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Environmental Effects of Dredging Technical Notes

Data Base for Polychlorinated Dioxins and Polychlorinated Furans

Purpose

This note provides initial information on the development of a computerized data base concerning dioxin and polychlorinated furans in aquatic media including sediments, animals, and bioassay results. The ultimate goal of compiling this data is to provide Corps elements with numerical and descriptive guidance so sediment, tissue, and bioassay results concerning dioxins and polychlorinated furans in the environment can be related to the potential for biological and environmental effects.

Background

The aquatic disposal of dredged material is regulated under two federal statutes: Section 404(b)(1) of the Clean Water Act, as amended (PL 92-500) and Section 103 of the Marine Protection, Research, and Sanctuaries Act, as amended (PL 92-532). The US Army Corps of Engineers (USACE) is responsible for ensuring that sediments are dredged and disposed in a manner that will not have an unacceptable adverse impact on the environment.

Over the past few years sediments in several areas slated for dredging have been demonstrated to have small, but measurable amounts of dioxins and polychlorinated furans present as contaminants. At least one dredging project was delayed because dioxin was detected by the US Environmental Protection Agency in a nearby paper plant settling pond. The mention of dioxin has become enough to cause public outcry and endanger the future of some dredging projects.

The extremely high cost of dioxin and polychlorinated furan determination in environmental samples coupled with the vanishingly small quantities of these analytes present in most environmental samples simply do not allow cases of suspected dioxin and polychlorinated furan contamination to be routinely evaluated like other contaminants.

Dioxins are a class of chlorinated, two-ring compounds. The word dioxin is commonly used interchangeably to mean either the class of compounds known as dioxins or, more commonly, to mean the most toxic member of the class of compounds, 2,3,7,8-tetrachloro dibenzo-*p*-dioxin. Polychlorinated furans are a closely related class of compounds that are also chlorinated, two-ring compounds. Figure 1 shows a polychlorinated dibenzodioxin (PCDD), and Figure 2 shows a polychlorinated dibenzofuran (PCDF). Chlorine atoms are substituted at each of the numbered sites on the two molecules, and the resultant name of the compound is given by the substitution numbers and a prefix designating the total number of substitutions. For example, 2,3,7,8-tetrachloro dibenzo-*p*-dioxin is substituted with four chlorines (tetra-) at the sites numbered 2, 3, 7, and 8. The names of the compounds are often abbreviated to the substituted sites, a hyphen, and the first letter of each word in the compound. For example, **2,3,7,8-t**etrachloro **d**ibenzo-*p*-**d**ioxin is abbreviated to 2,3,7,8-TCDD and **2,3,6,7,8-p**entachloro **d**ibenzo**f**uran is abbreviated to 2,3,6,7,8-PCDF. The chemicals that make up the class of compounds known as dioxins are all known as dioxin congeners. There are 75 **p**oly**c**hlorinated **d**ibenzo**d**ioxin (PCDD) congeners. Likewise, the members of the class of compounds known as **p**oly**c**hlorinated **d**ibenzo**f**urans (PCDF) are known as polychlorinated furan congeners. There are 135 polychlorinated furan congeners (Rappe 1984).

The relative toxicities of PCDD and PCDF congeners are the subject of current controversy. There is some agreement that congeners of both classes that are substituted in the 2, 3, 7, and 8 positions are toxic or more toxic than congeners not substituted in those positions. Congeners not substituted in the 2, 3, 7, and 8 positions are deemed less toxic or nontoxic. The relative toxicities of these compounds are discussed by McFarland and others (in preparation).

PCDDs and PCDFs are the product of incomplete combustion in the presence of chlorine or the product of certain industrial chlorination processes. They are released into the environment via industrial fugitive emissions or by the application of contaminated herbicide (Miller, Norris, and Hawkes 1973). It is clear that some natural mechanism for the synthesis of PCDDs and PCDFs also exists, particularly octachloro dibenzo-*p*-dioxin (Hashimoto, Wakimoto, and Tatsukawa 1990).

