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Environmental Effects of Dredging Technical Notes

REGULATORY IDENTIFICATION OF HYDROCARBON CONTAMINANTS IN DREDGED MATERIAL

PURPOSE: This note summarizes the findings of a workshop convened to assist Corps regulators in the evaluation of hydrocarbon contamination in dredged material. The workshop participants suggested a list of 15 compounds to be used in a tiered testing approach. The 15 compounds occur frequently in contaminated sediment, can be analyzed reliably, and are considered to be representative of hydrocarbons that are known in general to have toxic effects.

BACKGROUND: A 3-day workshop on regulatory evaluation of hydrocarbons in dredged material was conducted 13-15 May 1986 at the Waterways Experiment Station (WES). The workshop was requested by the US Army Engineer Districts, New York and Chicago. The purpose of the workshop was to provide the districts with assistance in identifying specific hydrocarbon compounds that would be the most appropriate to analyze in the regulation of dredged material disposal. The original focus was on petroleum hydrocarbons, but the scope of the workshop was broadened to consider any hydrocarbon contamination regardless of source.

Workshop participants from government agencies, private industry, and academia were selected for their expertise in analysis of hydrocarbons in sediment and in prediction of the potential environmental impacts of such substances. The workshop consisted of brief presentations and roundtable discussions focusing on various aspects of environmental chemistry and biological effects of hydrocarbons. The discussions culminated in the recommendation of specific hydrocarbons as indicator compounds and in the development of a suggested tiered testing approach for regulatory evaluation of hydrocarbon-contaminated dredged material.

ADDITIONAL INFORMATION OR QUESTIONS: Refer to the workshop proceedings (Clarke and Gibson 1986) or contact the authors, Ms. Joan Clarke (601) 634-2954 (FTS 542-2954) and Ms. Alfreda Gibson (601) 634-4027 (FTS 542-4027), or the EEDP Program Manager, Dr. Robert M. Engler, (601) 634-3624 (FTS 542-3624).

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The Nature of the Problem

Hydrocarbons comprise a large number of compounds, some of which pose potentially serious environmental threats. Hundreds of these compounds have been identified in sediment, water, and organism tissue samples. They span a wide range of water solubility, persistence, bioavailability, toxicity, bioaccumulation potential, carcinogenicity, and overall biological importance.

Hydrocarbons, by definition, are molecules composed only of carbon and hydrogen. Straight- or branched-chain hydrocarbons are called aliphatics; hydrocarbon ring structures are called cyclics. Hydrocarbons that contain only single bonds between adjacent carbon atoms are termed saturated (i.e., saturated with hydrocarbon atoms); the presence of double or triple bonds makes them unsaturated. Reactivity of hydrocarbons generally increases with degree of unsaturation. Aromatics, in the classic sense, are cyclics containing one or more 6-carbon rings in which the carbon atoms are joined by alternating double and single bonds (e.g., benzene and naphthalene). Heterocyclics are ring structures that include elements other than carbon and hydrogen (such as nitrogen, sulfur, or oxygen) and may or may not be aromatic. Cyclic hydrocarbons with side chains attached to a parent structure (nucleus) are alkylated. Examples of these structures are illustrated in Figure 1.

Hydrocarbons in aquatic systems can arise from several sources. Petroleum hydrocarbons originate only from petroleum products ranging from crude oil to highly refined products and often contain heterocyclics. Fuel-oil spills and miscellaneous disposal (e.g., municipal surface runoff) are major sources of petroleum contamination to the aquatic environment. Hydrocarbons may also be biogenic or pyrogenic in origin. Biogenic hydrocarbons are produced by living organisms and consist primarily of aliphatics. Pyrogenic hydrocarbons are generated by combustion or incineration of various organic substances including petroleum, coal, and wood products, and they enter aquatic systems mainly via atmospheric deposition.

