NATURAL ATTENUATION OF HEAVY OIL ON COARSE SEDIMENT BEACHES: RESULTS FROM BLACK DUCK COVE, NOVA SCOTIA, CANADA OVER 35 YEARS FOLLOWING THE "ARROW" OIL SPILL

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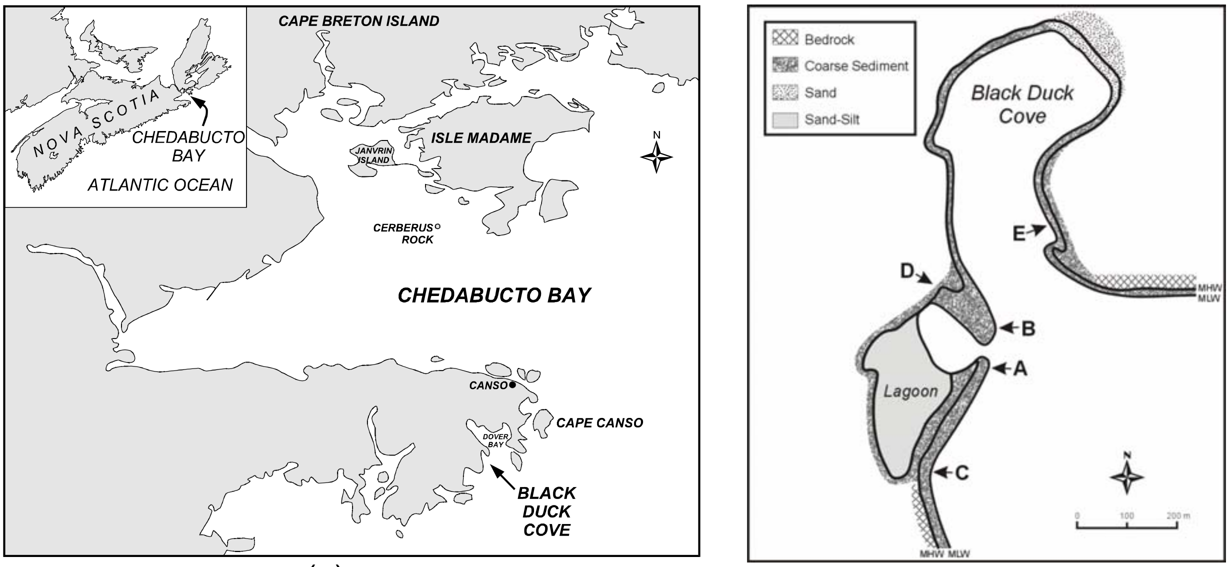
ABSTRACT
The 1970 wreck of the ARROW on Cerberus Rock, Nova Scotia, Canada, oiled much of the shoreline of Chedabucto Bay with Bunker C fuel. Most of the Bay was oil-free within a few years but some areas of Black Duck Cove have oil residues on coarse-sediment beaches and in fine-grained sediment in a protected lagoon. These areas have been sampled several times over the past 35 years and the site provides a laboratory for following the natural attenuation of heavy oil spills in the marine environment. Here we focus on the coarse sediments, including cobbles and boulders. The site has both surface and subsurface oil deposits in a variety of forms in all tidal zones. Asphalt pavements and sediments whose pore spaces remain filled with oil present examples of stable oil-sediment deposits. The pavements are being eroded by wave action at very slow but observable rates. Intertidal pore-filled sediments are also resistant to physical processes and sequestered subsurface residues coat the cobble-boulder sediments below the zone of sediment redistribution. Subsurface oil that fills the pores below the boulder surface layer is associated with the presence of finer sediments, which presumably have prevented deeper migration. These subsurface oils likely will remain until the sediment is disturbed by major storms or as a result of landward barrier migration. Samples from these environments show that the surface oil is extensively degraded, but that some of the deep subsurface oil is still very similar to the spilled material. Residual oil in the fine-grained sediment of the lagoon is extensively biodegraded, and has only very minimal environmental effects, indicating that if unweathered oil is released from the cobble areas into this environment it is rapidly degraded. The numerous observations since 1970 lead to the conclusion that the presence of subsurface oil residues in 2005 is not unexpected. As information has accumulated we have developed a better understanding of what has happened, what is happening, and what could be the fate of the oil residues at Black Duck Cove and elsewhere.

INTRODUCTION
Only a handful of coastal locations have long-term, persistent oil deposits following a spill with sufficient information on which to build a history of the changes in the physical and chemical character of the oil. One site is at Black Duck Cove (45° 16' N, 61° 01' W) on the Atlantic coast of Nova Scotia, Canada (Figure 1). This location was oiled in February 1970 by a bunker C spill from the tanker ARROW. The coarse sediment beaches of Black Duck Cove provide an accessible natural laboratory for the study of the long-term fate and persistence of stranded oil in a coastal marine environment. Numerous site visits have been made by various investigators and

observers including, in 1990, the Federal On-Scene Coordinator for the EXXON VALDEZ response operations, Admiral Ciancaglini, and his technical advisors. However, the site has not been studied in a systematic manner, spatially or temporally. The only mapping of the oil distribution was carried out in 1992 (Owens *et al.* 1994a). Samples have been collected at various times and analyzed to address particular issues related to weathering, including biodegradation and photo-oxidation, and to toxicity. Thus, although the site is well known to the oil spill scientific community, it has not been studied or documented systematically and there is probably much to be learned concerning the physical and chemical processes that have been going on, about the location and character of the oil residues, and the reasons for their persistence. The objective of this discussion is to summarize the knowledge that has been acquired collectively over the last 35 years.



