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REPORT TITLE: Fate and Effects of N-, O-, and S- Heterocycles (NOSHs) from Petroleum and Pyrogenic Sources in Marine Sediments

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BACKGROUND: N-, O-, S- heterocycles (NOSHs) occur in crude oils, coal- and petro-chemicals, produced waters, and pyrogenic products found in marine systems. Detailed studies on the environmental chemistry and toxicology of these compounds in marine sediment and water are necessary for evaluating the impacts of energy development/transportation, industry, and waste disposal in coastal marine systems.

OBJECTIVES: (1) To provide quantitative data on the fates of prominent NOSH compounds in three marine sediments under oxidized and reduced electrochemical conditions. (2) To determine the transformation pathways of selected compounds and evaluate the toxicological significance of NOSH transformation in situ. (3) To provide information on the environmental chemistry and microbiology of NOSHs introduced to marine sediments from petroleum and pyrogenic sources.

DESCRIPTION: The fates and toxicological significance NOSH compounds and mixtures in different marine sediments were evaluated in laboratory microcosms. Methods were developed for chemical analysis, transformation pathway determination,

isolation microbial degraders, and deuterated tracer/metabolic pathway experiments. Relative rates of degradation of a complex mixture of NOSHs were determined in three marine sediments under oxidized and reduced electrochemical conditions. The cytotoxicity of water and sediment samples was determined over a time course of NOSH compound degradation. The identities of stable transformation products were determined using mass spectrometry, and deuterated tracer compounds were synthesized and used to confirm product analysis and postulate metabolic mechanisms involved in the transformations of selected NOSHs. Microbes degrading the NOSHs were isolated and characterized. Mechanisms of NOSH sediment chemistry also were evaluated.

SIGNIFICANT CONCLUSIONS: Many NOSH compounds can be degraded in sediment water systems under oxidized and reduced conditions if those sediments are constantly stirred. In quiescent sediment profiles characteristic of natural marine systems, NOSHs are transformed to a much lesser extent. In both stirred and unstirred systems, partial transformation products accumulated. Several of these products were mobile, toxic and/or potentially carcinogenic. Although not transformed rapidly under natural conditions in sediments, NOSH compounds can be mobile in heterogeneous sediment water systems. Mechanisms of NOSH transport through these systems include complexation with soluble and/or redox active metals (e.g., Fe), protonation to water soluble ion pairs, electrochemical oxidation or reduction to polar species, and entrainment in colloidal or soluble organic matter.

STUDY RESULTS: The effects of redox potential (Eh) and sediment particle size distribution on NOSH degradation were examined using stirred, controlled Eh sediment-water microcosms, and sealed, unstirred microcosms approximating natural sediment profiles sediment-water microcosms, and sealed, unstirred microcosms approximating natural sediment profiles. Results from the controlled Eh microcosms showed that most NOSHs were transformed in the mixed sediment slurries under oxidized and reduced conditions. Unstirred microcosms simulating field conditions showed much less NOSH degradation. In both stirred and unstirred sediments, NOSH degradation proceeded more slowly and on fewer compounds in fine grained clay than in coarse grained sand and silt. In unstirred sediments, however, reduced redox conditions generally favored NOSH compound degradation relative to oxidized conditions, while this effect was attenuated under stirred conditions. The sediment microbial communities of the microcosms were affected by NOSHs: within 7 days of exposure to 19 NOSH compounds (50 ppm each), aerobic samples showed reduction or elimination of gram (+) bacteria and termination of fungal growth. The anaerobic community was not appreciably affected by NOSHs. Microbes isolated from both oxidized and reduced NOSH microcosms showed rapid growth on single and crude oils containing NOSHs. Single compound growth favored mainly one or two *Psuedomonas sp*., with an actinomycete also observed when co-substrates were introduced along with the NOSHs (e.g., alkanes and aromatics in the carbon black). The cytotoxicity of aqueous phase samples from the stirred microcosms generally decreased with time and progressive NOSH degradation. The level of measured aqueous cytotoxicity, however, oscillated before becoming consistently low after about 7 weeks. Under oxidized and reduced

conditions, stable NOSH transformation products accumulated. These tended to be oxygenated, water soluble system with potentially significant chemical and toxicological characteristics (e.g., redox cycling, metal complexation). The major metabolic processes represented by the transformation products were 1) oxidation to phenols, ketones, carboxylic acids, and alcohols, 2) saturation of aromatic rings and disproportionation of heterocyclic atoms (e.g., protonation of N and O, oxidation and S), 3) opening of aromatic rings followed by b oxidation (or decarboxylation of oxidized alkyl groups), and 4) a complex series of addition reactions (observed with benzothiazole). Some NOSH products were structurally similar or identical to know carcinogens, so the effects of microbial action were to increase toxicity and availability of some NOSHs, at least temporarily. Reactions including iron-NOSH complexation and chemical redox reactions in situ were found to be important to NOSH fates in sediments. The stirring and vigorous mixing of the sediments in the controlled Eh microcosms obscured this effect, and stimulated the degradation of most NOSH compounds under oxidized and reduced conditions. Hence the stirred microcosms gave over-estimates of NOSH degradation in sediment-water systems typical of most estuarine environments.

STUDY PRODUCT: Catallo, W. James and Robert P. Gambrell. Fates and Effects of N-, O-, and S-Heterocycles (NOSHs) from Petroleum and Pyrogenic Sources in Marine Sediments. Final report submitted to the U.S. Dept of the Interior, Minerals Management Service, Gulf of Mexico Region, OCS Office, New Orleans, LA. Contract Number: 14-35-0001-30470. OCS Study MMS 94-0056, 81 pp.

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