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Review paper

Organic geochemistry applied to environmental assessments of Prince William Sound, Alaska, after the *Exxon Valdez* oil spillâ€"a review

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Abstract

Organic geochemistry played a major role in the environmental assessments conducted following the *Exxon Valdez* oil spill, which occurred on March 24, 1989, and released about 258,000 bbls (41 million liters) of Alaska North Slope crude oil into Prince William Sound. Geochemical analyses of more than 15,000 sediment, tar, and biological samples and about 5000 water samples provide the largest database yet collected on oil-spill chemistry, and we review the results here. The marine environment of the Sound has a complex background of petrogenic, pyrogenic, and biogenic hydrocarbons from natural

and anthropogenic sources. Geochemical evaluation of the fate and effects of the spilled oil required that this oil and its residues be distinguished from the background. A variety of molecular and isotopic techniques were employed to identify various hydrocarbon sources and to distinguish quantitatively among mixed sources in the samples. Although the specific criteria used to distinguish multiple sources in the region affected by the *Exxon Valdez* spill are not necessarily applicable to all spill situations, the principles that governed their selection are.

Distributions of polycyclic aromatic hydrocarbons (PAH) and dibenzothiophenes distinguish *Exxon Valdez* oil and its weathered residues from background hydrocarbons in benthic sediments. Ratios of C2-dibenzothiopheneC2-phenanthrene and C3-dibenzothiopheneC3-phenanthrene were particularly useful. Carbon isotopes and terpane distributions distinguished *Exxon Valdez* residues found on shorelines from tars from other sources. Diesel and diesel soot were identified by the absence of alkylated chrysenes and a narrow distribution of *n*-alkanes, whereas pyrogenic products were distinguished by the dominance of 4- to 6-ring PAH over 2- to 3-ring PAH and by the dominance of non-alkylated over alkylated homologues of each PAH series. The presence of 18Î±(H)-oleanane in benthic sediments, coupled with its absence in *Exxon Valdez* oil and its residues, confirm another petrogenic source.

Results of geochemical studies suggest that the petrogenic component in the background of benthic sediments is derived from oil seeps in the eastern Gulf of Alaska. In 1990 and 1991, *Exxon Valdez* residues, generally forming a small increment to the pre-spill background, were found to be only sporadically distributed in some shallow, near shore sediments adjacent to shorelines that had been heavily oiled in 1989. In 1994, occurrences of *Exxon Valdez* tars on shoreline surfaces were rare, although residues could be found buried in shoreline sediments at some isolated locations along the spill path where they were protected from wave action. Spilled oil residues collected 16 months after the spill were degraded, on average, by nearly 50%. Shoreline residues from sources other than the spill were also identified and are widespread throughout the Sound. These residues include (1) geochemically distinct tars and oils imported from California oil fields to Alaska for fuel and construction purposes prior to the discovery of the Cook Inlet and North Slope oil fields, (2) diesel and diesel soot, and (3) more highly refined products.

Of the more than 2700 chemical analyses of biological samples of higher life forms (fish, birds, and mammals) about 150 (6%) indicate recognizable residues of *Exxon Valdez* oil,

which were identified by their distribution of polycyclic aromatic hydrocarbons (PAH). Most of these samples (138) were collected in 1989 and most were associated with external surfaces or the gastrointestinal tract. Rarely do internal tissues or fluids contain recognizable fingerprints of spilled oil. This observation includes samples from marine mammals that were visibly oiled externally. Other hydrocarbon sources, including diesel and a non-petroleum artifact that occurs when concentrations of individual PAH are at or near their method detection limit, are also identified in biological samples.

Keywords

oil spill; *Exxon Valdez*; hydrocarbon fingerprinting; polycyclic aromatic hydrocarbons; biomarkers; hopane; carbon isotopes; subtidal sediments; environmental assessments; oil seeps; fate, effects; environmental geochemistry; Prince William Sound; Alaska

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