(a) (b)

Figure 1 (a) Location of Chedabucto Bay and Black Duck Cove: (b) site sketch

BLACK DUCK COVE

Black Duck Cove is on the western shore of Dover Bay (Figure 1a). The southwest shore of the cove is fronted by a cobble-boulder barrier beach that is presently separated into three longshore segments by two breaches that allow tidal flow into the cove. The central segment of the barrier is 40 to 50m wide with highest elevations up to 3.5m above low water. The western segment is a short barrier which evolved following the development of the 50–m wide washover channel (location C on Figure 1b) that separates the two beach segments. The only remnant of the northeast segment of the barrier is a coarse lag shoal which is submerged at high tide (location B). Orford *et al*. (1991) recognized that drift-aligned coarse sediment barriers evolve into complex, organized systems through time mainly as a result of sediment supply changes. They identified three stages in coarse sediment barrier development: (1) initiation of drift-aligned forms; (2) consolidation and stabilization when drift-aligned forms can become swash-aligned; and (3) breakdown as sediment supply fails and/or sea level rises. The emergence of a clast-organized structure, in terms of shape and size sorting, e.g., cobble-boulder frame, reduces the potential for longshore sediment transport and the proximal barrier is no longer capable of satisfying the sediment supply demands of the distal barrier. The barrier reaches a threshold condition where it reorganizes into discrete cells in which weak structural positions develop and breaches can occur, as we observe at Black Duck Cove. The central segment of the Black Duck Cove barrier beach is presently more swash-aligned and is slowly migrating landward during episodic storm events as waves transport the large clasts from the beachface, over the ridge crest onto the back barrier. During this rollover process, the crest can become elevated as shown by the clean clasts which have accumulated on top of the oiled clasts in the upper part of the Black Duck Cove central barrier beach.

Vertical aerial photography (1974, 1980, 1991, 1998) combined with ground observations, show clearly, that over the last 35 years: (1) the crest of the storm ridge has migrated landward; (2) the distal end of the barrier thinned and moved landward between 1991 and 1998; and (3) landward movement is evident on the outer north shore of the cove where two small ponds have been gradually filled by cobbles and boulders. The changes are small, on the order of a few meters over a 20-year period, but show that the sediments are being reworked and redistributed in the short term.

Tides in the area are mixed semi-diurnal with a mean range of 1.2 m, and 1.8 m at springs. This is a storm-wave environment in which wave energy is concentrated in winter months associated with the passage of low-pressure systems across the region.

THE SPILL

The tanker ARROW grounded and sank on Cerberus Rock in Chedabucto Bay, Nova Scotia (45° 28’ N, 61° 06’ W)(Figure 1a), on 4 February 1970, with a cargo of 108,000 barrels of Bunker C fuel oil. The forward tanks were damaged on grounding and oil began to spill immediately. The vessel broke in half on 8 February and the stern sank on 12 February in 30 m of water, by which time an estimated 50% of the cargo had been released. The stern tanks contained about one third of the cargo, almost all, 36,924 barrels, was recovered by pumping. Strong SSE winds blew for the first two days following the grounding. These then subsided to NE and NW winds that moved oil towards the southern shores of Chedabucto Bay. Oil was first observed in Black Duck Cove from the air during mid-late February (Ministry of Transport, 1970). A recreational sand beach on the north shore of the cove was cleaned by mechanical and manual removal in the spring of 1970 but the southern area, which is characterized by a cobble-boulder barrier backed by a sand-silt lagoon, was not treated or cleaned.

ACTIVITIES AND OBSERVATIONS

Site visits to Black Duck Cove have been made by numerous investigators over the past 35 years and the authors’ observations are summarized below in chronological order.

1970

Frequent site visits were made between 25 April and 1July, primarily in conjunction with the cleanup of the north shore sand beach (Owens, 1971). Oil was observed on the lagoon shore of the barrier and on the mainland shore but no systematic observations or measurements were made in the barrier-lagoon area, other than random aerial and ground photography (e.g. Figure 2), nor were samples collected.

Figure 2 Aerial photograph of Black Duck Cove, 30 April 1970, showing the cobble-boulder barrier beach, lagoon, and shoal in the foreground, The only area cleaned by work crews was the sand beach at the head of the cove.

