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Fate of Crude and Refined Oils in North Slope Soils

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ABSTRACT. Prudhoe Bay crude oil and refined diesel fuel were applied to five topographically distinct tundra soils at Prudhoe Bay, Alaska. The penetration of hydrocarbons into the soil column depended on soil moisture and drainage characteristics. Biodegradation, shown by changes in the pristane to heptadecane and resolvable to total gas chromatographic area ratios, appeared to be greatly restricted in drier tundra soils during one year exposure. Some light hydrocarbons, C_9—C_{10}, were recovered from soils one year after spillages. Hydrocarbons were still present in soils at Fish Creek, Alaska, contaminated by refined oil spillages 28 years earlier, attesting to the persistence of hydrocarbons in North Slope soils.

RÉSUMÉ. Du "brut de Prudhoe Bay" et du fuel de diesel, raffiné, étaient répandus sur 5 sols de toundras, topographiquement distincts, à Prudhoe Bay, Alaska.

La profondeur de pénétration en hydrocarbures dans le sol dépendait de l'humidité du sol et des caractéristiques de drainage. Les rendements de chromatographie gazeuse d'un gaz entiérement analysé montraient des changements dans l'importance des pristanes et heptadecanes, ceci indiquait une biodegradation, apparaissant plus restreinte dans les sols plus secs de toundra, au cours d'une expérience d'un an. Quelques hydrocarbures légers C_9 — C_{10}, étaient récupérés du sol, un an après la pollution. A Fish Creek, Alaska, des hydrocarbures étaient encore présents dans le sol contaminé par des fuites de pétrole raffiné, 28 ans plus tôt; ceci atteste la persistance des hydrocarbures dans les sols du "North Slope". Traduit par Alain de Vendigies, Aquitaine Co. of Canada Ltd.

INTRODUCTION

In previous studies we have examined the fate of Prudhoe Bay crude oil and the microbial response to crude oil in several topographically distinct tundra soils near Barrow, Alaska (Sexstone and Atlas, 1977a; 1977b; Sexstone *et al.*, 1978). In the present study the fate of Prudhoe Bay crude oil in five topographically distinct soil types at Prudhoe Bay, Alaska were examined. Equivalent soil types (e.g. low center basin), are drier at Prudhoe Bay than near Barrow. The pH also is higher in Prudhoe Bay soils than soils from Barrow. The purpose of examining additional soil types at Prudhoe Bay was to determine if the fate of crude oil was similar in spacially separated areas o coastal tundra. During this study an accidental spillage of Prudhoe Bay crud oil occurred at Franklin Bluffs, Alaska, approximately 55 km south of o Prudhoe Bay study site. Samples were collected from this site shortly af the spillage occurred.

In addition to examining the fate of crude oil, this study included examination of the fate of diesel fuel in the same five soil types used ir

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crude oil study at Prudhoe Bay. Spillages of refined oils frequently occur around oil development and production camps. Frequent small chronic spillages of refined oils may be a greater environmental problem than rare accidental spillages of crude oil on tundra soils. We included in this study an examination of the hydrocarbons remaining at sites around a former drilling operation at Fish Creek, Alaska that had been contaminated in 1949 by three separate fuel oil spillages.

MATERIALS AND METHODS

Study Sites

Experimental crude and refined oil spill sites were established at Prudhoe Bay, Alaska in July 1976. Prudhoe Bay crude oil and refined diesel fuel were applied to sites at an application rate of 12 l/m^2. Comparable reference sites were also established. Oil was applied through a perforated plate to ensure even coverage. Each plot was surrounded with a sheet of polyethylene inserted to a depth of 10 cm. The study sites were arranged along a topographic moisture gradient. Sites were chosen to represent unique soil-vegetation-landform types (Walker *et al.*, 1977). Sites included: 1) a reticulate tundra site; 2) a transitional site between reticulate and low center polygonal tundra; 3) a low center basin; 4) a low center rim; and 5) a pond apron.

An area of 1949 diesel fuel spillages at the Fish Creek, Alaska west drill site was included (28 km s of Atigura Point). Three spillages occurred from camp maintenance equipment covering an area of approximately 30 m^2. Samples were collected at the three separate spillage sites. Soils at Fish Creek are tussock soils underlain by sand.

