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Short-Term Weathering Rates of Buried Oils in Experimental Sand Columns over North-Temperate Temperature Range

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Petroleum residues are degraded (weathered) at different rates, depending on various conditions. Degradation in slicks generally has time scales of days to weeks for loss of low molecular weight alkanes and aromatics (Calder and Boehm et al. 1981). This largely involves physical processes of wind-driven evaporation, and dissolution into the water column. Weathering in homogeneously oiled surface sediments, not having the benefit of evaporation, has time scales of months to years (Fusey and Oudot 1984; Page et al. 1989). Tidal submergence and temperature can influence this significantly. For example, Prudhoe Bay crude oil in sediments placed in trays on the bottom of a near-arctic bay showed virtually no weathering (Haines and Atlas 1982).

Here we report on weathering rates and qualitative changes of oils, buried within constantly submerged and irrigated sandy beach sediments for up to 11 mon. Such conditions occur when coastal stranded oil becomes buried subtidally, or becomes mixed into intertidal beach sediments below the water table. Experimental conditions included continuous sea water irrigation, indigenous microbial populations, and continuous complete submergence. For preliminary microbial incubation and weathering results, see Thorpe et al. (1986). We expected that oil degradation within sandy sediments would be comparatively slow, as organic material and nutrients are more limited, thereby limiting microbial activity. Lower temperatures and submergence also should limit the weathering process.

MATERIALS AND METHODS

The test oils were Venezuelan crude oil, Bunker C fuel oil (Esso Petroleum Refinery, Nova Scotia), and West Venture C-62 condensate (Mobil Oil Canada Ltd, Nova Scotia). Oil:sand mixtures (1% crude oil or Bunker C, 3% condensate) placed in mesh bags (sediment only for con-

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trols) were buried in experimental sand columns (beach sand, 1:3 ratio 75-177 μm to 177-600 μm) with top surfaces level with the sand surface. The 10-L sand columns (circa 50-cm diameter) were continuously irrigated from the bottom up via a central standpipe fitted with a perforated base. The entire sea water volume in each column was recirculated daily by maintaining circulation flow at 300 mL hr^{-1}. A charcoal filter was fitted to the standpipe to trap leached materials. There was no evidence of channelling of water through the sand column during long-term incubations. To simulate tidal washing out of leached material, 50% of the recirculating sea water was replaced each day with sand-filtered sea water from the Dalhousie University Aquatron facility. Sand columns were set up in controlled temperature rooms, three for each test oil, at 5°C, 10°C and 15°C, respectively, plus two controls. In-sand nutrient levels were maintained at not less than 10 μg atom L^{-1} NO_3 and 1.5 μg atom L^{-1} PO_4 by additions of enriched sea water containing 0.5 g L^{-1} K_2HPO_4 and 2.0 g L^{-1} KNO_3. Preliminary incubation of beach sand with crude oil (liquid medium, 250 mL shaking flasks, 2 wks, 10°C) indicated ample indigenous hydrocarbon utilizing microbes (45% to 75% reduction in C17:pristane and C18: phytane ratios). Water flow rates within the sand columns averged 0.02 mm sec^{-1}, less than half of an estimated 0.5 mm sec^{-1} for a high energy beach (Riedl 1971), ranking our conditions as moderate to low-energy. Oil:sand ratios used (1:100, 3:100) were quantitatively within the ranges found after coastal oiling (e.g., Hess 1978; Owens et al. 1987).

Mesh bags were retrieved for hydrocarbon analysis at 24-hr, 7-d, 1-mon, plus at 2-mon intervals, up to 11 mon. Hydrocarbon analysis was by gas chromatography (GC/FID) after Soxhlet-extraction of wet oil:sand mixtures into dichloromethane, drying with Na_2SO_4, and concentration to 10 mL (rotary evaporator, 10°C) (HP Model 5830A GC/FID, 0.25 mm i.d. 30-m silicone fused-silica capillary column, injector temp. 250°C, He at 0.5 cm^3 min^{-1}; detector temp. 275°C; oven temp. 35°C for 5 min, programmed to 260°C @ 8°C min^{-1}). Parallel, spiked samples served to correct for losses of volatile hydrocarbons (C12) during extraction and solvent concentration steps. Known amounts of the test oils served as reference material. Average recovery for low boiling point hydrocrbons (C12) was 93%.