1973

A one-day study at Black Duck Cove included two nearshore bathymetric profiles, one through the center of the cove to the sand beach on the north shore and the second perpendicular to the barrier beach (Owens and Rashid, 1976). A beach profile was surveyed from the low tide line on the ocean side of the barrier across the lagoon to the mainland shore. Grain size estimates were made at a 3-m interval and the per cent surface oil distribution was documented on a 1-m wide swath along this transect. Observations on the transect documented the following oil features (Note: the oil terms Thick, Cover, Coat, Stain and OP are defined in Owens *et al*. 1994a):

- **OUTER BARRIER BEACH**: A 1- to 2-m wide band of oil at the top of the beach face above the mean high water level, with up to 50% Cover on the boulders, which in some sections had been buried by clean cobbles and boulders.
- **STORM RIDGE CREST**: A 10-m wide band of surface splashes on the boulders on the beach crest and landward of the crest, with a less than a 10% Coat and Cover distribution (Figure 5 in Owens, 1978).
- **BACK BARRIER BEACH**: A 1-m wide band of 100% Thick (10-25 cm) oil on the boulders, granules and coarse sands below the mean high water level, and a 2-3-m wide band of 50% oil below that deposit.
- **MAINLAND BEACH - LOWER HALF INTERTIDAL ZONE:** A 20-m wide band just above the mean low water level with between 5 and 50% Thick (10-25 cm) oil between the boulders and cobbles “as a sediment-oil matrix” and on cobbles, granules, coarse sands and silt.
- **MAINLAND BEACH - UPPER HALF INTERTIDAL ZONE:** A 15-m wide band of 100% asphalt pavement on cobbles, pebbles, granules, and coarse sands that ended at the mean high water level.

The oil deposits on the mainland shore of the lagoon were observed to be fluid and mobile on an earlier site visit in May (Figure 6a in Owens, 1978). A sample was collected from the fine sediments in the lagoon. The viscosity of the oil was high and the residue had a high hydrocarbon content (Rashid, 1974).

1982

The Black Duck Cove area was surveyed on 17 July during an aerial videotape flight to provide data for shoreline mapping of the coast of Nova Scotia as part of spill response planning. The helicopter landed on the barrier and ground photographs were taken on both the barrier beach and on the mainland shore asphalt pavement. No measurements or samples were taken at the time.

1990

A ground site visit on 21 August documented the following oiling conditions:

- **OUTER BARRIER BEACH**: A narrow band of oil approximately 2 m above the high tide level in the central section of the barrier just below the beach crest. Digging at this location revealed subsurface oil as a Coat or Stain on the cobbles. Oil filled the pore spaces between the cobbles in the washover channel at the proximal west end of the barrier (location C in Figure 1b) and was present as a band at a higher elevation on the sides of the channel.
- **BACK BARRIER BEACH**: A 15-cm thick layer of oil at the high water level was present with "pads" of oil resting on sand sediments lower in the intertidal zone.
- **MAINLAND BEACH**: A 7 to 10 cm layer of oil with grasses that had grown through the oil. Parts of the hard pavement had been buried by sand.

1992

A complete ground survey of the coasts of Chedabucto Bay oiled from the ARROW was carried out that involved walking 247 km of coast following SCAT procedures to document the location, distribution, and character of any oil that was observed (Owens *et al*., 1994a). In addition to the regional survey, detailed site surveys were carried out and samples collected at a number of locations, including Black Duck Cove. Specifically, the pavement on the mainland shore (D on Figure 1b) and the oil residues on the lagoon shore of the barrier were mapped and surveyed in detail.

The observations on the residual oil twenty two and a half years after it had been stranded are summarized as:

- **OUTER BARRIER BEACH:** No visible surface oil. A pit dug just below the storm ridge crest found Stain and Coat on boulders and cobbles below a surface layer of clean boulders (Plate 3 in Owens *et al*. 1994a). This layer most likely represented the surface layer observed in 1970 that had been buried.
- **BACK BARRIER BEACH:** An approximately 100-m section of the beach was mapped in detail (Figure 8 in Owens *et al*. 1994a). The northern half of the area was mapped as 10-20% surface Cover with Oil-Filled Pores (OP) between cobbles; the southern half area was a mixture of continuous Asphalt Pavement, 40-50% surface Cover with OP between cobbles and some pebbles, or buried Patchy Asphalt Pavement mixed with sand lower in the tidal zone.
- **MAINLAND BEACH**: An approximately 100-m section of the beach to the south of the shoal at the lagoon entrance was mapped in detail (Figure 9 in Owens *et al*. 1994a). The area was dominated by a 10- to 15-m wide continuous Asphalt Pavement (Table 1) which was buried by clean sand or clean pebbles and cobbles in parts of the mid-intertidal zone.