Also examined was an area near Franklin Bluffs, Alaska, site of a 1977 crude oil spillage (estimated at 5,000 barrels of hot Prudhoe Bay oil), from a rupture in the Trans-Alaskan Pipeline. Soils in the contaminated area are wet bog soils located on an inland extension of the coastal plain and are situated on a low terrace of the Sagavanirktok River underlain by gravel.

Soil Analysis

Soil cores were analysed for morphology, moisture, bulk density, soil reaction (pH) and electrical conductivity. General soil morphology was used as a measure of uniformity of the soil core. For determining soil moisture, wet volumes were measured and cores weighed. Then the cores were dried for 24 hours at 105 °C and the dry weight and volume were obtained. Percent moisture was calculated using the formula: (wet weight — dry weight/wet volume) × 100. Dry bulk density was calculated using the formula: dry weight/dry volume. Soil reaction was obtained from a soil water suspension of one part soil to five parts water with a pH meter (Beckman expandomatic). No correction was made for weight differences. Electrical conductivity was obtained on the same soil-water suspension as the soil reaction with an inverted sensor.

Enumeration of Hydrocarbon Utilizing Microorganisms

Hydrocarbon utilizing microorganisms were enumerated utilizing a modified 14 C radio-respirometric MPN technique (Roubal and Atlas, 1978).

Oil Analysis

Crude oil and diesel fuel were extracted from acidified soil sections using diethyl ether and Soxhlett extraction (Sexstone *et al.*, 1978). Extracted oils were weighed and analysed by gas liquid chromatography using a Hewlett Packard 5830 reporting gas chromatograph equipped with flame ionization detector and stainless steel columns (3 m × 0.3 cm) packed with 3% 0V101 on Supelcoport (Sexstone *et al.*, 1978). The ratio of resolvable to total area was calculated as an index of biodegradation.

Selected extracts were also analysed using 30 m glass capillary columns coated with SP2100. The following conditions were used for these analyses: 1) initial temperature, 80 °C; 2) 5 °C/min to 300 °C; 3) 15 min isothermal at 300 °C; and 4) flow rate 3 ml/min. Pristane to heptadecane ratios were calculated for crude oils as a further index of modification of oil composition. Additionally, volatile components C_1 — C_9, were analysed by head space gas chromatography (McFadden *et al.*, 1977).

RESULTS

Soil Analysis

No significant difference in soil moisture, dry bulk density, electrical conductivity or soil reaction (pH) could be related to crude or refined oil application at the Prudhoe Bay sites. Variation in these soil parameters could be related to differences in soil morphology and drainage, except for electrical conductivity at one site. Typical values for these soil measurements are shown in Table 1. At the Fish Creek spill sites the depth of thaw was 67 cm in the contaminated areas compared to 21 cm in uncontaminated reference areas. Depth of thaw was not measured in the Prudhoe Bay soils studied.

Hydrocarbon Utilizing Microorganisms

Hydrocarbon utilizing microorganisms in reticulate and transitional tundra soils were observed to increase from 7×10^1 and 3×10^3, respectively, to greater than 10^5 organism/gm dry wt soil when treated with either crude oil or diesel fuel. Hydrocarbon utilizing organisms were abundant, $>10^5$/gm dry wt, in basin, rim, and pond apron soils, regardless of treatment.

TABLE 1. Typical parameters of Prudhoe Bay soils at 0-2 cm

Soil Type	Moisture	Bulk Density	Electrical μMohs/cm	pH
reticulate	15	11	180	8.1
transitional	30	7	*	7.6
basin	40	5	150	7.5
rim	30	4	150	7.5
pond apron	80	3	220	7.3

Differences were found in treated plots at this site: control = 200; crude oil = 120; diesel fuel = 70.

TABLE 2. Weight of solvent extractable material (mg hydrocarbon/gm wt soil) from oiled tundra soils at Prudhoe Bay, Alaska

Depth (in cm)	SOIL TYPE Reticulate	Transitional	Basin	Rim	Pond Apron
			CRUDE OIL		
0-2	73	47	185	41	37
2-4	45	22	88	2	16
4-8	37	49	15	2	3
			DIESEL FUEL		
0-2	7	7	20	3	3
2-4	11	3	3	1	—
4-8	2	2	3	2	—

Analysis of Oils

The weights of recoverable oils from the Prudhoe Bay sites showed that the crude oil sites retained ten times more extractable "oil" than the diesel spill sites (Table 2). Lighter hydrocarbons which are abundant in diesel fuel are lost more readily than the heavier hydrocarbons which are abundant in crude oil. Gas chromatography confirmed the distribution of the remaining hydrocarbons in the soil (Figs. 1 and 2), shown by the weight of residual "oil" determinations.

