

STUDY TITLE: University Research Initiative on the Effects of Offshore Petroleum Development in the Gulf of Mexico

REPORT TITLE: Fate and Transport of Particle-Reactive Normal, Alkylated, and Heterocyclic Aromatic Hydrocarbons in a Sediment-Water-Colloid System

CONTRACT NUMBER: 14-35-0001-30470

SPONSORING OCS REGION: Gulf of Mexico

APPLICABLE PLANNING AREA: Central Gulf of Mexico

FISCAL YEARS: 1989 through 1993

COMPLETION DATE OF REPORT: June, 1993

COSTS: FY 89: \$70,734; FY 90: \$69,173; FY 91: \$73,443; FY 92: \$0; FY 93: \$0

CUMULATIVE PROJECT COST: \$213,350

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KEY WORDS: Produced water, brine, hydrocarbons, sorption, desorption, sediments, fate, transport, Louisiana, GC/MS analysis

BACKGROUND: The Northwestern Gulf of Mexico region is an area of intensive oil and gas exploration and production. Produced water separated from OCS oil and gas is discharged into coastal and OCS waters, resulting in the contamination of sediments. The U.S. Department of the Interior, Minerals Management Service is charged with the assessment of short- and long-term impacts of OCS oil and gas production activities. This study addresses the physical-chemical processes which determine the distribution and lifetime of aromatic hydrocarbons in sediment-water systems.

OBJECTIVES: 1) To study the sorption/desorption equilibria and kinetics of selected normal, alkylated and heterocyclic PAH on various sediment types (a range of organic carbon and particle sizes) over a range of salinities; 2) to study the relationship between the carbon fraction of sediments and the equilibrium K_{oc} (partition coefficient) for selected normal, alkylated and heterocyclic PAH; and 3) to study the kinetics of desorption of aromatic hydrocarbons from bedded sediments.

DESCRIPTION: The overall study framework was designed to investigate the fate, transport and chemical transformations of normal, alkylated and heterocyclic aromatic hydrocarbons associated with produced water discharges in coastal marine and estuarine systems. The study area encompassed both estuarine and near-shore coastal regions of Louisiana receiving such discharges.

SIGNIFICANT CONCLUSIONS: Sorption/Desorption Equilibria: Sorption equilibrium partition coefficients on sediments were determined using standardized procedures. Desorption kinetics were investigated using: batch and sediment microcosms. The kinetics of the sorption/desorption process in marine/estuarine sediments were studied as a function of salinity changes. An empirical predictive model of the effects of salinity upon sorption equilibria was developed and reported.

Fate of In-place Petrogenic Contamination in Sediments: An extensive methods development effort was directed at the trace determination of 58 specific positional isomers of alkylated naphthalenes, phenanthrenes and dibenzothiophenes with the result that much new information on the distribution and fate of these substances was obtained in field assessments and laboratory experiments. The mean detection limits achieved for water samples (2000 ml) and sediment samples (<2 g) using selected ion monitoring gas chromatography/mass spectrometry are 0.005 ppb and 0.5 ppb, respectively.

Microcosm Development and Testing of PAH Desorption Kinetics: A microcosm system to study the desorption of alkylated PAH from contaminated sediments for extended periods was developed. Results of these investigations have led to the development of a predictive model for evaluating desorption rate constants for several groups of alkylated and heterocyclic PAH.

STUDY RESULTS: Sorption/Desorption Equilibria: The results of the study on the effects of increasing salinity upon sorption and desorption equilibria represent some of the most detailed data published to date. In all cases, sorption/desorption K_d values were dependent upon salinity. The effects salinity on partitioning were examined in terms of the salting out effect as described by the Setchenow equation and incorporating the established regressions of partition coefficients with the inverse of aqueous solubility. This equation was: $\log K_dS/K_dO = \sigma M_s - \log Y_{O_j}$. Plots of experimental values of $\log K_dS/K_dO$ against the molar concentration of seawater (M_s) yielded a slope of σ and an intercept of $\log Y_{O_j}$. The values of Y_{O_j} determined (~ 0.80) were close to unity or the expected theoretical value. Similarly, the Setchenow constants (σ) determined were 0.55, close to values measured in solution of ~ 0.3 . Analytical Methods Development: The new analysis method which was developed was applied to field collected sediment cores and yielded comprehensive data on the spatial and depth distributions of parent, alkylated and heterocyclic PAHs. Detection limits for water samples of 0.005 ppb and for sediment samples of 0.5 ppb were achieved with excellent recoveries of surrogates (80-110%). Standard QA/QC procedures, including analysis of duplicate and spiked samples, and daily tuning and calibration of the GC/MS system were performed. Field Applications: An extensive body of information was

acquired for surface and depth sections of cores collected seasonally at various distances from produced water discharges located at Pass Fourchon, Bayou Rigaud and Eugene Island (OCS) in South Louisiana. Variations in the relative concentrations of alkylated and heterocyclic PAH were seen at various distances from the two discharge sites. We have applied ratioing of analytes and multi-variant statistical analysis techniques in order to further examine patterns in this and other data to determine if there are selective mobilization/ removal processes which may be active in the field for various members of the class of alkylated and heterocyclic PAH.

Microcosm Studies: A microcosm test apparatus was designed. Sediment cores were incubated in the microcosm for periods up to 120 days. Cores were then sectioned and analyzed according to the methodology developed and reported here. Desorption profiles were determined at each time point and an overall model of diffusion limited desorption based upon a semi-infinite solution to the Fickian diffusion model with respect to the concentrations was applied. The experimental data from the depth profiles for individual compounds at various times in our study were fitted to this model to estimate values for effective diffusivity (D_{eff}). Alternatively, values of D_{eff} estimated from compound molecular parameters were used to evaluate the fit of the Fickian diffusion model to profiles in the experimental cores. Precise measurements of the concentrations of several isomers of the same compound (eg. dimethyl naphthalenes), made multiple estimates of D_{eff} within a core possible.

STUDY PRODUCT: Means, J.C. and D.J. McMillin. 1993. Fate and Transport of Particle-Reactive Normal, Alkylated and Heterocyclic Aromatic Hydrocarbons in a Sediment-Water-Colloid System. A final report by the Louisiana Universities Marine Consortium for the U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico Region, OCS Office, New Orleans, LA. Contract No.: 4-35-0001-30470, OCS Study MMS 93-0018. 150pp.

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