Table 1 Mapped Oil Distribution at Two Sites within Black Duck Cove, 1992

	OIL DISTRIBUTION	
	Mainland Shore (m^2)	Back Barrier Shore (m^2)
Continuous pavement	228	864
Cover with *Fucus*	40	0
Broken (51-90%)	0	64
Patchy (40-50%)	200	164
Patchy (10-20%)	520	
TOTAL SURFACE OIL	**988**	**1092**
Buried Pooled Oil (m^2)	168	72

Oiled sediment samples were collected from both the ocean and the lagoon side of the barrier, and extracted into hexane/dichloromethane. GC/MS studies revealed that all the oil did indeed come from the ARROW spill, and that although samples enclosed beneath a crust of weathered oil were still similar to the cargo material, samples from the weathered surface and from the mid intertidal zone, were extensively degraded (Wang et al., 1994).

1997

Samples were collected from the tidal flat in the lagoon behind the barrier (Lee *et al*. 2003). They were tested for residual toxicity, and oil was extracted and analyzed by GC/MS. Not surprisingly, in view of the substantial populations of benthic invertebrates found in the affected sediments, residual oil in the sediments had rather limited toxicity (Lee *et al*. 1998, 1999, 2003). When winter flounder (*Pleuronectes americanus*) were exposed to the oil in the laboratory, hepatic CYP1A protein levels were elevated and mixed function oxygenase (MFO) was induced, but the response was weak (Lee *et al*., 2003). Sediment toxicity was detected by the Amphipod Survival Test (*Eohaustorius estuarius*) in four out of the eight contaminated samples, but no sediment toxicity was detected with the Microtox Solid Phase Test (*Vibrio fisheri*).

Interstitial water samples were determined to be non-toxic by the Microtox 100% Test (*Vibrio fisheri*) and the Echinoid Fertilization Test (*Lytechinus pictus*). Sediment elutriates were also found to be non-toxic in the Grass Shrimp Embryo-Larval Toxicity (GSELTOX) Test (*Palaemonetes pugio*) (Lee *et al*. 2003).

The ongoing recovery was attributed to the physical removal of much of the oil by natural processes such as storms and tides, and the biodegradation of the residual oil. In support of the latter mechanism, mineralization experiments showed that all test sediments had the capacity for hexadecane, octacosane and naphthalene degradation, while chemical analysis (Prince *et al*., 1998) confirmed the results of Wang *et al*. (1994) that the Bunker C oil from the ARROW had undergone substantial degradation since the spill.

2005

Three pits were excavated just below the storm ridge crest on the barrier during a half-day site visit in March 2005 to locate the subsurface Stains and Coats documented in 1992. No subsurface oil was observed to a depth of 60 cm. The beach character had changed since 1992 as a relatively recent "new" layer of sediment had been deposited on the upper beach face slope. Some surface boulders above the beach crest had a <10% Stain or Coat. Pebbles with Coats and Stains were encountered in pits on the back barrier shore. Digging was limited by frozen interstitial water.

Two samples collected in the back barrier pits had compositions consistent with weathered ARROW oil. They were substantially degraded, with from 60 to 87% loss of detectable (column resolvable) hydrocarbons. Oil exposed on the surface of a pebble on the lagoon shore was very photooxidized compared with a sample from within an adjacent “internal” oil layer, having lost 60-70% of alkylated three and four ring aromatics.

A two-day site visit in October 2005 involved surveying across the barrier beach (A and C; Figure 1b), through the washover channel (C), and on the mainland shoal/platform (B and D) as well as pit excavation and sample collection. A 150 m^2 area of exhumed sequestered subsurface oil was observed on the ocean side of the barrier near the distal point (A in Figure 1b). The area between 22 and 28 m distance on the profile in Figure 3 clearly had been excavated recently. The surface armour layer (Isla, 1993) was very unstable and the boulders showed signs of very recent contact abrasion where they had been chipped and/or algae had been removed. Some of the oiled boulders that had been exhumed had been thrown above the high water level on to the top of the ridge.

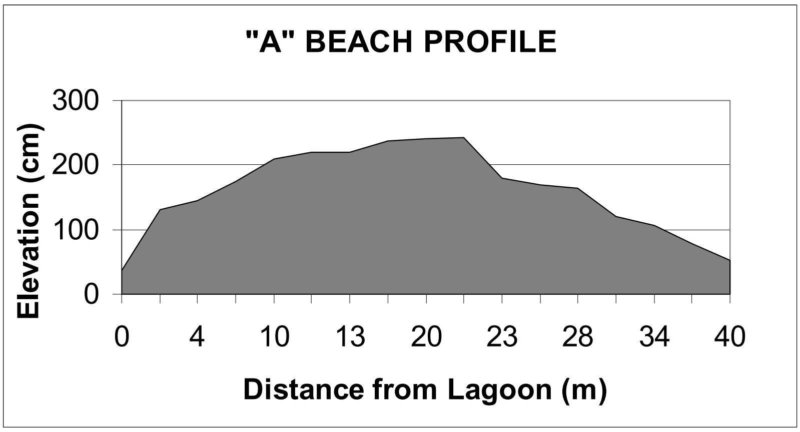


Figure 3 Profile from lagoon (left) to ocean (right) at the distal end of the barrier (“A” in Figure 1b) (VE approx. x 4)

Two winter storms with offshore significant wave heights >5m passed through the region on October 16 and 24-26. The earlier one coincided with a storm surge that generated water levels more than 0.6m above predicted high tides at Halifax. Either of these events could have triggered the excavation of the beach, and the short time between them means that the second storm could have had an additive effect.

