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CHANGING CONCEPTS AND IMPROVED METHODS FOR EVALUATING THE IMPORTANCE OF PCBs AS DREDGED SEDIMENT CONTAMINANTS

by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) <p>Polychlorinated biphenyls (PCBs) are highly persistent and widespread contaminants frequently encountered by Corps of Engineers personnel involved with dredged material disposal activities. Interpretation of the potential ecological effects of disposing PCB-contaminated sediments in open water or using other methods is a persistent difficulty in the preparation of environmental impact statements and other documentation necessary for informed decisionmaking. However, the understanding of the nature and behavior of PCBs as environmental contaminants has progressed rapidly within the scientific community with the advances in analytical technology of the past few years.</p> <p>PCBs are a group of 209 congeners that have up to ten chlorine atoms on the biphenyl molecule and that differ from each other in the number and positions of the chlorines. About 100 of these congeners are found in the industrial PCB formulations marketed</p> <p style="text-align: right;">(Continued)</p>					
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Preface

This research was conducted by the US Army Engineer Waterways Experiment Station (WES), Environmental Laboratory (EL), Vicksburg, Miss. Funding was provided by the Long-Term Effects of Dredging Operations (LEDO) Program, which is sponsored by the Office, Chief of Engineers (OCE), US Army. LEDO is managed within the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, Manager, and Mr. Robert L. Lazor, LEDO Coordinator. The Technical Monitors for OCE were Dr. Robert W. Pierce, Dr. William L. Klesch, and Mr. Charles W. Hummer.

Authors of this report were Mr. Victor A. McFarland, Ms. Joan U. Clarke, and Ms. Alfreda B. Gibson of the Contaminant Mobility and Regulatory Criteria Group (CMRCG), EL. The report was edited by Ms. Jamie W. Leach of the WES Information Products Division.

The study was conducted under the general supervision of Dr. Richard K. Peddicord, leader of the Biological Evaluation and Criteria Team, CMRCG; Dr. Charles R. Lee, Chief, CMRCG; and Mr. Donald L. Robey, Chief, Ecosystem Research and Simulation Division. Chief of EL was Dr. John Harrison.

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COL Allen F. Grum, USA, was the previous Director of WES. COL Dwayne G. Lee, CE, is the present Commander and Director. Dr. Robert W. Whalin is Technical Director.

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CHANGING CONCEPTS AND IMPROVED METHODS FOR
EVALUATING THE IMPORTANCE OF PCBs AS
DREDGED SEDIMENT CONTAMINANTS

Introduction

1. Polychlorinated biphenyls (PCBs) have been produced industrially worldwide since 1929. Their manufacture in the United States increased to about 120 metric tons annually in 1970 and declined sharply thereafter (Hutzinger, Safe, and Zitko 1974). In the late 1960s public awareness of the extent of environmental contamination caused by indiscriminant use and disposal of PCBs peaked, leading to voluntary restriction of production in 1971 by the sole US manufacturer. However, some PCB components are highly persistent in the environment (Ballschmitter, Zell, and Neu 1978), and since passage of the Clean Water Act and Ocean Dumping Act in the early 1970s and the Toxic Substances Control Act in 1976, Corps of Engineers personnel involved with dredged material disposal activities have increasingly been confronted with the presence of PCBs in sediments. Understanding the nature and behavior of PCBs has progressed rapidly with the advances in analytical technology of the past few years. Questions that arise repeatedly concerning the ecological importance of PCBs in sediments can now be given more definitive answers than in the past by scientists and engineers who are asked to make evaluations.

The Nature of PCB

2. Polychlorinated biphenyl is not a single chemical compound; PCB is the generic name for a group of related compounds (congeners) having 209 possible individual configurations. The congeners differ in number and position of chlorine atoms substituted for hydrogens on the biphenyl molecule (Figure 1). Congeners having the same number of chlorine atoms are isomers. Since there are 10 positions on the biphenyl nucleus at which substitution may occur, there are 10 isomer groups (monochlorobiphenyl through decachlorobiphenyl).

3. Zitko (1983) proposed a hexadecimal system for standardizing the nomenclature of PCB congeners. This offers the advantage of recalling the exact substitution pattern of a congener from a simple code. In Zitko's system the pentachlorobiphenyl congener shown in Figure 2 would be identified as "D6."

