Identification and Potential Biological Effects of the Major Components in the Seawater Extract of a Bunker Fuel

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INTRODUCTION

In January, 1971, approximately 840,000 gal of bunker fuel (Standard Oil Co. of California) was accidently discharged into San Francisco Bay. About 60% of the oil was recovered by methods capable of recovering only floating or beached insoluble residues (CHAN, 1973). Inevitably, escaping portions of the oil fouled littoral marine communities and water birds, often with fatal results (WHITE, 1972). Unknown amounts of the volatile fractions of oil escaped to the atmosphere, and some dissolved in the water column. We presently report the composition of the seawater extract of a bunker fuel similar to that spilled in 1971, and comment on previous methodology for obtaining the seawater-soluble fraction of bunker fuels (BOYLAN and TRIPP, 1971) as well as the possible significance of the dissolved oil to a local crab species.

"Bunker fuel" is a term applied to various mixtures of petroleum-derived compounds, which are often waste products of refineries. Although no two bunker fuels are identical, those produced by a single refinery are generally similar. We chose the present bunker fuel (identified as Chevron Tank 1899) because of its availability and similarity to that involved in a spill of major proportions, although this fuel is not necessarily representative of a uniformly formulated class of materials.

Few data have been published concerning the composition of water-soluble material released from crude or fuel oils, and meaningful conclusions regarding the biological effects of aqueous extracts of fuels are lacking (KITTREDGE, 1973; LICHOTOVICH et al., 1971). Seawater extracts of a bunker fuel have been shown to contain naphthalene as well as methyl and dimethyl naphthalenes (BOYLAN and TRIPP, 1971). The known toxicities of such compounds for fish (PICKERING and HENDERSON, 1966; HOLLAND et al., 1960) indirectly suggest that

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large scale release of water solubles constitutes a threatening, though less visible hazard than the more obvious fouling effects of floating oil.

METHODS

Seawater extracts of a test bunker fuel (Chevron Tank 1899) were prepared by mixing 1000 ml aged seawater and 50 g bunker fuel in a Waring, 4 liter blender at low speed for 1 minute. The dark brown aqueous phase was separated and filtered through Whatman #1 paper. The resultant solution was filtered through diatomaceous earth and then through a 0.45μ membrane filter. The final solution was clear and colorless with no visible emulsion and had a strong cresol-like odor. Other extracts were prepared by repeating the procedure with distilled water and by eluting the water-soluble components from sand impregnated with bunker fuel. Dissolved organic compounds were recovered by extraction, either with reagent chloroform or with reagent pentane. The resultant solution was concentrated on a rotary evaporator and analyzed by gas chromatography (GLC) on a column of 20% FFAP on 70/80 AW DMCS Chromasorb W (Varian Aerograph Co.) using an Aerograph Model A550 oven with A600 electrometer. Major components were purified by preparative gas chromatography on columns of Carbowax 20M and SE-30 as required. Individual components were identified by mass spectrometry and, as necessary, by infrared spectroscopy and thin-layer chromatography.

RESULTS and DISCUSSION

Gas chromatograms of seawater extracts of bunker fuel are shown in Fig. 1. When chloroform was used for recovery, the major component of the seawater extract (Fig. 1a) comprising 36% of the dissolved oil, was identified as acetophenone, based on its mass spectrum (parent ion m/e = 120 with major fragments at m/e = 105, 77 and 51 and infrared spectrum, $\nu_{C=O}$ 1965 cm^{-1}). The component responsible for the peak of retention time 6.7 min was identified as 2-phenyl-2-propanol by its mass spectrum (parent ion m/e = 136; major fragments at m/e 43 and 121), infrared spectrum and its thin-layer R_f-value on silica gel. Other components which were identified by their mass spectra and GLC retention times included naphthalene, phenol, and *o*- and *p*-cresol. In addition, the methylnaphthalenes were identified by coinjection with authentic samples. The presence of xylenols was indicated by minor peaks with retention