The observations and surveys in October documented the residual oil after 35 years:

- **OUTER BARRIER BEACH**:
    a. An area of exhumed subsurface oil that had not been observed on previous site visits, including the previous one in March 2005. The oil was at the distal end in a low-lying, recently-eroded part of the upper intertidal zone. Typical boulder size on the surface was on the order of 60-80cm. The exposed subsurface boulders and cobbles had a surface Cover, Coat, or Stain (Figure 4a) that had not been abraded since exposure as there were no signs of

abrasion or scraping on the oiled surfaces. In the lower intertidal zone there was extensive removal of algae indicating sediment mobility.

b. In the washover channel, oil was observed at two low-lying areas in the sediments in the middle and upper intertidal zones at a location where it had been observed in 1990 and on 1993 and 1982 aerial images. Oil filled the spaces between the pebble-cobble-boulder sediments and was described as OP (Figure 4b). Surface oil had been abraded from the top of the cobbles, leaving zones where the OP was clearly visible. The position of the oil suggested that this oil deposit could extend beneath adjacent higher sections of the washover channel. A band of oil also was observed on the channel margins below the last high tide swash line.

(a) (b)

Figure 4 (a) Exhumed subsurface oil from the upper intertidal zone, distal end of the barrier beach (“A”): (b) mid-tidal subsurface OP, washover channel (“C”). October 2005

- **BACK BARRIER BEACH**: Oil was observed in the sediments in the middle and upper intertidal zone at the same locations where it had been documented in 1992 (Figure 8 in Owens *et al.,* 1994a). Oil filled the spaces between the pebble-cobble-boulder sediments and was described as OP.
- **MAINLAND BEACH**: The extensive asphalt pavement mapped in 1992 was still present (Figure 1b, D) as was oil in the sediments in the middle and upper intertidal zones on the wide (30m) coarse-sediment shoal (Figure 1b, B) at the entrance to the lagoon. This oil had been documented or observed during previous site visits, most recently in March 2005. The oil filled the spaces between the pebble-cobble-boulder sediments and was described as OP.
- **NORTHEAST SHORE OF BLACK DUCK COVE** (Figure 1b, E): Oil was present in the sediments in the middle and upper intertidal zones, filled the spaces between the pebble-cobble-boulder sediments, and was described as OP. This deposit had been observed in 1992.

In summary, surface and subsurface oil has been observed at the same locations on various site visits (Table 2). The October 2005 visit documented a recently exhumed subsurface deposit that may be part of a more extensive layer that remains sequestered beneath the outer beach.

Table 2 Summary of Observations (locations A through E are shown on Figure 1b)

LOCATION	OIL DISTRIBUTION AND CHARACTER
Ocean side (outer) barrier beach (A)	• Subsurface oil located in berm crest pits oil in 1990 and1992 but not in 2005; recent deposition may have added sediment to this zone. • Subsurface oil in mid-upper intertidal zone exhumed by recent (October 2005) storm; may represent a more extensive deposit of oil.
Ocean side washover channel (C)	• Surface and subsurface OP in the sediments in the middle intertidal zone; observed on previous site visits, can be identified in early (1973 and 1982) aerial images, and was documented in 1990.
Back barrier upper intertidal zone	• Extensive asphalt pavement in upper intertidal zone; only slowly degrading by edge erosion. • Extensive area of surface and subsurface OP in the cobble sediments in northern upper intertidal zone; has been observed on several site visits.
Mainland shore intertidal zone (B, D)	• Extensive asphalt pavement in upper intertidal zone (D); only slowly degrading by edge erosion. • Extensive area of surface/subsurface OP in the sediments in the middle-lower intertidal zones on the wide shoal at the mouth of the lagoon (B); observed on several prior site visits.
Northeast shore (E)	• Surface-subsurface OP in the sediments in the middle-upper intertidal zones; has been observed on several site visits.