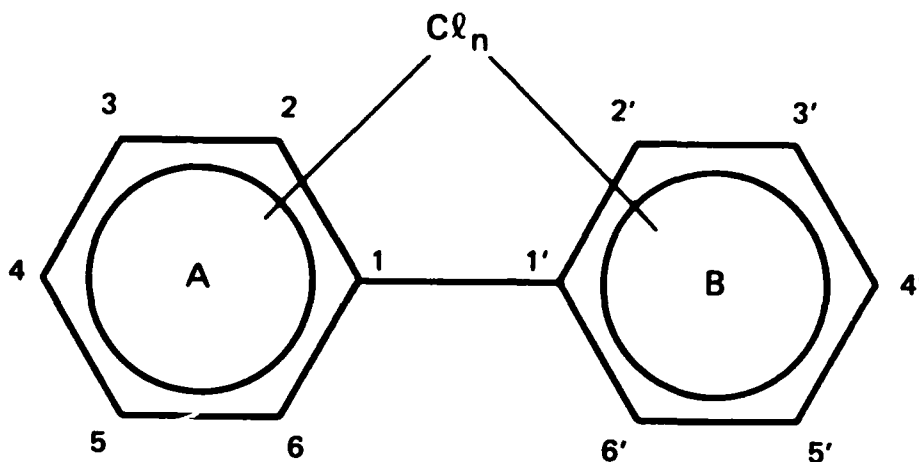


Figure 1. Polychlorinated biphenyl; chlorines (Cl) may be substituted at any or all of positions 2-6 and 2'-6' ($n = 1, 2, 3, \dots, 10$), yielding 209 possible configurations. The nucleus of the molecule consists of two phenyl ring structures (A and B) covalently bonded at carbons numbered 1 and 1'

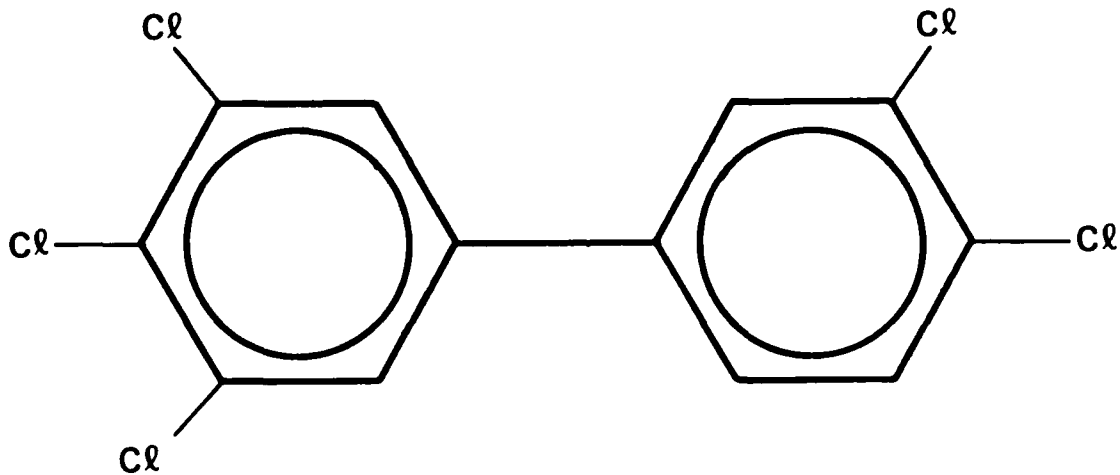


Figure 2. Example of a toxic PCB congener: 3,3',4,4',5-pentachlorobiphenyl, or congener No. 126 by the numerical nomenclature system of Ballschmiter and Zell (1980)

Although the code is simple to decipher, once learned, it is not yet widely used. The numerical nomenclature system developed by Ballschmiter and Zell (1980), however, is frequently used in scientific reports involving specific PCB congeners, although a table is required to convert the "congener number" to its corresponding structure (Appendix A). In Figure 2 the correct nomenclature using Ballschmiter and Zell (1980) is 3,3',4,4',5-pentachlorobiphenyl and the congener number is 126.

Aroclors and analysis

4. The mixtures of PCB congeners that were originally marketed as Aroclors and entered the environment as waste transformer oils, hydraulic fluids, pesticide extenders, plasticizers, etc., were formulated to contain differing percentages of chlorination. Hence, Aroclor 1242 (A1242) contained 42-percent covalently bonded chlorine; A1254 contained 54-percent chlorine, and so on. The formulations thus prepared had differing physical properties of fluidity, dielectric constant, vapor pressure, solubility, etc., and were suitable for many industrial applications.

