.2	0.04	0.3	
Bay 103	L-1+L-2	1.5	7.3	—	n.d.	n.d.	0.07	0.1	0.05	0.1	

<sup>a</sup>With respect to dry weight of sediment sample.<sup>b</sup>Weight of extract or fraction thereof determined gravimetrically.<sup>c</sup>CPI = carbon preference index.<sup>d</sup>Determined by GC<sup>2</sup>/FID.<sup>e</sup>Sum of all the resolved peaks in chromatogram.

n.c. = not calculated.

n.d. = not detected.

FIG. 7. Representative capillary gas chromatograms of liquid chromatography fractions  $f_1$  and  $f_2$  of beach sediment sample extracts.

>0.1), although the confidence level increased. Even though weak positive correlation was found (at the 80% confidence level), the results indicated that the UV/F method of analysis

may well be responding to three- and four-ring PAHs, among other fluorescent compounds.

Perylene was found to be a prominent PAH in three of the

TABLE 10. Concentrations of aromatic compounds in beach sediment samples by GC/MS — 1980 samples

Compound <sup>b</sup>	Concentration (ng·g <sup>-1</sup> ) <sup>a</sup>				
	9		10		11
Sample:	9-C-L	9-C-H	10-N-L	10-N-H	11-C-L
Phenanthrene	0.3	0.3	2.6	0.5	0.3
Methylphenanthrenes	0.4	n.d. <sup>c</sup>	5.6	0.9	0.5
Dimethylphenanthrenes	0.2	n.d.	3.1	0.5	n.d.
Trimethylphenanthrenes	0.1	n.d.	1.9	0.3	n.d.
Fluorene	0.03	n.d.	0.4	0.03	n.d.
Methylfluorenes	0.1	n.d.	1.6	0.2	n.d.
Dimethylfluorenes	n.d.	n.d.	1.7	0.2	n.d.
Trimethylfluorenes	n.d.	n.d.	1.0	n.d.	n.d.
Methyl dibenzothiophenes	n.d.	n.d.	0.8	n.d.	n.d.
Fluoranthene	0.4	n.d.	0.3	0.1	0.05
Pyrene	0.3	n.d.	1.6	0.2	0.15
Benz[a]anthracene	0.1	n.d.	1.0	0.1	0.07
Chrysene/triphenylene	0.1	n.d.	1.0	0.1	0.07
Benzofluoranthenes	0.1	n.d.	1.6	0.2	0.02
Benzopyrenes	0.1	n.d.	1.8	0.2	0.04
Perylene	n.d.	n.d.	3.3	0.1	0.2

<sup>a,b,c</sup>See footnotes to Table 6 for explanation.

beach sediments analyzed by GC/MS, corroborating the UV/F results that indicated its presence. In the five beach sediments analyzed there was also a positive correlation of modest significance between the concentrations of perylene and those of total hydrocarbons and extractable organics ( $r_s = 0.83$ ,  $0.2 > p > 0.1$ ).

In contrast to what was observed for the three offshore sediment samples studied by GC/MS, the beach sediment samples with detectable monomethyl phenanthrenes contained measurable quantities of 1- and 9- (and/or 4-) methylphenanthrenes as well as the 2- and 3-methylphenanthrenes. Also, three beach sediment samples contained measurable quantities of dimethyl- and trimethylphenanthrenes, which were below the detection limit in the subtidal sediment samples analyzed. In general, the distributions of alkylated phenanthrenes and fluorenes were more like oil than combustion product. In contrast to the petrogenic appearance of the phenanthrene and fluorene distribution, the distributions of the four- and five-ring PAHs were distinctly pyrolytic in appearance — i.e., only the parent PAHs were detectable.

The presence of what appeared to be azaarenes was indicated in the two beach sediments studied, 10-C-L and 11-C-L. The identification was based on mass spectral searches for molecular ions in the quinoline, acridine/phenanthridine and benzacridine/phenanthridine series and on retention times. Although the compounds were at the detection limit of  $1 \text{ ng}\cdot\text{g}^{-1}$  in beach sediment samples 10-C-L and 11-C-L, alkylated acridines/phenanthridines appeared to be present in distributions similar to that of Lagomedio crude oil.

