PERSISTENCE OF PHENOLS IN AQUATIC MICROCOSMS RECEIVING CHRONIC INPUTS OF COAL-DERIVED OIL

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(Received January 20, 1983; revised May 18, 1984)

Abstract. The environmental fate of constituent phenols of a coal-derived oil spilled intermittently on water was evaluated in aquatic microcosms. Phenols dissolved rapidly from the oil into the water, and initially accumulated with sequential oil additions. The major process removing phenols from the microcosms was microbial degradation—other processes were negligible in comparison. After phenols attained maximum concentrations in the first 28 days of the study, degradation rates exceeded input rates in all microcosms during the second 28 days the study and total phenol concentrations decreased. Significant differences were apparent in the rates of degradation of various alkylphenol isomers and isomer groups, but no compounds were observed to be refractory. Upon discontinuation of oil inputs at day 56, dissolved phenols disappeared within several weeks. Microcosm exposure history and the presence of other phenol isomers affected the rate of removal of individual isomers, complicating prediction of the rate of removal of individual toxicants.

1. Introduction

Phenol and alkylated phenols are major industrial raw materials and important constituents of many coal-derived substitutes for natural crude oil or boiler fuel. Since these phenols are highly toxic to aquatic life (Giddings, 1982; Giddings and Washington, 1981; Giddings et al., 1980; Becker et al., 1983; Dauble et al., 1982) and dissolve rapidly into water contacting phenolic liquids (Herbes et al., 1983), spills of phenolic liquids in waterways can pose a threat to aquatic resources. The degree of hazard of any spill will be determined in part by how rapidly the toxic contaminants are removed from the water column by natural processes. Predicting how rapidly toxicant concentrations will be reduced by these processes requires knowledge of the processes that dominate the fate of the toxicant and estimates of the rates of those processes in the aquatic system (Baughman and Lassister, 1978). An important consideration is the role of factors such as the presence of other contaminants and the response of the biotic component of the system to prior or continuing toxicant exposure. Microcosm experiments provide the opportunity to investigate the importance of such factors.

As part of a larger study undertaken to evaluate the responses of aquatic ecosystems to chronic inputs of coal-derived oil, this study (Franco et al., 1984; Giddings et al., 1984) investigated the ability of aquatic microcosms to accommodate chronic pollution by phenolic liquid fuels. Our objectives were to determine the rates and mechanisms of

removal of phenols in microcosms, to assess the extent to which prior and continuing exposure affects the system's ability to degrade phenols, and to identify persistent water soluble components of synthetic liquid fuels that may not be rapidly removed from surface waters.

2. Methods

2.1. Microcosm Studies

The aquatic microcosms used in this experiment are described in detail by Franco et al. (1984). They were aquaria containing 55-L of pond water and 6 cm of natural sediment. *Elodea canadensis*, the dominant aquatic plant, filled the lower two-thirds of the water column, with many shoots reaching the surface. A pH of 10.2 was typical at the start of the experiment, with a value of 7.5 typical at the end in the oil-treated microcosms. The chamber housing the microcosms controlled the temperature at 15.5 °C during the night and 21.5 °C during the day. Illumination was 160 to 213 μEin m⁻² s⁻¹ daylight fluorescent lighting for 12 h daily.

In the larger study (Franco et al., 1984), pairs of microcosms received equivalent oil doses, one weekly, the other daily. Seven dose rates were administered, ranging from 0.28 to 7 mL of oil per week. In our study, only the four microcosms receiving the two highest dose rates were monitored. They are referred to in this paper by the nomenclature used in the larger study (Franco et al., 1984). Thus, microcosm 7D received 7 mL oil week⁻¹, administered 1 mL day⁻¹, and microcosm 7W received 7 mL oil week⁻¹, administered in a single dose once each week. Microcosms 6D and 6W each received 2.8 mL oil week⁻¹, with daily and weekly inputs, respectively.

The oil used in the study was a distillate (boiling range ~ 196 to 268 °C) from the H-coal process containing approximately 10% total phenols, and is identified as sample No. 887 in the ORNL sample repository (Cowser, 1982). Oil was added in the morning, when the microcosms were at the daily minimum temperature. Water samples were taken daily though siphons and frozen and stored at −20 °C. Oil addition ended after 56 days.

The most abundant class of water soluble compounds in the oil used was phenols, represented primarily by cresols, xyleneols, and other alkyl phenols containing two to four alkyl carbon atoms. We analyzed phenols by using a VARIAN Model Vista 5000 high performance liquid chromatograph equipped with a 30-cm × 4-mm MCH-10 reverse phase column. Centrifuged water samples were injected directly into the HPLC and were eluted at 2mL min⁻¹ with an acetonitrile/water gradient starting at 80% water and terminating at 73% acetonitrile in 20 min. A variable wavelength UV absorption detector was used at 230 nm to detect the phenols. Peaks were quantified against appropriate standards when possible. When peaks contained more than one possible isomer, a mean response factor was obtained from coeluting standards. If no coeluting standards were available, peaks were quantified by using mean response factors for a group of isomers that were close to the elution position of the unidentified peak.