In some circumstances, the potential for a toxic environmental impact of a dredged material may be determined by its particular mixture of hydrocarbon compounds. Analysis of hydrocarbons in a sediment sample as oil and grease or as total petroleum hydrocarbons or other summary type measures cannot provide sufficient information for accurate evaluation of potential environmental impacts. On the other hand, qualitative and quantitative analyses of <u>all</u>

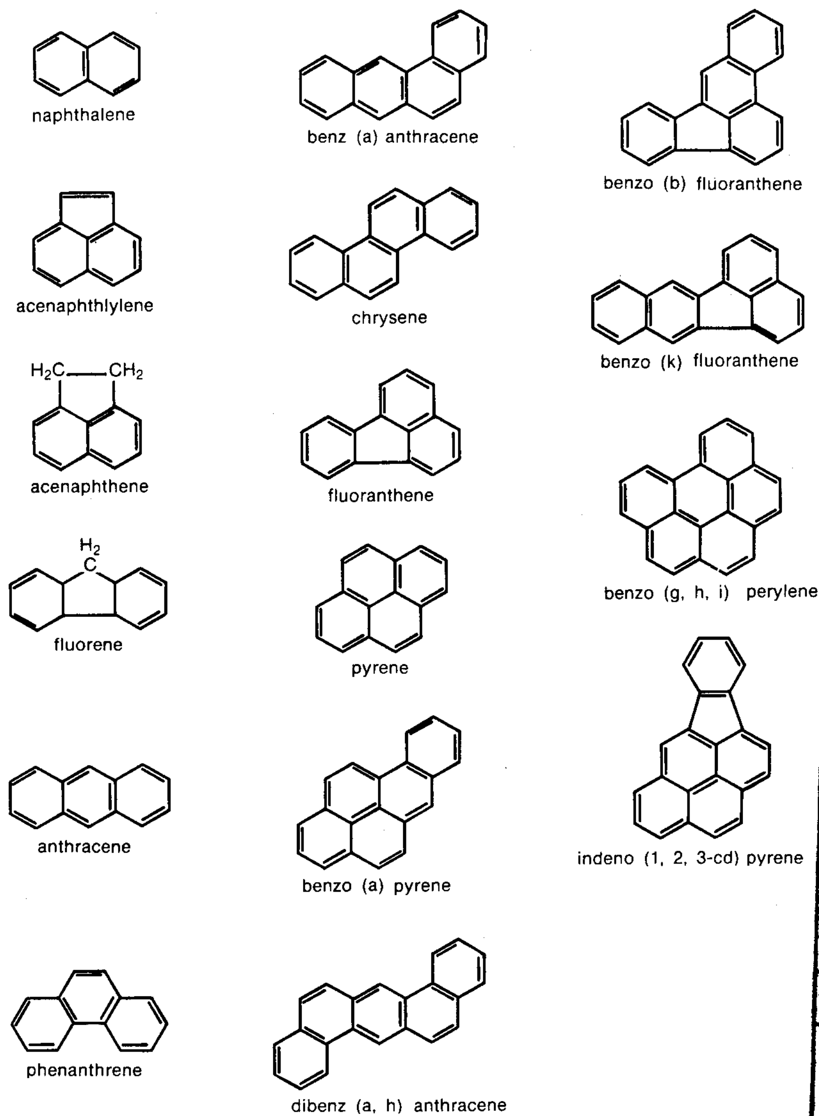

Figure 1. Examples of basic hydrocarbon and heterocycle structures

hydrocarbon compounds present would be virtually impossible. Even a _relatively_ comprehensive analysis would be too time-consuming and expensive and would produce an excessive volume of data to be reviewed as part of the regulatory process. Thus, an intermediate approach is needed for adequate and informed regulatory evaluations of potential toxic impacts of hydrocarbons in dredged material.

The objective of the workshop was achieved by formulating such an intermediate approach based on identification of a limited number of hydrocarbon compounds to be used in a regulatory testing scheme.