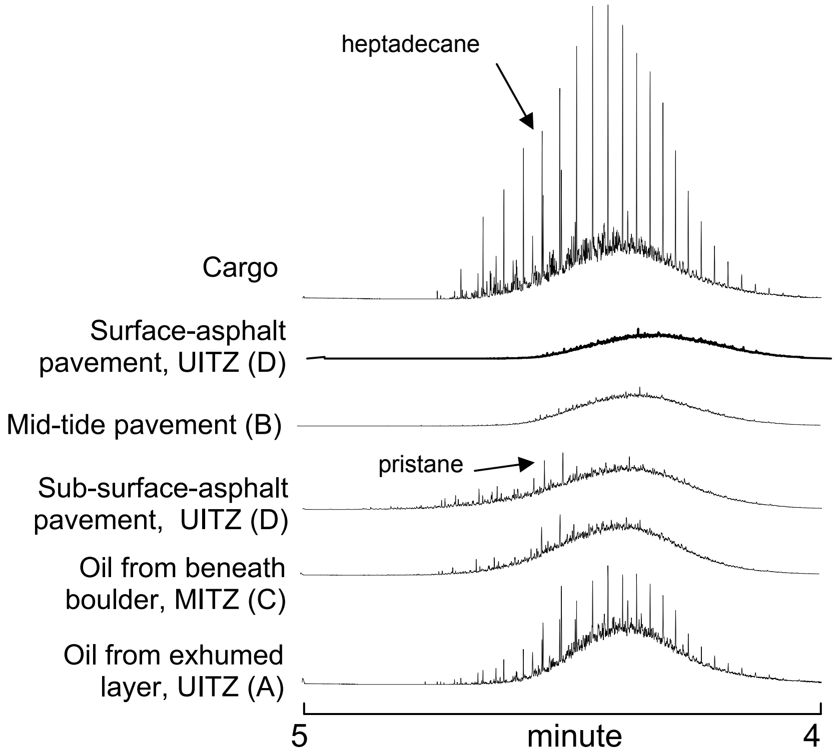
SAMPLE ANALYSES RESULTS

Samples from Black Duck Cove have been subjected to extensive analysis, for both major hydrocarbon types (polars, resins, aliphatics and aromatics by thin layer chromatography (Prince *et al*. 1998)) and individual hydrocarbon species by GC/MS (Wang *et al*. 1994; Prince *et al*. 1998, 2003).

Different samples show substantial differences in the extent of weathering, depending on their location and exposure, but the losses can be attributed to biodegradation and photochemical oxidation (Prince *et al*. 2003). The latter process only affects surface samples and is limited primarily to the destruction of polycyclic aromatic hydrocarbons (PAHs), especially the larger and more alkylated ones (Garrett *et al*. 1998).

Biodegradation has typically removed all the n-alkanes and many of the polycyclic aromatic hydrocarbons, starting with the smaller and less-alkylated ones and progressing to the larger ones. Typical samples have lost about half of the GC-detectable hydrocarbons by this process, although some samples are likely buried sufficiently deep, or are in sufficiently large “tarballs” that they are essentially preserved from biodegradation. The oil recently exhumed on the outer spit has the biomarker fingerprints of the ARROW cargo, and still has some *n*-alkanes and *iso*-alkanes, and seems relatively well preserved over the 35 years since the spill.

Figure 5 shows chromatograms of the cargo oil collected soon after the spill and oil samples collected in Black Duck Cove in October 2005. The chromatograms are normalized to C30 hopane, which served as a conserved internal marker (Prince *et al*. 1994). All samples were determined to be ARROW oil. The most biodegraded and photooxidized sample was scraped from the surface of the upper intertidal zone (UITZ) asphalt pavement at location D (Figure 1b). The next three samples (from locations B, D, and C) were collected within an oil layer or deposit and only the sample from the mid-tide pavement (B), collected at the surface, shows signs of some photooxidation, but it is critical to note that all three have been biodegraded to one degree or another. This means that, although the pore spaces at locations B and C appear to be completely filled with oil, the layers are not impervious as there must be or have been water movement in order for that biodegradation. The least weathered sample was collected from just above the fine sediment layer at the site of the exhumed oil at location A. Comparison of the samples from the surface and subsurface of the asphalt pavement at D shows that the sample collected within the pavement was less degraded than one scraped from the surface. In particular, the more photolabile benzo[a]pyrene is more depleted in the surface sample (Figure 6).



Bio degradation	Photo oxidation
+++++	++++
++++	+
+++	-
++	-
+	-

Figure 5 Chromatograms of cargo oil and samples collected in October 2005 ranked according to degree of biodegradation and photooxidation.

The various toxicological assays used by Lee and his colleagues (Lee *et al*. 1998, 1999, 2003) show that the sediment and interstitial water within the cove exhibit relatively low toxicities, and there are thriving invertebrate populations even in samples with some obvious residual oil.

DISCUSSION

The observations and results of sample analyses over the past 35 years provide an insight and understanding into the character of the residual oils and the processes that affect weathering and persistence. The key points are summarized in the following five questions.

1. <u>What are the key observations regarding oil and coarse sediment beaches?</u>

- Surface oil remains as (i) pavements with a hard crust that resists erosion: these have formed in the upper intertidal zone in sheltered locations or above the limit of normal wave action; and (ii) splash Coats and Stains on sediment above the normal limit of wave action. Pavement formation occurred with and without sands.