Pentacyclic triterpanes were present, if at all, in concentrations less than the detection limit in the six beach samples examined (10-C-L, 10-N-L and -H, 9-C-L and -H and 11-C-L). The sediment sample 10-C-L was a possible exception in that peaks in the  $m/z$  191 ion chromatograms corresponding in retention time to homohopanes and bishomohopanes were present.

#### DISCUSSION

Consideration of the results of the hydrocarbon survey of the Cape Hatt area of Baffin Island indicates that the nature of the area is predominantly pristine and therefore ideally suited to experiments such as the BIOS Project. Despite this predominantly pristine nature, however, there is evidence of low-level inputs of combustion or petroleum-derived hydrocarbons into the sediments. Further, the results spotlight some interesting features of the hydrocarbon geochemistry, whose in-depth study was beyond the original scope and intent of the BIOS Project.

The evidence that was gathered using the IR, UV/F, GC/FID and GC/MS methods of analysis indicates that the sediments of the study area are naturally impacted by a variety of hydrocarbon sources. There is no evidence of more than trace oiling from any oil seeps that may be nearby or from the more distant ones at Buchan Gulf on Scott Inlet. Indeed, a case can be made for long-range eolian transport and local biogenesis to account for the sedimentary hydrocarbon content.

The quantitative analyses of the sediment samples show that the hydrocarbon concentrations found in the Cape Hatt study areas are as low as those reported for remote marine sites anywhere (Clarke and MacLeod, 1977). The concentrations of "petroleum residues" in the bottom sediments of Buchan Gulf and Scott Inlet troughs as determined by UV/F analysis are

generally in the range  $5.0\text{--}7.5 \mu\text{g}\cdot\text{g}^{-1}$ , with concentrations  $>10 \mu\text{g}\cdot\text{g}^{-1}$  in the seep zones (Levy and Ehrhardt, 1981). Levy and Ehrhardt (1981) also report concentrations  $<2.5 \mu\text{g}\cdot\text{g}^{-1}$  in sediments some tens of kilometres from the seep zones but within a few kilometres of shore. If it is assumed that the oil concentrations expressed as Bunker C and Lagomedio crude oil equivalents do not differ by more than a factor of two to three, then the Cape Hatt sediments would appear to be at worst no more contaminated than the Baffin Island Shelf sediments some tens of kilometres from the identified oil seeps in the Buchan Gulf and Scott Inlet areas.

The concentrations of individual PAHs in beach and subtidal sediment samples in the low to sub  $\text{ng}\cdot\text{g}^{-1}$  (parts per billion) range are as low as has been reported for sediments in areas remote from industrial civilization (Laflamme and Hites, 1978; Windsor and Hites, 1979; Platt and Mackie, 1979; Sporstøl *et al.*, 1983). Thus, the quantitative methods employed in the study all attest to a lack of significantly larger inputs of petrogenic or pyrogenic hydrocarbons into the study area compared to other similarly isolated locations in the world.

Although the low hydrocarbon concentrations found in the sediment samples severely tested the analytical methods used, some useful qualitative information is obtainable from the gas chromatograms, mass chromatograms and synchronous UV/F scans regarding the source of some of the sedimentary hydrocarbon components. Components are identifiable as likely being marine or terrestrial biogenic, pyrogenic or petrogenic. High concentrations of pristane relative to phytane in most of the beach and subtidal sediments indicate a marine biological source for some of the sedimentary hydrocarbons. This indication is supported by the presence of a cluster of prominent peaks in the chromatograms of subtidal sediments having retention times close to that of *n*-heneicosane. This cluster is a common feature of coastal marine subtidal sediments and is believed to be of marine biological (planktonic or bacterial) origin (Barrick *et al.*, 1980; Requejo and Quinn, 1983).

A terrestrial biological source of other sedimentary hydrocarbons is indicated by the predominance in the *n*-heneicosane to *n*-triacontane range of *n*-alkanes having an odd number of carbon atoms (CPI values from 3-12). As noted above, a local source of plant waxes may be questioned and the possibility that the *n*-alkanes may have been imported from the lower latitudes on eolian particles (Radke *et al.*, 1984) must be considered as possible. Airborne particles collected elsewhere have been characterized by CPI indexes in the 2-10 range (Simoneit, 1977; Simoneit *et al.*, 1977; Marty and Salot, 1982).