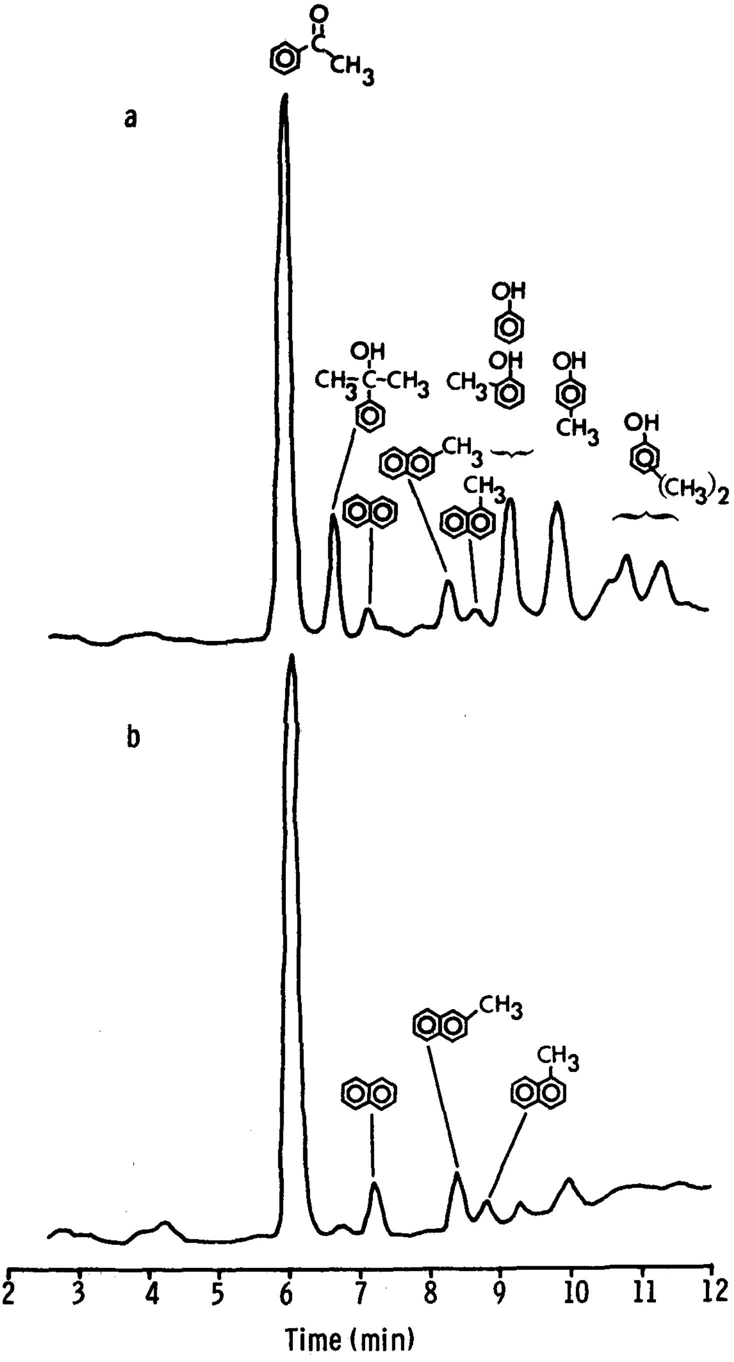

Fig. 1. Gas chromatograms of seawater extracts of bunker fuel. a. Recovered by chloroform extraction. b. Recovered by pentane extraction.

times approximately 11 min resulting from components readily extracted by 5% NaOH. Thus, the major components of the seawater extract of this bunker fuel are acetophenone, 2-phenyl-2-propanol, phenol and cresols. Naphthalene and its methyl derivatives are present in comparatively minor amounts (Fig. 1a). Similar results were obtained with distilled water extracts and when samples were eluted from oil-impregnated sand.