Additional Information

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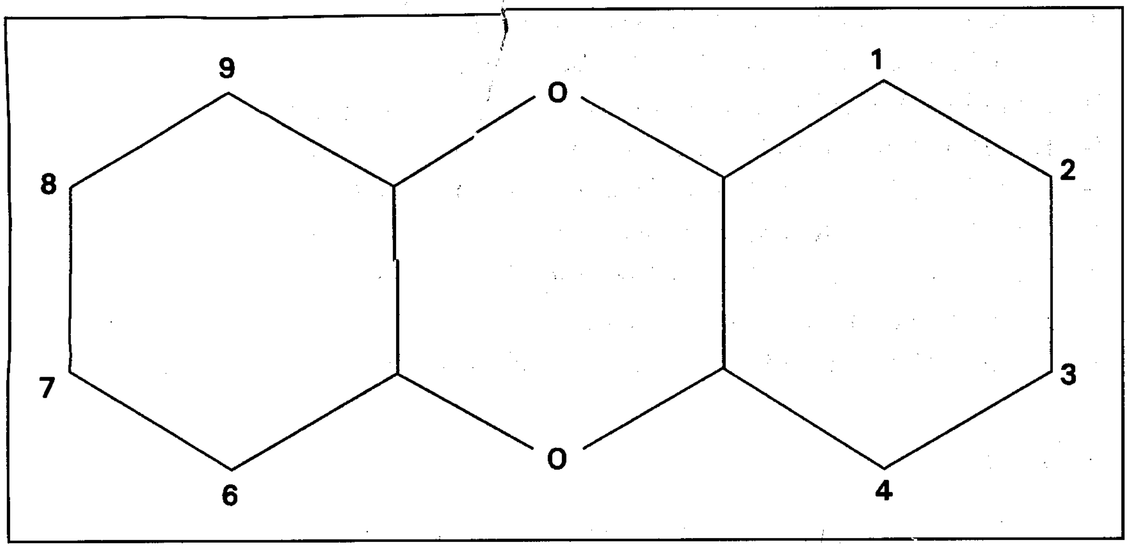

Figure 1. Polychlorinated dibenzo-p-dioxins (PCDDs); chlorine atoms are substituted at one or more of the numbered locations on the molecule

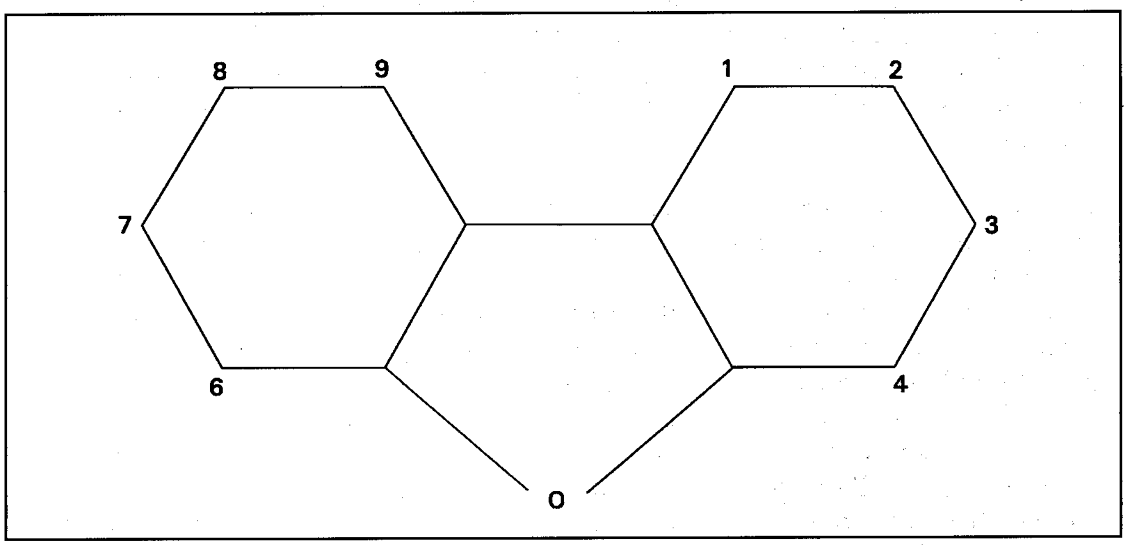

Figure 2. Polychlorinated dibenzofurans (PCDFs); chlorine atoms are substituted at one or more of the numbered locations on the molecule