Weathering indices for crude oil and Bunker fuel were 1) general loss of volatile hydrocarbons, 2) decreases in peak heights for C17, C18, C21 relative to isoprenoids pristane (Pr) and phytane (Phy), 3) changes in the ratio of resolved peaks (especially C18, C21) relative to the size of the unresolved complex mixture (UCM) (C18:UCM, C21:UCM). For the condensate, composed largely of low molecular compounds, we monitored percent composition of

Table 1. Percent loss by weathering from buried oil in continuously irrigated experimental sand columns; determined by peak-height analysis of gas chromatograms.

	0-16 hr	16 hr-1 wk	9-11 mon	Total loss
Crude oil (10 mon)				
5 °C	ND[1]	ND	5	ND
10 °C	ND	ND	7	ND
15 °C	25	15	15	55%
Bunker fuel (11 mon)				
5 °C	ND[1]	ND	<1	ND
10 °C	ND	ND	<1	ND
15 °C	15	7	5	27%
Condensate (9 mon)				
5 °C	ND	ND	<<1	ND
10 °C	ND	ND	<1	ND
15 °C	35	14	<1	49%

[1] not determined

hydrocarbon groups (<C10, C10-C14, C14-C17, >C17). Total hydrocarbon losses were calculated from the peak heights /areas as compared to non-weathered oils. Precision in CG peak areas was ±5%. Degradation rates were estimated from these.

RESULTS AND DISCUSSION

Weathering was highest at 15°C, and proceeded in two distinct phases. Substantial amounts of hydrocarbons were lost from all oil:sand mixtures during the first eight experimental days, most rapidly during the first 24 hr, levelling off after week 1 (Table 1). Losses were highest in condensate; 35% and 14% by weight at 15°C during the first 16 hr and the following week, respectively. Losses in crude oil were intermediate; 25% by weight during the first 16 hr, and 15% during the subsequent week. Bunker C lost 15% and 7% during the first 16 hr and the first week, respectively. These rapid initial losses were expected, as all three oils at the outset were unweathered and therefore contained their normal mobile lower molecular weight fraction.

Qualitatively, the most obvious changes during this initial period were in the lighter molecular weight hydrocarbons and then primarily for crude oil. In crude oil these were mainly below C9 (Table 2), probably by selective dissolution into the circulating sea water. For example, in standard reference crude oil, about 21% of total resolved material occurred below C9, but after 1 mon at 15°C, the same fraction below C9 constituted only 3% of the total. The higher molecular weight com-

Table 1. Weathering indices for crude oil and Bunker C fuel in submerged beach sand.

	5°C				10°C				15°C			
	<C10 (%)	C17 :Pr[1]	C18 :Phy	C21 :UCM	<C10 (%)	C17 :Pr	C18 :Phy	C21 :UCM	<C10 (%)	C17 :Pr	C18 :Phy	C21 :UCM
VENEZUELA CRUDE												
start	25	1.3	1.4	3.5	25	1.3	1.4	3.5	25	1.3	1.4	3.5
month 1	3.8	1.2	1.4	3.3	1.0	1.3	1.4	3.1	ND[2]	1.2	1.5	3.2
2	ND	1.2	1.4	3.3	ND	1.2	1.4	3.2	1.7	1.2	1.4	3.0
10	ND	1.4	1.5	3.0	ND	1.3	1.5	3.0	ND	1.1	1.0	2.0
BUNKER C FUEL												
start	0.5	1.6	1.5	2.4	0.5	1.6	1.5	2.4	0.5	1.6	1.5	2.4
month 1	0.3	1.4	1.5	2.4	<0.1	1.5	1.6	2.2	ND	1.4	1.5	2.4
3	<0.1	1.3	1.4	2.7	<0.1	1.4	1.6	2.8	ND	1.2	1.4	2.8
10	ND	1.5	1.5	2.7	ND	ND	ND	ND	ND	1.1	0.9	1.8
11	ND	ND	ND	ND	ND	1.5	1.6	2.8	ND	ND	ND	ND

[1] Pr=pristane, Phy=phytane, UCM=unresolved common mixture; [2] ND = not determined

Table 3. Percent compositional changes in condensate in submerged beach-sand columns.