The remaining oil showed similar patterns of penetration of "oil" from both diesel fuel and crude oil. Hydrocarbons were found in similar concentrations throughout the upper 8 cm of the drier and better drained reticulate and transitional tundra sites. In the wetter and poorer drained basin, rim, and pond apron soils, the greatest concentrations of hydrocarbons were found in the upper 2—8 cm. High concentrations of crude oil were recovered from the Franklin Bluffs spill site shortly after spillage (Fig. 1). Hydrocarbons were also recoverable decades after spillage in contaminated soils at Fish Creek in concentrations equal to the remaining diesel fuel at Prudhoe Bay. The refined fuel spillage at Fish Creek obviously had a different composition than the diesel fuel at Prudhoe Bay (Fig. 2). Hydrocarbons were distributed throughout the upper 40 cm at the Fish Creek site (Table 3).

Although most light hydrocarbons had been lost from the oils during one year exposure in soils at Prudhoe Bay, light alkanes in the range C_9—C_{10} were present in some of the recovered oils. Gas head chromatography failed to detect low molecular weight hydrocarbons from these soils. Compared to artifically weathered oil, there were more low molecular weight hydrocarbons remaining in the oils recovered from Prudhoe Bay (Fig. 1). Artificially

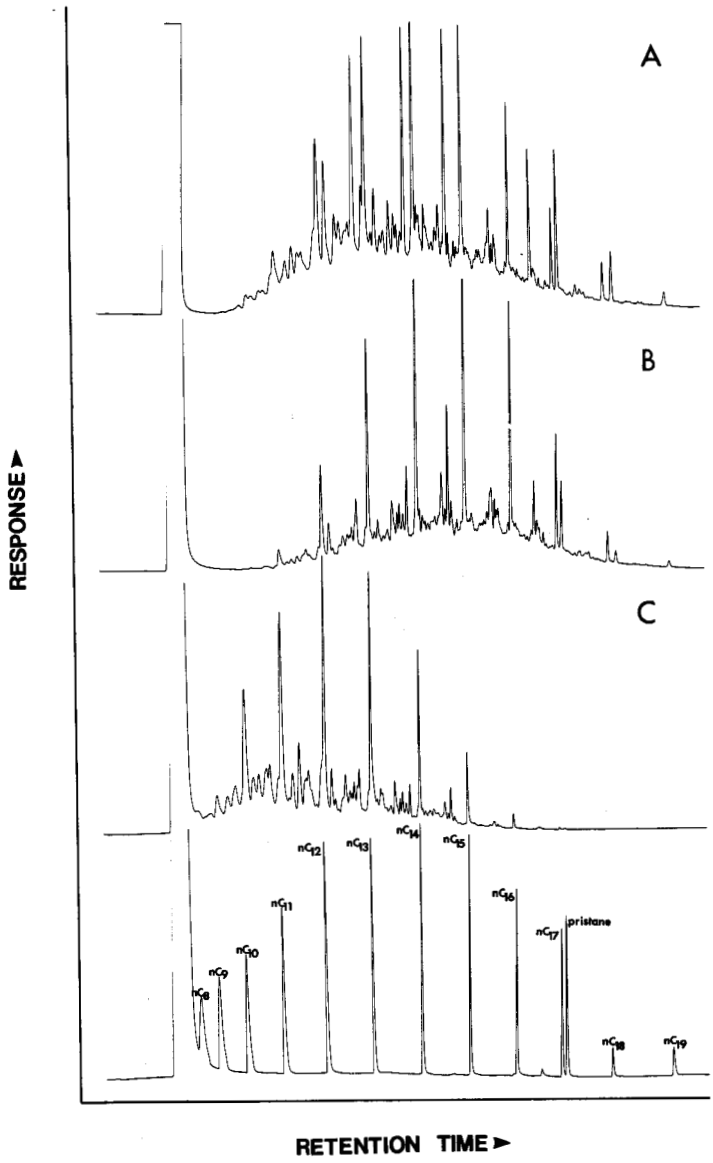

FIG. 1. Glass capillary gas chromatographic tracings of recovered crude oils: A. Oil from Franklin Bluff spill; B. Oil from Prudhoe Bay reticulate tundra; C. Artificially weathered oil; D. Known hydrocarbons.

