

STUDY TITLE: Biodegradation of Aromatic Heterocycles from Petroleum Produced Water, and Pyrogenic Sources in Marine Sediments

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PROJECT MANAGER: W. James Catallo

AFFILIATION: Louisiana State University

ADDRESS: Department of Veterinary Physiology, Pharmacology & Toxicology, Baton Rouge, LA 70803

PRINCIPAL INVESTIGATOR: W. James Catallo

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BACKGROUND: The wetland and coastal marine environments are being impacted by discharges from OCS production and other industrial activities. The potential exists for the impairment of function and quality for habitat and other living resources. Biodegradation and bioremediation research attempts to develop treatment approaches that detoxify pollutant mixtures as well as remove these compounds from affected systems. This requires detailed knowledge of the transformation rates and pathways of chemicals under different environmental conditions as well as data on the results of these reactions in terms of bioavailability and toxicity.

OBJECTIVES: Marine sediment is being collected and exposed to oxidized and reduced conditions in microcosms where each sample is exposed to mixtures of heterocycles. The microcosms are incubated and sampled for heterocycles and their intermediates. Attempts are being made to enhance the biodegradation of heterocycles by selecting for effective microbial communities. This work examines in detail the biodegradation pathways and rates of degradation for toxic organic chemicals in marine sediments by indigenous microflora. A series of heterocyclic chemicals found in

produced waters and pyrogenic products is being examined for biodegradation under different physicochemical conditions in sediment-water microcosms maintained in the laboratory.

DESCRIPTION: This report summarizes laboratory studies and associated technical development on the influence of hydrology on biogeochemical processes, particularly those that govern the transport and transformation of pollutant organic chemicals in wetland sediments. The goals were to: 1) determine the effects of static vs. dynamic hydrology on biogeochemical behavior of tidal wetland sediment systems, with respect to central variables (e.g., redox potential dynamics) and pollutant transformation, 2) design and build hydrodynamic microcosms for this purpose that are reproducible, well controlled, and adequately monitored in the laboratory and, 3) develop analytical approaches for target pollutant chemicals that allow for detection of small but significant concentration differences between time points and treatments. The pollutant chemicals examined here included representative N-, O-, and S- heterocycles (NOSHs) that occur in coal chemicals, crude oils, and pyrogenic mixtures. The target analytes were quinoxaline, 2-methylquinoxaline, 2,3-dimethylquinoxaline, benzothiazole, dibenzofuran, phenazine, dibenzothiophene, phenothiazine, acridine, and phenanthridine. These and other NOSHs are found in pollutant mixtures near certain industrial activity, hazardous waste sites, and major harbors. They are of interest because of their apparent stability in aquatic sediments except for certain (turbulent, well-oxidized) conditions under which they are labile. Further, many NOSH compounds are acutely toxic, with some also mutagenic and/or carcinogenic in mammals.

SIGNIFICANT CONCLUSIONS: It was found that the physicochemical and biological behavior of the sediments in the microcosms was similar to that observed in natural settings, and in accord with prevailing theory. Redox potential time series and sediment trace gas signatures from the different treatments were analogous to those encountered in field settings continuously flooded and drained systems had reduced (mean - 428 mV) and oxidized (+ 73 mV) Eh values, respectively, with no evidence of daily or longer periodic variation. The tidal systems exhibited oscillating Eh values, with significant amplitudes (40 – 180 mV/0.5 d). Biogeochemical gas mixtures leaving the sediments also reflected the hydrological status of the treatments: the major gases observed were CO₂ from microbial respiration (drained) vs. CO₂ with small sulfide and methane outputs (tidal), vs. relatively large amounts of sulfides and methane. Transformation of the NOSH analytes was different in each of the hydrologic regimes, with the rate of transformation and the number of NOSHs degraded decreasing in the following order: drained > tidal > flooded.

STUDY RESULTS: The results indicated that sediments and associated biota exposed to tidal pulsing (analogous to a streamside salt marsh ecophene) removed more NOSH compounds faster and to lower levels than a flooded sediment (analogous to a flooded interior ecophene or an impounded system). Of the two wetland possibilities (tidal vs. flooded), the tidal systems were better able to transform the NOSH compounds. From a contaminated sediment perspective, an optimal remediation strategy for these NOSHs would encompass dredging of affected areas followed by upland placement and tilling to

maintain well-oxidized conditions. From an ecological perspective, promoting *in situ* remediation of NOSHs and other organic pollutants would involve exposing as much contaminated sediment as possible to the action of tides, while minimizing the area exposed to prolonged flooding.

STUDY PRODUCTS: W. J. Catallo. 2000. Biodegradation of Aromatic Heterocycles from Petroleum-Produced Water and Pyrogenic Sources in Marine Sediments. OCS Study MMS 2000-060. A final report by the Louisiana State University for the U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. Contract No. 14-35-0001-30660-19920.