	5 °C				10 °C				15 °C			
	<C10	C10-14	C14-17	>C17	<C10	C10-14	C14-17	>C17	<C10	C10-14	C14-17	>C17
start	48.5	27.6	19.1	4.8	48.5	27.6	19.1	4.8	48.5	27.6	19.1	4.8
day 3	43	30	21	6	ND[1]	ND	ND	ND	44	32	18	6
6	ND	ND	ND	ND	41	34	20	5	43	33	19	5
month 3	ND	ND	ND	ND	ND	ND	ND	ND	26	44	26	4
8	ND	ND	ND	ND	ND	ND	ND	ND	28	39	19	8
9	34	39	19	8	34	37	19	9	ND	ND	ND	ND

[1] ND = not determined

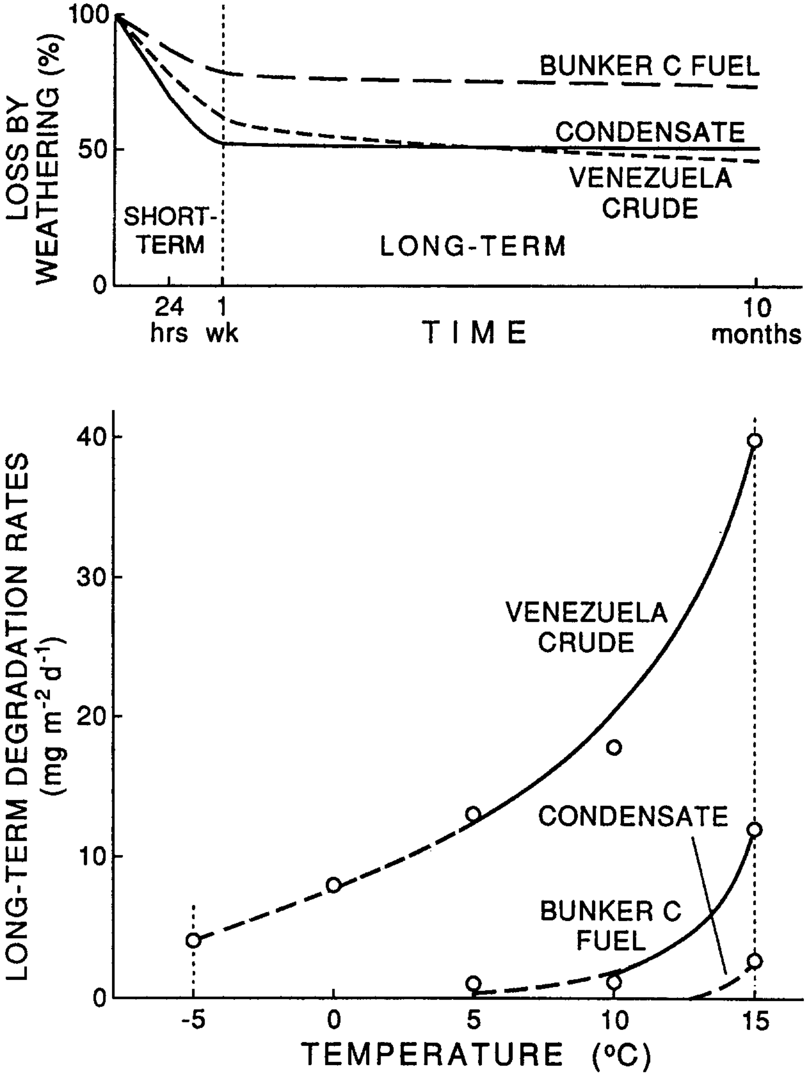

Figure 1. 8-11 mon weathering of oils buried in continuously submerged experimental beach sand columns. A - percent bulk loss; B - degradation rates for north-temperate temperature range; -5°C and 0°C values were extrapolated using calculated Q_{10}.

pounds (i.e., >C9) did not show appreciable change. There was little short-term qualitative change in Bunker C fuel and in Venture condensate. The pattern of the losses, and principally of the lower molecular weight fractions, suggests that initial weathering was mainly by dissolution into circulating sea water.

Table 4. 11-mon degradation rates (mg m^{-2} d^{-1}) for oils buried within experimental sand columns.