Approach

In order to construct this data base the published literature was reviewed. A good deal of literature is available concerning PCDDs and PCDFs in general and the mammalian health effects of these classes of compounds. This data base, however, was specifically limited to references of an aquatic nature. More than 20 technical journals were reviewed in their entirety for the information contained in the data base. The papers selected for inclusion in the data base were used to construct nine tables, the contents of which are:

- Table 1a - Dioxin Levels in Selected Sediments
- Table 1b - Furan Levels in Selected Sediments
- Table 2a - Dioxin Residues in Bioassay Exposed Organisms
- Table 2b - Furan Residues in Bioassay Exposed Organisms
- Table 3a - Dioxin Residues in Field-Collected Organisms
- Table 3b - Furan Residues in Field-Collected Organisms
- Table 4a - Dioxin Levels in Fish-Eating Birds and their Eggs
- Table 4b - Furan Levels in Fish-Eating Birds and their Eggs
- Table 5 - Dioxin Residues Associated with Known Biological Effects

Analysis

The tables will be published in their entirety in a Miscellaneous Paper currently being prepared, but are too extensive to be included in this note. Significant information, however, can be gleaned from the tables that could be of immediate benefit to USACE field elements. Summaries of the information contained in these tables have been prepared. The information contained in Table 5 has been summarized and commented on in a technical note (Gibson and Reilly 1992). The information gleaned from all the tables and some other sources has been included in a Miscellaneous Paper dealing with Toxic Equivalency Factors (McFarland and others, in preparation).

Tables 1a and 1b summarize data published concerning PCDD and PCDF levels in selected sediments and other aquatic substrates including some data concerning fly ash settling ponds, sewage sludge, and other types of sludges. There are over 750 data arranged by congener with individual data concerning each congener's concentration, the location of the collection, and the reference from which the data were obtained. In some cases, the detection limit is given, particularly when a nondetect value was reported. Some data are grouped by congener class (for example, the total of all hexa congeners). Detection levels reported for nondetect data range from 0.2 part per trillion (pptr) for 1,2,3,7,8-PCDD from the Baltic Sea to 88 pptr for sediments from the Saigon River in South Vietnam. The lowest reported value of 0.001 pptr was for total PCDDs in treated sludge collected near Ontario. The highest reported sediment value was over 99,000 pptr OCDD in sediments collected near Sheffield, United Kingdom.

Tables 2a and 2b summarize data published concerning PCDD and PCDF levels in organisms that were exposed to materials contaminated with PCDDs and PCDFs under bioassay conditions. Over 140 individual measurements were reviewed. The data base is arranged by congener and by organism. The level of exposure and the tissue residue of the exposed organism is given, as are some salient features concerning the exposure. Data exist concerning the uptake of PCDD in freshwater fish and invertebrates and saltwater invertebrates. The only PCDF data currently available are for carp exposed to fly ash.

Several interesting facts can be extracted from this data set. Under a variety of exposure times and conditions, the bioaccumulation of various PCDD and PCDF congeners was assessed. In no reported case did the organism ever bioaccumulate a higher concentration of contaminant than the concentration of the substrate to which they were exposed. Other information from this data set seems to indicate that because of differences in bioavailability of the various congeners, it would be inadvisable to apply Toxic Equivalency Factors (TEQ Methodology) to sediment concentrations to perform an estimation of environmental risk.

