Deleterious properties retained by diesel fuel spilled in northern Canada in winter


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Abstract

In March 1983, a fuel truck overturned at a bridge crossing the Cameron River, near Yellowknife, Northwest Territories, Canada, and spilled a quantity of diesel fuel. The spilled diesel fuel penetrated the snow cover, moved along the frozen surface of the ground and entered the ice-covered Cameron River. A sample of diesel fuel was recovered from beneath the river ice eight days after the initial spill. This sample from the river was compared with that from the original cargo in the truck in three quantitative and independent ways, namely gas chromatography with a comparison of the sample patterns by principal component analysis, acute toxicity to fish, and tendency to taint fish with an oily taste. The two samples were essentially the same in all respects, except for some subtle but consistent differences in the relative proportions of some individual hydrocarbons. The river samples were shown to contain slightly higher proportions of the C_3 to C_9 alkane components. Slightly lower proportions of alkanes eluted after C_{12}, possibly as a result of losses due to sediment adsorption or fractionation under the ice. Evidently the low ambient temperatures and cover by ice and snow reduced greatly the 'weathering' phenomenon often described with spilled oils, and permitted the oil to retain its toxic and tainting properties.

Introduction

Petroleum oils discharged into natural waters undergo changes in composition described as "weathering" [1] with the result that the oil becomes less harmful to
aquatic life. Rates of weathering depend on factors such as temperature, sunlight, mixing processes in both air and water, and metabolism by microorganisms. Consequently, weathering in polar regions during winter is relatively slow [2-6].

Weathering has been difficult to describe mathematically because of the changing properties of the oil remaining after components have been partially lost. Evaporation is principally responsible for early weathering of oil at sea [7,8]. Rate-controlling variables include temperature and mixing within both oil and air phases [9,10]. Oil spilled experimentally on snow has been observed to penetrate and to spread slowly at the surface of the ground (11).

The acute toxicity of oils to fish has been attributed to the low-boiling components most soluble in water, principally normal and cyclic alkanes up to C₄ and alkylated derivatives of benzene and naphthalene [12-14], and to compounds formed photochemically from oil [15]. Generally, toxicity testing with petroleum oils has been done using an aqueous extract of oil, the ‘water-soluble fraction’ (WSF) prepared by mixing oil and water and collecting the water phase after allowing the layers to separate. Even in the absence of overt toxic effects, oil components have been taken up by fish and shellfish [16,17] resulting in offensive flavors and odors [18,19].

On March 1, 1983, a fuel truck loaded with diesel overturned about 15 m from the bank of the Cameron River, some 58 km from Yellowknife, Northwest Territories, Canada. Most of the cargo was spilled the following day during removal of the truck, and a sample of diesel was collected from the truck at that time. The spilled diesel fuel penetrated through the snow (ca. 60 cm deep), and moved toward the river at the frozen surface of the ground. In spite of efforts to burn the oil, some did enter the river. On March 9 a fresh hole was cut in river ice about 25 m downstream from the point where oil entered the river, and a lens of diesel was found at the ice-water interface. Air temperatures during this period ranged from -7 to -39°C. The sample of diesel recovered from the river was compared with the earlier sample from the truck by three independent means: gas chromatography of dilutions of the samples in hexane, acute (96-hour) toxicity tests against larval whitefish (Coregonus clupeaformis), and sensory (taste) evaluation of fillets from large whitefish exposed to both samples of diesel in the laboratory.

Methods

Gas chromatography of oil samples

Both samples of diesel fuel were collected in screw-cap bottles filled to the brim and capped tightly, and were stored unfrozen. For gas chromatographic analyses, the samples of diesel were diluted (1:2000 v/v) with hexane. A Varian 6000 instrument was used fitted with a 15-m DB 5 bonded fused silica capillary column using splitless injection at 240°C, with nitrogen carrier gas flowing at 20.5 cm sec⁻¹. Column temperature was held at 35°C for 2 min, and then programmed to 250°C at 10°C per min. The flame ionization detector was
maintained at 260°C with flows of hydrogen and air at 20 and 200 mL min⁻¹ respectively. An internal standard of n-decylbenzene was added to each sample and a Varian model 4270 integrator was used to calculate peak areas, with the "baseline logic" command operating. Counts for peaks were converted to quantities from their ratios to the counts produced by a known amount of the internal standard, assuming equal response factors for the FID detector. Very small peaks were excluded by setting the integrator to ignore peaks with fewer than 1000 counts. Under these conditions about 240 peaks were integrated. Each sample was injected six times. A P30 and a P50 diesel fuel sample were analyzed using the same gas chromatographic conditions and integrator settings.