Recommendations of the Workshop

Key compounds

Aromatics, particularly the polycyclic (or polynuclear) aromatic hydrocarbons (PAHs), are the most important class of hydrocarbon contaminants in dredged material from a regulatory standpoint. The PAHs are those aromatics having two or more fused rings. Not all PAHs are readily bioavailable, and most do not attain concentrations in water that are acutely toxic to aquatic organisms. However, concern over PAHs as environmental pollutants stems from the acute toxicity of some 2- and 3-ring compounds, such as anthracene and phenanthrene, and the chronic toxicity (especially carcinogenicity) of the higher molecular weight compounds.

Sixteen of the 129 toxic chemicals on the EPA priority pollutant list are PAHs (Richards and Shieh 1986, Keith and Telliard 1979). These 16 priority pollutant PAHs are illustrated in Figure 2. The workshop participants recommended 15 of the 16 priority pollutant PAHs as key compounds for regulatory evaluation of hydrocarbons in dredged material. Naphthalene was not included in the list because it is too water soluble to persist in sediment and too volatile to give accurate analytical results. The behavior, fate, and effects of the other 15 PAHs are representative of hydrocarbons that are known in general to have biological effects, and some are known carcinogens.

Aliphatics, another major class of hydrocarbons, need not be included in regulatory evaluations of dredged material because they generally do not cause major environmental impacts in the context of dredging and disposal.

Testing approach

A tiered testing approach was suggested for regulatory evaluations of PAHs in dredged material. This type of evaluation would begin with a general assessment of the likelihood of contamination. If hydrocarbon contamination is considered likely, then the first testing tier would be conducted. This tier includes an acute toxicity test and analysis of the sediment for the 15 priority pollutant PAHs selected as key compounds. Acute toxicity tests exposing crustaceans (such as *Daphnia* in fresh water and *Mysidopsis* in salt water) to contaminated sediment are commonly done and have accepted standard procedures; the results are easy to interpret. If acute toxicity is seen, then regulators might decide to impose dredging or disposal restrictions without conducting any further tests.