A case for long-range transport of hydrocarbons, in this case combustion derived, into the study area can be made from the alkyl distributions of four- and five-ring PAHs (Laflamme and Hites, 1978) in the intertidal and beach sediment samples from the Cape Hatt area. PAHs such as pyrene, fluoranthene, chrysene, benz(a)anthracene and benzo(a)pyrene are found in a strong excess over their alkylated congeners where measurement was possible. Distributions strongly favouring alkyl unsubstituted PAHs are also characteristic of some long-range transported particulates (Lunde and Bjorseth, 1977), and evidence is mounting for the transport of airborne pollutants in general to the Arctic from industrial centres in Eurasia and North America (Kerr, 1981; Oehme and Ottar, 1984).

The possibility of *in situ* genesis of PAHs is indicated by the presence of perylene as a major PAH in almost all the beach and subtidal sediments. Perylene concentrations covary with extract-

able organic concentrations in the sediment samples studied. Unfortunately, a definitive source identification for the perylene must await further study, because it is also produced in combustion processes. Despite probable modes of *in situ* diagenesis (Laflamme and Hites, 1978; Wakeham *et al.*, 1979), the correlation may be coincidental and not signify a common source (Prah and Carpenter, 1983).

The distributions of alkylated three-ring aromatic hydrocarbons in the beach and subtidal sediment samples suggest that there may be petroleum source contributing to the sedimentary hydrocarbons in the study areas. The methylphenanthrene/phenanthrene ratios generally fall in the range 1-2, which is between the ranges accepted for combustion (0.5-1) and petroleum (2->6) (Prah and Carpenter, 1983). The distribution of the alkylated acridines/phenanthridines in the two beach samples studied supports this view. Aside from possible local contamination by vessel traffic and human activities, the possibility of seep oil as a source comes to mind. In this regard a local seep source need not be postulated, if it can be accepted that oil-containing aerosols emitted from the sea by bursting bubble processes (Marty *et al.*, 1984) in the area of Buchan Gulf and Scott Inlet may be borne by the wind and deposited in the Cape Hatt area. Also, water-borne oil may be transported by water currents, although the currents flow predominantly southerly along the northeast coast of Baffin Island (Lemon and Fissel, 1982).

The apparent absence in the subtidal sediments in the 1- and 9- (and/or 4-) methylphenanthrenes and their more alkylated homologues, even though easily measurable amounts of the 2- and 3-methylphenanthrenes are present, is a mystery. One is led to ponder the possibility of a diagenic pathway from some biogenic precursor, although the evidence does not point to a tricyclic diterpenoid precursor, such as abietic acid, because of the absence of hydrocarbons predicted by the commonly accepted pathway (Cranwell, 1982). Wakeham *et al.* (1980), however, have presented evidence suggesting alternative diageneses of the phenanthrenes in sediment. Another possibility is selective biodegradation. The available evidence seems not to support this proposition. For example, Rowland *et al.* (1986) have shown that the laboratory biodegradation of North Sea Brent crude oil in the presence of a recent marine sediment from Scotland occurred with a more rapid utilization of 1-, 2- and 3-methylphenanthrenes than 9-methylphenanthrene.

The pentacyclic triterpanes of the hopane family, which were detected at low concentrations (20 ng·g<sup>-1</sup>) in the subtidal sediments, but not in the beach sediments, indicate the presence of mature sediments or ones contaminated by petroleum oil. The presence of a distinctive and very broad unresolved complex mixture in the GC/FID traces from several subtidal sediments is a common feature of mature or petroleum-contaminated sediments. As possible sources of the UCM and pentacyclic triterpanes, atmospheric aerosols from the seep area or particulates from the lower latitudes must be considered along with local anthropogenic oiling or petroleum-like residue from the original sedimentary rock via erosion and deposition.