When the seawater extract of the oil was extracted with pentane, incomplete recovery of the phenolic aromatics and the 2-phenyl-2-propanol was observed (Fig. 1b). The amounts of these more polar, and consequently more water-soluble components, were substantially reduced relative to the less water-soluble naphthalene and methylnaphthalenes. Therefore, a representative recovery of the dissolved petroleum components cannot be obtained by the use of a saturated hydrocarbon, such as pentane, for extraction.

The appearance of polar aromatics, including acetophenone, and phenols as major constituents of the original seawater extract of our bunker fuel, contrasts with the findings of BOYLAN and TRIPP (1971) that naphthalenes are the major constituents of seawater extracts of bunker fuels (Northeast Petroleum Co., No. 6 oils) recovered by pentane extraction. This apparent contradiction stems, in part, from the variable composition of bunker fuels from different sources. However, the failure of pentane and similar nonpolar solvents to extract phenols completely may have been a significant factor. To characterize the composition of dissolved oil, we feel that chloroform or other polar solvents must be employed for extraction of oil from water samples. Accurate characterization of the dissolved oil is mandatory if realistic toxicological assays are to be performed using marine organisms.

Due to the partition coefficient, the blender extraction procedure produced only about 10 mg/liter of dissolved oil from 50 g of bunker fuel, but we found that water-soluble components which leach from an oil film exposed to a large volume of water constituted about 0.1% of the fuel. Under field conditions (e.g., during the 1971 San Francisco spill) the combined effects of tidal currents, beaching of the oil, agitation during cleanup operations, and exposure of the oil to water for several days produced significant elution of the water-soluble components of the oil.

We have prepared and analyzed a seawater extract of a sample of bunker fuel recovered from a beach on San Francisco Bay two days after the 1971 spill. The most water-soluble compounds present in the test bunker fuel were not detected in the seawater extract of this sample. Major components were naphthalene compounds; polar aromatics apparently had been removed by prior exposure to seawater. This behavior was reproduced using our test bunker fuel. Two grams of our mixture placed in 4.5 l of seawater for 12 hrs with mild agitation resulted in essentially complete loss of acetophenone, 2-phenyl-2-propanol, phenol and cresols to the aqueous phase; naphthalene derivatives remained the major water-soluble components in the residue. The loss of acetophenone during weathering is shown in Table I. These observations support our contention that significant amounts of low molecular weight polar aromatic compounds present in the spilled bunker fuel rapidly dissolved at the time of the 1971 spill.

TABLE I

Percentage Acetophenone in Seawater Extracts of Bunker Fuels

Bunker Fuel	Percent of Total Seawater Extract
Fresh Tank 1899	36%
Weathered Tank 1899	< 1%
Recovered from Beach Voyage 1456	< 1%

The actual amount of oil that dissolved from the 1971 spill remains unknown. A hypothetical, yet realistic minimum estimate of oil fraction leaching into the water from the spilled bunker fuel might have been 100 mg per liter of oil based on our laboratory extraction of the test bunker fuel. With 840,000 gal (ca. 3.18×10^6 liters) of oil spilled, approximately 317 km^2 of the top meter of seawater could have been fouled with water-soluble components at the 1 ppb level. The fouling of Duxbury Reef, about 20 km north on the coast from San Francisco, suggests that some water-soluble components could have been transported to that location in the oil slick and concurrently dissolved in surface water. Sedentary littoral animals on Duxbury were severely affected by floating oil which became thickly deposited on a great part of the reef. The vagile population of the shore crab *Pachygrapsus crassipes*, which may have been able to escape the physical effects of the oil, was nonetheless decimated over a large portion of the reef (CHAN, 1973). Similar effects were observed within the Bay at a breakwater near the city of Sausalito. A possible explanation of the disappearance of the crabs is that they were adversely affected by the water-soluble components as identified above. This conclusion is supported by the results of KITTREDGE (1973) who has shown that the water-soluble components of fuel oils seriously impaired feeding and sexual behavior of this species at ppb concentrations. This is the first report, to our knowledge, of a potential environmental effect of identified water-soluble components of an oil spill. Considering the active crab fishing along the California Coast, continued research into the effects of dissolved oil on these animals (particularly the juvenile plankton stages) is merited.

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