	-5°C	0°C	5°C	10°C	15°C
Venezuela crude	4.2[1]	8.4[1]	13[2]	18[2]	40[2]
Bunker C fuel	NA[4]	NA	< 2[3]	< 2[3]	12[2]
West Venture condensate	NA	NA	NA	NA	< 5[3]

[1] extrapolated, using calculated Q_{10} = 3.2 at 5-15°C; [2] calculated by GC peak height analysis; [3] estimated from GC chromatograms; [4] NA = not available

Quantitative changes for all three oils over the 9-11 mon period were small, even at 15°C (Table 1, Figure 1). Based on peak area analyses, total percent loss of resolved material from crude oil over the 10-mon period was between 5% (5°C) and 15% (15°C). For Bunker C, estimated hydrocarbon losses were from 1% at 5°C to approx. 5% at 15 °C. For condensate, after the initial rapid changes of the first week, less than 1% of buried condensate was lost during the subsequent 9 mon. Qualitatively, changes for crude oil included a small increase in UCM, evident by month 2, but only at 15°C (Table 3). This was followed by a slight reduction in C17, C18 and C21 concentrations by month 9. Bunker C fuel changed little over the 11-mon period. Minor weathering changes occurred in the mid-range n-alkanes (C17-C21), mainly at 10°C and 15°C, but most changes fell within ±0.1-0.2 of the indices in the reference material. At 15°C, a small decrease in the C21:UCM ratio was noted after 2 mon, with an increasing UCM by month 10. At 10°C some minor weathering changes were seen after 5 mon. No qualitative changes in peak patterns were observed at 5°C. Qualitative changes in condensate were minimal over the 9 mon, restricted mainly to the lower molecular weight fractions (Table 3). Some losses of hydrocarbons up to C10 (at 15°C) were seen in week 3, with further losses after 3 mon. No losses were evident at the lower temperatures (5°C, 10°C) until months 4 to 5.

The lack of changes for Bunker fuel and crude oil over 9 to 11 mon may in part have been due to a surface:volume effect; i.e., the oil was dispersed within the sediments in such high concentration that microbial activity was restricted to outer exposed surfaces only. For example, Owens et al. (1987) noted that weathering and biodegradation of stranded crude oil on an arctic beach progressed slowly where oil-in-sediment concentrations exceeded 1%. Temperature also undoubtedly was a major factor, especially in the 5°C experiments, by reducing microbial metabolism. Another explanation, that the native microbial population might have become washed out of the system, seems unlikely. The experimental system was continuously resupplied, and therefore reinnoculated, with freshly collected ambient sea water, and periodic monitoring showed that microbial populations were continuously present in all systems. Also, nutrient levels were not limiting.

The large losses of condensate during the initial 2 weeks are consistent with its large low-molecular weight fraction (16.5% <C21), but the subsequent long-term persistence of peacks in the condensate GC spectra was unexpected. Strain (1985) similarly observed that condensate components as light as C7 and C8 could persist for more than 6 mon, provided the condensate were buried within surface sediments. He speculated that strong adsorption of condensate onto sand grains and strong oil-particle interaction might explain this unexpected persistence. Whatever the reasons, this requires further study as it runs counter to theoretical expectations (Ross 1982; Nadeau and MacKay 1978).

Specific degradation rates over the full experimental temperature range (5-15°C) could only be calculated for crude oil. Degradation rates for crude oil at lower temperatures (0°C and -5°C) were obtained by extrapolation using $Q_{10} = 3.1$ calculated from degradation rates at 5°C and 10°C [$Q_{10}=(\text{rate}_n-\text{rate}_{n-1})/(T_n-T_{n-1})$]. This value agrees with values for Q_{10} of 2.7-3 reported in the literature (oil oxidation studies, Zobell 1964; crude oil weathering in experimental beach gravel columns, Gibbs and Davis 1976). The calculated degradation rates (Table 4, Figure 1B) compare well with reported values from the literature (50 mg m^{-2} d^{-1}, Atlas 1981; 260 mg m^{-2} d^{-1}, 12°C, Gibbs and Davis 1976; 40-90 mg m^{-2} d^{-1}, 10°C, Johnston 1970). The extrapolated degradation rates at 0°C and -5°C also seem reasonably within range, although we suspect that in reality they may be even lower with the north-temperate microbial populations used here. For Bunker fuel we were able to obtain a measured degradation rate only at 15°C. For the lower temperature ranges, for both Bunker fuel and condensate, the longer term losses were so small as to allow estimates only. The degradation rates for condensate seem low, but we note that these rates are based on the more persistent, i.e., less degradable, hydrocarbon fractions in the residual oil.

The data indicate a potential in-sediment persistence of crude and bunker oils and condensate (at 1 to 10% concentration oil:sand) that extends well beyond 11 mon, when buried in continuously submerged non-reworked sandy sediments under low-energy north-temperate conditions. This persistence is influenced inversely by temperature.

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