Principal component analysis (PCA) was performed on the four fuel chromatographic data sets using the program 'Conaco for Windows'.

**Acute toxicity of oil-water mixtures**

Water-soluble fractions of both diesel samples were prepared by stirring oil with water (1:100 v/v) magnetically in a closed container for 2 h and then allowing the mixture to stand for a further 48 h period to separate the oil and water layers. The water layer, representing the WSF, was collected and diluted with untreated water to give solutions of 50, 30, 11, and 6.5% WSF. These dilutions, together with untreated water controls, were used to fill duplicate 1 L glass jars to overflowing, and five larval whitefish were placed in each before the jars were capped tightly. Fish were observed regularly over a 96 h period and the time to the death of each fish was recorded. Hydrocarbon concentrations in the water were measured at the onset of exposure and after 96 h by solvent extraction and gas chromatography [20], and the exposure concentration was taken as the mean of the initial and final oil concentrations. Dissolved oxygen measurements at the end of the 96 h period ranged from 8.1 to 10.2 ppm. Mean survival times (MSTS) were estimated manually by plotting percentage survival (probit scale) against exposure time (logarithmic scale). MSTS were then plotted against exposure concentrations, so that concentration required to kill half the fish over 96 h (96 h LC₅₀) was read from the graph [21]. The same data were used to calculate LC₅₀ values by probit analysis using a computer program [22].

**Fish tainting experiments**

Oil (10 mL) was added to about 400 mL of water in a 1 L jar and shaken vigorously by hand for 5 min. The resulting emulsion was added with stirring to 148 L tanks containing four whitefish per tank. After exposure periods of either 2.5 or 5 h at 10°C with no aeration the fish were removed, rinsed in cold water, and sacrificed. Fish were then eviscerated, washed, and kept on ice while being prepared for sensory evaluation [23]. Skinless fillets prepared from each fish were homogenized in a food processor for 30 sec, portioned into samples of approximately 15 g and sealed in aluminum foil. Sets of foil packets were placed in plastic freezer bags, vacuum sealed and frozen at -30°C. Untreated whitefish were prepared in the same way. Prior to each sensory panel session
samples were removed from frozen storage, placed on a rack in a stainless steel steamer and steamed over boiling water for 15 min. The sealed packets were then placed on warming trays for presentation to judges.

Sensory panel evaluations

Each sensory panel session consisted of the evaluation of eight samples presented in random order to each of nine judges. Samples were not swallowed but were expectorated after evaluation; water and unsalted soda crackers were supplied for use after each sample to allow judges to clear the previous sample from their palates before continuing. Samples were presented in random order and each sample was evaluated twice by each judge. Panel members were experienced in the evaluation of fish products and were selected for their ability to perceive hydrocarbon off-flavors in water solutions and to rank those solutions in the correct order of concentrations. The rating procedure was a modification of the quantitative descriptive analysis [24,25] where a 15 cm line was provided with end points marked weak and strong. Panelists were asked to record their response to each sample by placing a mark on the line at a point corresponding to their perceived intensity of any petroleum off-flavor in the sample. Responses were then converted to numerical scores with a template marked in millimeters.

Results and discussion

Chromatograms of diesel recovered from the truck and from the river

Chromatograms of the samples recovered from the truck and from the river were quite similar (Figure 1). The integrated areas of each of the nine large peaks identified as n-alkanes from nonane (C9) to heptadecane (C17) were expressed as proportions of the total for all nine hydrocarbons and their distributions in the two samples were almost identical. They were very similar to those for 'arctic diesel 40' reported by Regnier et al. [10] and for Exxon Valdez oil reported by Short et al. [26]. Weathering by evaporation and dissolution of the spilled diesel would be expected to have preferentially removed the lower boiling and more soluble alkanes, leaving the river sample depleted in those compounds relative to the truck diesel. Clearly this did not occur as the river sample was slightly but consistently richer in nonane (C9), decane (C10) and undecane (C11), while the truck sample was generally slightly richer in the remaining alkanes.