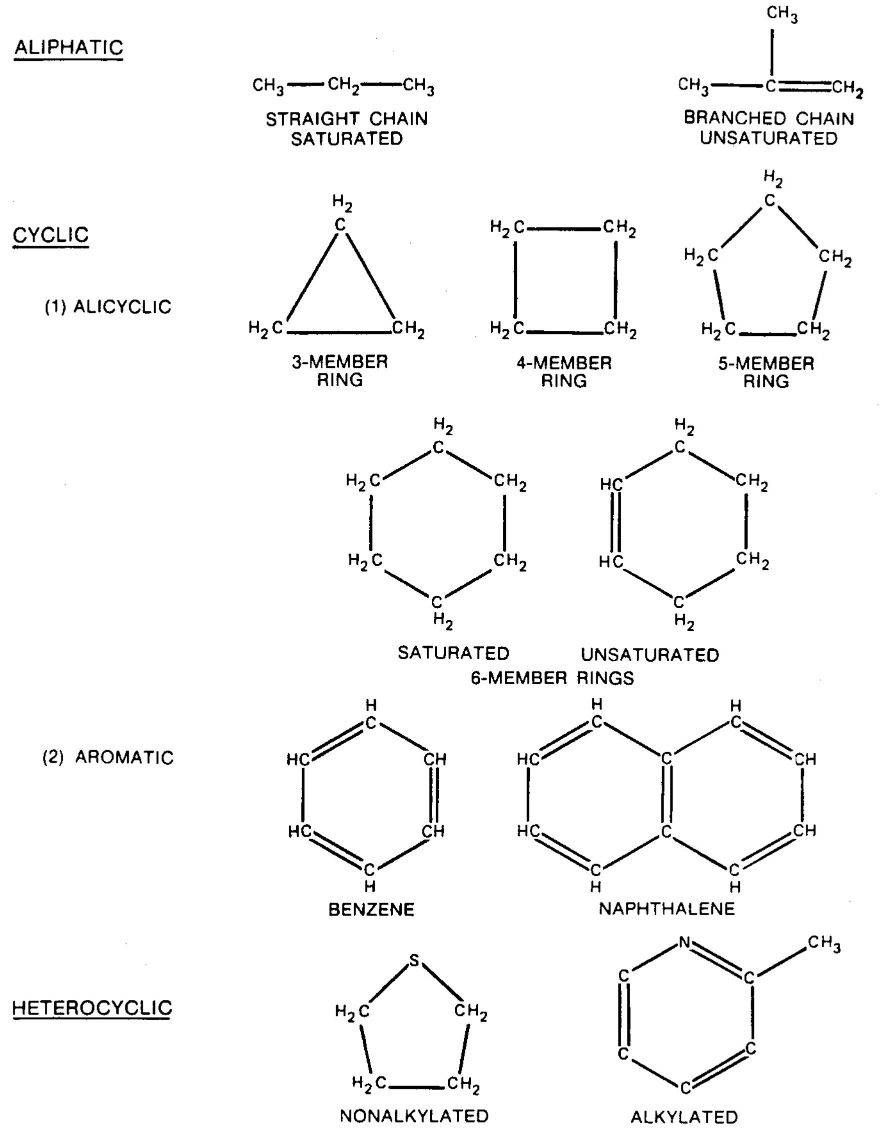

Figure 2. Structures of the 16 priority pollutant PAHs. (Note: Naphthalene was not recommended for use as a key compound.)

The first testing tier would accomplish two main purposes. First, the acute toxicity tests would indicate any acute toxicity due to any contaminants in the dredged material, not just to the 15 priority pollutant PAHs. Second, the sediment analysis would signal levels of the 15 PAHs that were not acutely toxic but that might cause concern over chronic toxicity problems. Recommending scientifically defensible levels of concern for the 15 PAHs will be the primary objective of a second workshop to be held during 1987.

If concern over chronic toxicity is suggested by the results of the sediment analysis in the first testing tier, then a second tier test would be conducted. The second tier would consist of a 10-day bioaccumulation test to demonstrate bioavailability. If any of the 15 PAHs is found in organism tissues after 10 days of exposure to the contaminated sediment, then that compound is bioavailable and may cause chronic effects. In the second-tier assessment, it is important to use organisms that have limited or no ability to metabolize PAHs. Appropriate saltwater species might include the clam *Mercenaria* or a suitable substitute bivalve or, in freshwater sediment, an amphipod such as *Pontoporeia*. Analysis of tissues for unmetabolized parent compounds is thus simplified. Although some metabolites may be more toxic to aquatic organisms than the parent PAH, analysis for metabolites of PAHs is not recommended for a routine regulatory program until more research is completed and analytical methods are better established.

Quality assurance/quality control (QA/QC) evaluations and procedures are a critical need, especially when a variety of laboratories are used by a regulatory agency for testing and review purposes. Strong QA/QC guidelines need to be developed.

Future Research

The problem of hydrocarbon contamination in dredged material is complex because hundreds of compounds may be involved, spatial heterogeneity can be great, and many environmental factors can influence bioavailability. The recommendations of this workshop represent only a starting point for informed and environmentally sound regulatory evaluation. Research is needed to develop standard analytical procedures and biological testing protocols for the evaluations of PAH metabolites and of toxic hydrocarbons other than the priority pollutant PAHs. These include some of the alkylated PAHs, heterocyclics, nitroaromatics, and aromatic amines. Bioaccumulation tests can demonstrate bioavailability under specific circumstances but cannot pinpoint chronic effects. Biological tests that need to be refined and standardized include assays for such chronic effects as carcinogenicity, genotoxicity, and reproductive effects.

Literature Cited

Clarke, J. U., and Gibson, A. B. 1986. "Regulatory Identification of Petroleum Hydrocarbons in Dredged Material; Proceedings of a Workshop," Miscellaneous Paper in preparation, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Keith, L. H., and Telliard, W. A. 1979. "Priority Pollutants, I--A Perspective View," *Environmental Science and Technology*, 13(4):416-423.

Richards, D. J., and Shieh, W. K. 1986. "Biological Fate of Organic Priority Pollutants in the Aquatic Environment," *Water Research*, 20(9):1077-1090.