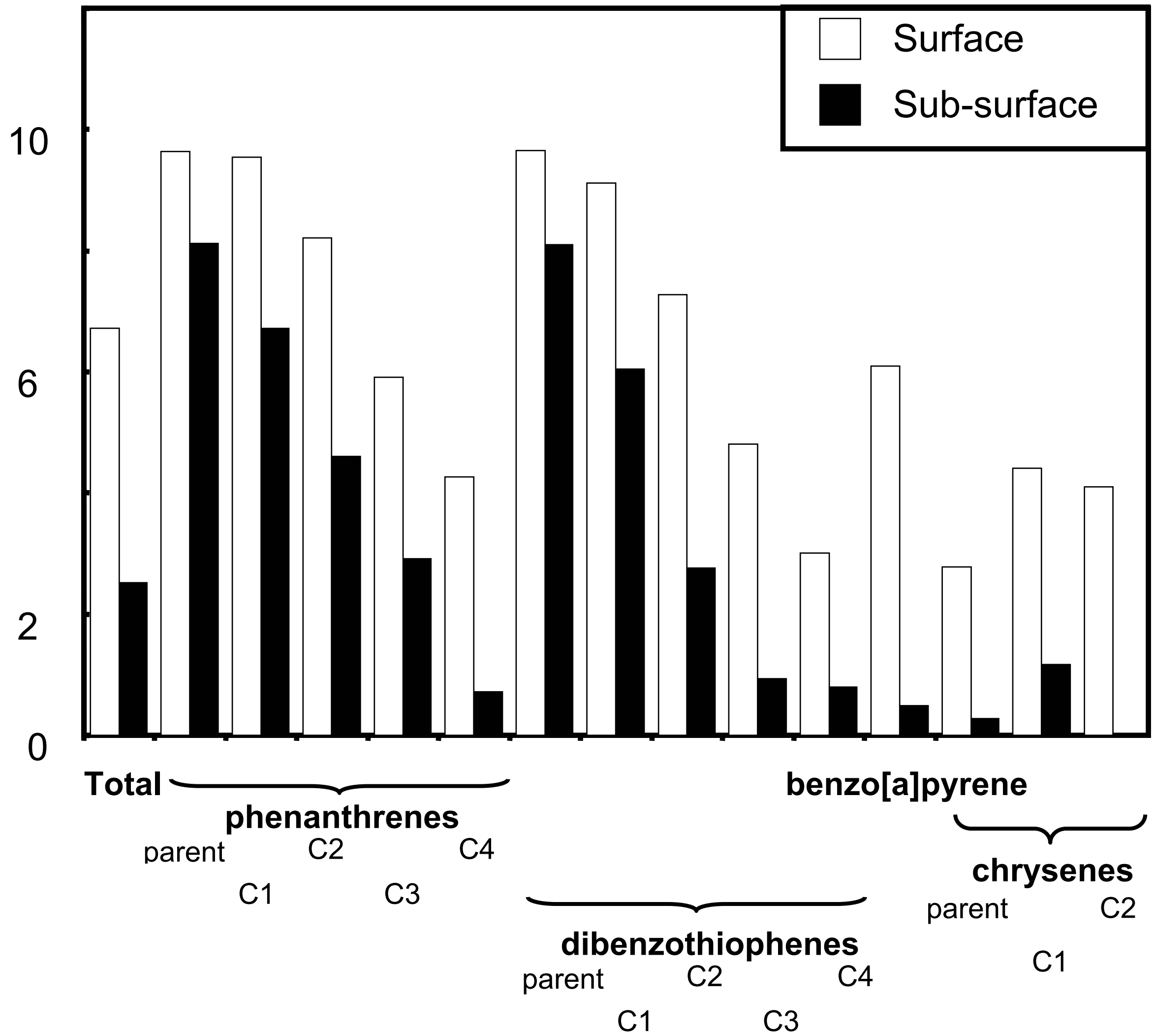


Figure 6 Surface and subsurface samples collected from the mainland beach upper intertidal zone asphalt pavement in October 2005 (D in Figure 1b)

- Oil that fills in the pore spaces between pebbles and/or cobbles as OP has stabilized the sediment. Normal reworking of the sediment by wave action was restricted once the exposed oil and sediment formed mutually saturated "asphalts". Filling the pore spaces limited infiltration and dramatically increased the entrainment threshold to initiate movement. Mid-intertidal zone examples of this effect are in the washover channel (Figure 1b, C) and on the lagoon shoal (B); upper intertidal examples are on the back barrier beach and on the northeast shore (E). The pores appear to be filled with oil, but are not impervious.
- Oil that penetrated deeply into pebbles, cobbles, and boulders below the normal zone of sediment redistribution has been protected from physical abrasion. The oil typically is a Coat, Cover, or Stain on the surface of sediment particles. Most likely, oil would have been carried through the large pore spaces by falling tidal water levels until it encountered the water table and/or areas of interstitial fine-grained sediment where further penetration would have ceased. Weathering processes such as biodegradation oil-mineral fine interaction and solubilization (OMA) would act only slowly on these sequestered residual oils. As there are very few fines in the Black Duck Cove sediments (Bragg and Owens, 1994) it is only biodegradation and the long-term reworking of the beach sediments that can remove this oil if it remains sequestered below the zone of sediment reworking.