PCA analysis was conducted on chromatographic data from four sample groups (river sample, truck diesel fuel, P30 diesel fuel and P50 diesel fuel). Peaks were aligned by relative retention time, then normalized to zero mean, unit variance within each replicate. PCA was performed with 'Conaco for Windows' using peaks common to all sample groups (n=92). The first three principal components explained 90.2% of the variation between components. The clusters for the P30 and P50 diesel fuels were tight and distinct from one another. The River and Truck diesel fuels were distinct from the other diesel fuels and formed a cluster of their own. (Figure 2).
Toxicity of diesel recovered from the truck and from the river

Mortality curves for the two samples were very similar (Figure 3), both 96h LC50 values were 1-2 ppm. Comparable results were obtained by probit analysis [22] and the LC50 values were calculated to be 1.6 and 1.8 ppm for truck and river samples respectively. These estimates of acute toxicity agree with earlier literature on water-soluble fractions of oils, [13] and they show that weathering processes over several days in the river removed little or no toxic material.

![Figure 3. Fish mean survival times plotted against nominal concentrations of diesel in the diesel-water mixtures. Mean survival times were plotted manually and the 96-hour LC-50 values were estimated from the curves.](image)

Tainting of fish by diesel recovered from the truck and from the river

Both samples produced undesirable flavors in the fish (Table 1), with almost the same intensity of off-flavor produced by 2.5h exposure as by 5h exposure. Clearly both samples of diesel fuel retained the property of tainting fish.

Tainting of fish confirmed in fish from the river

About five months after the spill, a fisherman complained that whitefish caught below a waterfall some 500 m downstream from the spill site were inedible due to their oily taste. No other oil spills had been reported in the area. Sensory analysis of additional fish obtained by angling below the waterfall on August 25, of the same year, confirmed the presence of an oily off-flavor. These fish would
have been present in that same reach of the river over the interval between the spill and their capture because they form a resident population confined between two impassible waterfalls 16 km apart.

<table>
<thead>
<tr>
<th>Exposure group</th>
<th>Exposure time (hours)</th>
<th>Mean panel score ± Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control, no oil</td>
<td>5</td>
<td>0.70 ± 0.76</td>
</tr>
<tr>
<td>Truck diesel</td>
<td>2.5</td>
<td>8.12 ± 1.73</td>
</tr>
<tr>
<td>Truck diesel</td>
<td>5</td>
<td>8.53 ± 2.24</td>
</tr>
<tr>
<td>River diesel</td>
<td>2.5</td>
<td>6.57 ± 2.41</td>
</tr>
<tr>
<td>River diesel</td>
<td>5</td>
<td>7.93 ± 2.39</td>
</tr>
</tbody>
</table>

Means with the same superscript do not differ at the 5% probability level. The reading of 0.70 for the intensity of off-flavor in the control samples results from a carryover effect of a strongly flavored sample on a subsequent weakly flavored sample. The problem of carryover is minimized but not eliminated by presenting samples to each panelist in a different random order.

Summary

In summary, diesel fuel spilled in winter in northern Canada penetrated through the snow and spread under it, with some oil reaching a river nearby. Diesel fuel recovered from under the ice of the river eight days after the initial accident had retained its original alkanes and other hydrocarbons. It had also retained its acute toxicity to fish, and its ability to taint fishery products with an offensive taste. This latter property would be sufficient to close any fishery experiencing such a spill. The normal weathering phenomenon often described for oils under temperate and open-water conditions did not occur during the first week after the spill, and probably not for much longer. As far as we are aware this is the only report showing the retention of chemical, toxicological, and tainting properties by a light refined oil spilled into water under northern winter conditions.

Case histories provide valuable illustrations of actions of pollutants under real environmental conditions and can serve to test theoretical expectations resulting from calculations and laboratory experiments. This case history is recorded in legal records because it resulted in court prosecution under the Canadian Fisheries Act but it has not been recorded in the scientific literature. The case confirms the importance of physical factors in limiting weathering of even a light refined oil in the Arctic in winter. It also documents a real incident in which pollution by diesel fuel was harmful to the fishery of a small Arctic river.
References


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