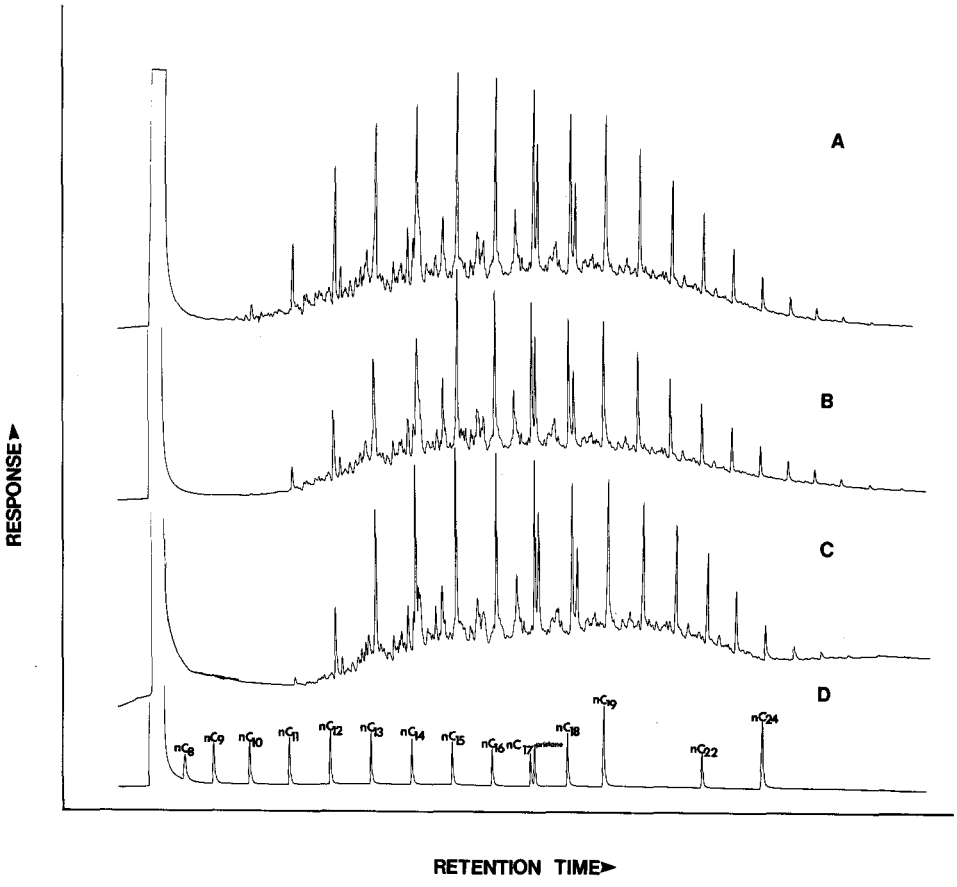

FIG. 2. Glass capillary gas chromatographic tracings of recovered refined oils: A. Hydrocarbons from Fish Creek spillage; B. Hydrocarbons from Prudhoe Bay reticulate tundra; C. Fresh Arctic diesel fuel; D. Known hydrocarbons.

weathered oil had been prepared by blowing air on Prudhoe Bay crude oil for 96 hours at 25 °C in sterile soil. The spilled oil at Franklin Bluff retained more low molecular weight hydrocarbons at the time of sampling, four days after spillage, than the one year old Prudhoe Bay oils. Even after four days exposure, much of the light hydrocarbon fraction, though, had been lost from the Franklin Bluff spill. Low molecular hydrocarbons below C_{11} were not found in the old fuel contaminated soils at Fish Creek (Fig. 2).