Tables 3a and 3b summarize the published data concerning PCDD and PCDF levels in field-collected organisms from a variety of contaminated and relatively uncontaminated areas. Over 1,500 individual measurements are reviewed. The data base is arranged by individual congener, although some data are given as summations of congener groups (for example, total hexa). The specific organism and tissue (if available) as well as the concentration and collection information are given for each measurement. Only a few of the studies reported give environmental levels that resulted in the reported tissue residues. From the scant information concerning the relationship between exposure and resultant tissue concentration, it is possible to conclude that the organisms nearly always show higher tissue residue concentrations than reported for water at the collection site, but never show higher tissue concentrations than sediment concentrations reported for the collection site.

Tables 4a and 4b summarize the published data concerning PCDD and PCDF tissue residues reported for fish-eating birds and their eggs. Over 30 individual measurements are given. Most of the measurements are for 2,3,7,8-TCDD and 2,3,7,8-TCDF. Some measurements summarize all the PCDD or all the PCDF congeners, but no studies summarized report on any other congeners for either PCDDs or PCDFs. Information concerning exposure levels was not given in any of these studies. The highest level reported for total PCDDs was 214 pptr in a night heron collected from Lake Michigan, Wisconsin, but the highest total for 2,3,7,8-TCDD was only 59 pptr, in a night heron collected near Green Bay, Wisconsin. The highest value reported for 2,3,7,8-TCDF was from a kingfisher collected near Sheboygan, Wisconsin. The highest total PCDFs level reported in the literature was 53 pptr reported in a night heron collected near Lake Michigan, Wisconsin.

Table 5 summarizes the data concerning PCDD residues in organisms associated with specific biological effects. Published data linking effects with known residues rather than nominal doses are limited to two studies. Both studies are limited to data concerning the 2,3,7,8-TCDD congener. It is not currently possible to develop an effects threshold or a no-effects concentration. Further information concerning residue levels and effects can be found in Gibson and Reilly (1992).

Summary

The PCDD and PCDF Data Base was developed to provide information concerning the environmental concentrations and effects of PCDD and PCDF contaminated sediments. Nearly 2,500 individual PCDD or PCDF measurements have been reviewed, summarized, and included in the data base. This information is

available to aid field elements by providing specific numerical guidance concerning contamination by PCDDs and PCDFs and the potential for effect due to dredging and disposal of sediments that may be contaminated with PCDDs or PCDFs.

It appears clear from several lines of evidence that organisms exposed to sediments contaminated by PCDDs or PCDFs will not bioaccumulate levels of PCDD or PCDF higher than the concentrations of the sediments to which they are exposed. Equally clear is the fact that there is a real lack of the information necessary to make informed decisions regarding the biological consequences associated with body burdens of PCDDs and PCDFs. The PCDD and PCDF Data Base will be published in a later paper with a complete analysis of the data.

References

Gibson, A. B., and Reilly, F. J., Jr. 1992. "Residue Effects Data Base on the Relationship between Dioxin and Biological Effects in Aquatic Animals." *Environmental Effects of Dredging Technical Notes* EEDP-04-14, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Hashimoto, S., Wakimoto, T., and Tatsukawa, R. 1990. "PCDDs in the Sediments Accumulated about 8,120 Years Ago from Japanese Coastal Areas," *Chemosphere*, Vol 21, No. 7, pp 825-835.

McFarland, V. A., Reilly, F. J., Jr., Clarke, J. U., and Ferguson, P. W. "Dioxin Toxic Equivalents (TEQs) in Dredged Sediment Evaluation," Miscellaneous Paper in preparation, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Miller, R. A., Norris, L. A., and Hawkes, C. L. 1973. "Toxicity of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) in Aquatic Organisms," *Environmental Health Perspectives*, Vol 5, pp 177-186.

Rappe, C. 1984. "Analysis of Polychlorinated Dioxins and Furans," *Environmental Science and Technology*, Vol 18, No. 3, pp 78A-90A.