- Nothing really surprising has been observed with respect to the surface or subsurface oil residues. The subsurface oil on the outer barrier that was documented in 1990 and 1992 is now buried by sediment thrown up the beach during storm events as part of the rollover migration process. The exhumed oil had not been observed prior to October 2005 due to the physical difficulty of excavating the stable imbricated boulders that armour the surface of the beach. The mid-intertidal subsurface OP on the ocean side of the washover channel is remarkable only in the sense that it has been so resistant to wave processes.

2. **<u>What do the results of the sample analyses indicate regarding weathering and persistence?</u>**

- After the short- and medium-term physical removal and weathering processes have completed what they can achieve, the long-term biodegradation and, for surface samples, photooxidation processes are the principal mechanisms for removal of the oil residues (Prince *et al*. 2003). Accessible samples are typically substantially weathered by these processes but there may well be pockets of "fresher" oil buried in some locations, such as the cobble beaches that are occasionally reworked by major storms. GC/MS analyses of residual biomarkers (Wang *et al*. 1994) will probably allow detection of some ARROW oil for some time into the future, but the environmental impact of the oil now evidently is quite low (Lee *et al*. 2003).

3. **<u>How much surface and subsurface oil remains today?</u>**

- The surface oil distribution has changed little since the 1992 mapping. Time series measurements of the METULA asphalt pavement observations indicate maximum edge erosion rates on the order of 10 cm/year at that site (Owens and Sergy, 2005). Similar rates would be appropriate estimates for this location.
- The extent of the recently exhumed oil is a matter of conjecture but it is reasonable to assume that it is part of a larger deposit. Similarly, the exposed oil in the washover channel is located at two low points and may well extend beneath the sediments in higher parts of the channel.

4. **<u>How long will the residues persist?</u>**

- The upper intertidal zone pavements or oil patches are slowly eroding, primarily by edge effects, as the surface of the oil has been hardened by photooxidation into an asphalt-like material. Erosion could completely remove the pavements and patches within the next few decades, unless buried by sediment.
- The middle intertidal zone OP subsurface oil deposits at C and B (Figure 1b) are relatively stable and persistent. The surface of the exposed parts of the oil is hard and protected to some degree by the surrounding pebbles and cobbles. This relatively stable situation is likely to remain unchanged unless there is an intervention associated with the slow landward migration and deterioration of the barrier beach.
- The barrier beach is migrating slowly landward and, assuming that this movement continues, so the persistence of the sequestered subsurface oil is finite. Although the two storms that occurred in October 2005 are normal events, in terms of offshore wave height, the combination of the very high water levels during the first storm followed by another storm very shortly thereafter may have produced an unusual condition. In any event, the few changes that have been observed over the past 35 years point to an extremely long persistence of oil, unless there is a natural intervention that alters the rate of beach change.

5. **<u>Does the lingering oil pose an ecological threat?</u>**

- Lee and his colleagues (1998, 1999, and 2003) used a comprehensive suite of toxicological assays to assess the residual environmental impact of the spill from the ARROW and concluded that, although there were some detectable responses, these were limited to the most sensitive assays, such as the induction of aromatic hydrocarbon-degrading Cytochrome P450 monooxygenases which is a response to PAH-exposure (Goksøyr and Förlin, 1992). Several widely used assays, such as Microtox®, which monitors the bioluminescence of a sensitive bacterium (*Vibrio fischeri*), revealed no detectable toxicity. They also noted that sediment with noticeable residual oil had thriving populations of invertebrates such as polychaete worms and clams. They concluded that the environmental impact of the spill had been substantially reduced over time, and that biodegradation would likely continue to reduce this impact in the future.

CONCLUSIONS

Long-term observations at Black Duck Cove offer valuable insights into the character of persistent oil residues in coarse-sediment beach environments. Oil deposited on more than 250 km of the shoreline in 1970 has been weathered and attenuated naturally (Owens *et al*. 1994b). The oil deposits that persist in Black Duck Cove represent most of the residual oil that remains today from the ARROW spill. They are, however, a miniscule fraction of the total oil that was originally stranded in 1970.

The residual surface and particularly the subsurface oil deposits remaining are very stable because of their location. The exposed surface pavements are being eroded, albeit slowly, primarily by water action, including by freeze-thaw phenomena in the winter. The subsurface oil that remains as OP in the middle and upper intertidal zones has effectively prevented normal sediment reworking and redistribution, even on the exposed beach, and will be removed naturally only when the present environmental conditions change, for example, as might occur with barrier beach migration and breakdown. The deeply sequestered oil in the barrier beach was discovered in 2005 only because a storm event or events had occurred immediately prior to the site visit. Without such events the oil would likely remain below the normal level of sediment redistribution, and only weather slowly. Biodegradation of this subsurface oil, which continues at the surface oil-water interface, to this point has only removed a portion of the most degradable components in the oil, the *n*-alkanes. Similar, but undisturbed, subsurface residues will likely remain essentially sequestered and unaltered for the foreseeable future.

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