A major reason for characterizing the hydrocarbons in the subtidal and beach sediments was to determine which characteristics could be used to differentiate between oiled and unoled sediments in the post-oil release period of the BIOS experiment. To this end, as well as to determine properties of the oil relevant to the oil dispersal systems (Dickins *et al.*, 1987), chemical characterization of the artificially weathered Lagomedio oil to be used in the experiment was undertaken (Boehm, 1981;

Boehm *et al.*, 1982; Dickins *et al.*, 1987). The generally high CPI values (2-12) found for the sediments, which reflected the plant wax origin of the sedimentary *n*-alkanes, indicated the possible utility of this index and related indexes in distinguishing between oiled and unoled sediments. The Lagomedio crude oil was found to have a CPI of 1 (Boehm *et al.*, 1987), which is typical of crude oils. Because the range of CPI values found for the sediments was so broad, however, this index would give equivocal evidence of oiling at concentrations of Lagomedio oil *n*-alkanes approaching background levels.

The low abundance of phytane in the sediments (< 1 ng·g<sup>-1</sup>) and high pristane/phytane ratios (>3 for subtidal and >10 for beach sediments) indicated that the abundance of phytane and the ratios would be useful for the determination of oiling by Lagomedio crude oil, which has a ratio of 0.74 and contains 0.64% phytane by weight (Boehm *et al.*, 1987). In principle, it would be practical to detect oil-derived phytane at concentrations of perhaps as little as twice the background maximum concentration or 2 ng·g<sup>-1</sup>, which would be the concentration of phytane from the oil present in a gram (dry weight) of sediment contaminated with 312 ng of the artificially weathered Lagomedio crude oil.

The presence of a UCM in several subtidal sediments indicated that this feature would have usefulness as a qualitative indicator of oiling by the released crude oil limited to the beach sediments.

Because the sediments showed measurable quantities of three- to five-ring unsubstituted aromatic hydrocarbons and no detectable quantities of their alkyl derivatives, the presence of the released oil, in which, typical of crude oils, the alkyl derivatives exceed in amount the parent PAHs, would be indicated by detectable amounts or more of alkylated PAHs. The azaarenes also showed potential as a tracer for the Lagomedio crude oil, because these compounds were present in relatively large amounts in the oil (Boehm, 1981). Nevertheless, the detection of a suite of azaarenes, albeit in low concentrations, in the two beach sediments analyzed that had a composition almost identical to that of the Lagomedio crude oil and financial considerations made this tracer less attractive than it might have been.

Because the *n*-alkanes and alkylated aromatic hydrocarbons from the oil would be particularly susceptible to biodegradative alteration and removal (Jones *et al.*, 1983) in the apparently non-accumulating sediments of the BIOS study areas, they were considered unlikely to be good long-term tracers of the released oil. For this reason, the pentacyclic triterpanes, which were known to be resistant to biodegradation (Dastillung and Albrecht, 1976), were investigated in the sediments and Lagomedio crude oil. The pentacyclic triterpanes of the sediments were identified as components of the (17 $\alpha$  H, 21 $\beta$  H) hopane series in which members with more than 30 carbon atoms were present as 1:1 mixtures of the two diastereomers at position 22. The sediment pentacyclic triterpanes were thus characteristic of ancient mature sediments of crude oils and were indistinguishable in a practical sense from those in the Lagomedio crude oil.

## CONCLUSIONS

The primary objective of this baseline hydrocarbon study was to verify that petroleum residues were not in high enough concentrations or variable enough from site to site to compromise the goals of the overall BIOS Project. A major concern was

the possibility of oiling from nearby undiscovered oil seeps. This study revealed, however, that the sediments in the proposed study area were at least as pristine as those in many remote areas of the world and, with respect to the petroleum hydrocarbon burden, were entirely suitable for the BIOS experiment.

At concentrations generally so low that the analytical procedures chosen for the study were insensitive or barely sensitive enough to make measurements, evidence of petroleum or combustion derived hydrocarbons in samples was obtained. With respect to the latter, a possible explanation is found in the recently discovered long-range transport of combustion products from the industrial mid-latitudes to the arctic regions. Nevertheless, this study did not address specifically the source and pathways of combustion-type and other hydrocarbons found in the region. There is a need for detailed geochemical studies in the Arctic to address questions regarding the sources, pathways and sinks of hydrocarbons there. Aside from providing the necessary baseline for the BIOS experiment, the present study should prove useful by raising specific questions regarding the hydrocarbon geochemistry of arctic nearshore sites.

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