The ratio of resolvable area to total area in the gas chromatographic analyses indicated biodegradative changes had occurred in the crude oil exposed in the wetter Prudhoe Bay soils (Table 4). Compared to artifically weathered crude oil there was greater than 50% reduction in this ratio in the wetter soils. Oil recovered from the drier reticulate tundra soils had the same ratio of resolvable to total area, as the artificially weathered oil, indicating abiotic but not biotic changes had occurred. Oil from the transitional tundra soils showed

TABLE 3. Weight of solvent extractable material (mg diesel fuel/gm wet wt soil) from soils at Fish Creek exposed to refined oil

Depth (in cm)	SITE A	B	C
0 - 10	26	2	9
10 - 25	15	4	5
25 - 40	—	2	1

TABLE 4. Indices of degradative change in crude oils recovered from 0-2 cm depth

	Resolvable Area/ Total Area Ratio	Pristane/nC_{17} Ratio
ARTIFICIALLY WEATHERED OIL	20.6	0.64
PRUDHOE BAY		
reticulate	20.5	0.63
transitional	16.4	0.67
basin	9.8	0.66
rim	7.0	0.71
pond apron	9.0	0.64
FRANKLIN BLUFF	—	0.64

a 25% decrease in the ratio of resolvable to total area indicating limited biodegradative changes. The pristane to heptadecane ratios also indicated some minor biodegradative changes had occurred in the wetter Prudhoe Bay soils (Table 4). A pristane to heptadecane ratio of 0.64 indicates no biodegradation. Statistical analyses have shown that ratios of 0.7 or greater are indicative of biodegradation. The pristane to heptadecane ratios indicated less biodegradation had occurred than indicated by the resolvable to total area ratios. The greatest change in the pristane to heptadecane ratio, observed in rim soils, was only 10%

DISCUSSION

The use of the pristane to heptadecane and resolvable area to total area ratios as indices of biodegradation is based on the assumption that different hydrocarbons in oil are degraded at different rates. Assuming that biodegradative modification of oil had occurred during one year exposure in Prudhoe Bay soils, the ratio of resolvable area to total area appears to be a more sensitive index of biodegradation than the pristane to heptadecane ratio. If, however, modification of the oil was almost entirely abiotic, the pristane to

heptadecane ratio would be a more accurate index of degradation. The high numbers of enumerated hydrocarbon utilizers could have supported extensive biodegradation of the oil. In either example, both ratios indicated greater degradation in the wetter tundra soils at Prudhoe Bay than in drier soils. This finding contrasts with results found in soils at Barrow, where the change in the pristane to heptadecane ratio indicated more biodegradation had occurred in the drier high center polygon soils than in the wetter basin and trough soils (Sexstone and Atlas, 1977b). One must remember that soils at Barrow have higher moisture contents than comparable soils at Prudhoe Bay. Also, the extent of degradation indicated by the pristane to heptadecane ratio was greater in soils in Barrow than in the Prudhoe Bay soils.

Our studies indicate that soil moisture and drainage characteristics are extremely important, not only in affecting rates of degradative modification of the oil, but also in determining the degree of penetration of the oil into the soil column. Both crude and refined oils penetrated to a greater extent in the drier soils at Prudhoe Bay. This was also true for previously studied soils at Barrow (Sexstone and Atlas, 1977b). Extensive penetration of hydrocarbons was found in the soils at Fish Creek contaminated in 1949.

It is likely that the low molecular weight C_9—C_{10} compounds that remained in some soils at Prudhoe Bay were bound somehow to soil particles or blocked by water from reaching the soil surface. Otherwise, these compounds should have evaporated as occurred in the artificially weathered oil. There are some indications that more low molecular weight hydrocarbons were retained in soils treated with crude oil at Prudhoe Bay than at Barrow, but the evidence is not conclusive because of some difference in the preparation of samples for chromatographic analyses.

Attempts at removal of the oil from the Franklin Bluffs spill obviously were not successful within the first few days at the sites samples. We are uncertain as to whether attempts to physically clean up the oil, that continued past the time of our sampling, were any more successful.

With respect to persistence of oil in tundra soils, we have previously predicted that contaminating oil would remain for more than a decade (Sexstone and Atlas, 1977b). The examination of the 1949 fuel oil spillages certainly confirms that hydrocarbons can persist for decades in surface tundra soils.

ACKNOWLEDGEMENTS

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