5. The manufacturing process tended to favor chlorination of the biphenyl nucleus in certain combinations of substituent positions over others. For example, the most commonly chlorinated positions on either ring were 2 or 4 for the addition of a single chlorine, 2 and 5 or 2 and 3 when two chlorines were added to the same ring, etc. Chlorination tended to be equally distributed over the two phenyl rings rather than to be concentrated on one ring alone (Hutzinger, Safe, and Zitko 1974). Consequently, the Aroclor mixtures comprised only about 100 of the possible 209 molecular configurations, and any one particular Aroclor generally contained only about 70 or fewer of these congeners (Hutzinger, Safe, and Zitko 1974). Although the specific composition of Aroclors could vary from batch to batch, the manufactured product could easily be matched with an Aroclor standard in routine laboratory procedures using packed column gas chromatography (GC) with electron capture detection (ECD). This analytical methodology was carried over into the analysis of environmental samples by employing quantitative procedures developed by Webb and McCall (1973).

6. However, due to degradation and differential affinities of congeners for various environmental compartments, PCB mixtures in environmental samples rarely match Aroclor standards well (Duinker and Hillebrand 1983; Duinker, Hillebrand, and Boon 1983; Bush et al. 1985). Data reported as Aroclor

mixtures or as "total PCB" contain no information regarding presence or absence, or proportion and amount of toxic components relative to those of little or no biological consequence (Bunyan and Page 1978). Thus, the convention of reporting "total PCB" or "PCB as Aroclor standards" (A1242, A1254, etc.) contributes to the difficulty in evaluating environmental consequences of PCB in sediments under differing disposal scenarios. Modern glass capillary column GC/ECD methods, which are capable of much greater resolution of complex mixtures of organic chemicals than were the original packed column GC techniques, are now available in most analytical laboratories, but Aroclor standards continue to be used and the data reported accordingly.

Where the differences arise

7. PCB isomer groups differ greatly in physical characteristics such as solubility and partitioning and in their biological properties. Each additional chlorine substantially increases the molecular mass, and as mass increases so does the relative insolubility in water and the "preference" of the molecule for mineral surfaces and organic solvents. The organic carbon of sediments and tissues of organisms may be thought of as organic solvents in this context.

8. Congeners within an isomer group also differ in physical and chemical properties, and in their biological activities. In addition to the number of chlorines substituted on the nucleus, position of substitution is a key determinant of whether a particular congener may be highly stable or susceptible to degradation, relatively water soluble or hydrophobic, and toxicologically inert or potent (Stalling et al. 1979; Shaw and Connell 1980; Bruggeman et al. 1981).

9. The two phenyl rings which compose the nucleus of all PCBs are joined by a single carbon-carbon bond (Figures 1 and 2). Because of this, the rings are capable of rotation with respect to each other and do not necessarily lie in the same plane (i.e., co-planar). In general, substitution at the 4 and 4' (para-) positions increases co-planarity of the molecule and "preference" for mineral surfaces and organic phases such as tissues or organic matter in sediment as opposed to water. Co-planarity has also been linked to increased persistence, bioavailability, and toxicity (Shaw and Connell 1982, 1984). Conversely, chlorine substitution at the 2, 2', 6, and 6' (ortho-) positions (Figure 1) tends to twist the molecule out of a co-planar configuration. Congeners having more ortho-substitutions show decreased affinity for

surfaces and organic phases and decreased biological activity compared with congeners of the same isomer group but having greater para- or meta- (3, 3', 5, and 5') substitution.

Toxic congeners

10. The most toxic congeners fall mainly within the isomer groups tetra-, penta-, and hexachlorobiphenyl (four to six chlorines per molecule). Congeners in the first three isomer groups (mono- through trichlorobiphenyl) are abundant in some environmental matrices but are also inert or nearly non-toxic (Goldstein et al. 1977; Safe et al. 1982; Bush et al. 1985). Congeners in isomer groups hepta- through decachlorobiphenyl are much less abundant in the environment than are the lower molecular weight compounds. Some of these, particularly among the heptachlorobiphenyls, are toxic. The highly chlorinated biphenyls tend to be enriched through food chain transfer in terrestrial and avian ecosystems (Smith et al. 1985).

11. The underlying characteristic for receptor binding, and therefore for direct toxicity of a PCB congener, appears to be the potential for polarization of the molecule (McKinney and Singh 1981). Optimum polarizability requires the substitution of at least four lateral chlorines (meta- or para-substitution) on the biphenyl nucleus arranged so that the molecule occupies about a 3 by 10 Angstrom space. Congener No. 126 (Figure 2) is one such molecule. Co-planarity favors fitting the molecule to the space, and net polarizability is buttressed by the presence of adjacent chlorines (McKinney and Singh 1981). These structural requirements limit the number of directly toxic PCB congeners to a relative few. Of the 209 possible PCB molecular structures, less than 20 possess this steric configuration and intramolecular distribution of forces (i.e., are isosteres). However, this is also the stereochemistry characteristic of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which is thought to be the most toxic xenobiotic substance in the environment. These few PCB congeners are thus isosteres of 2,3,7,8-TCDD and are similar to that compound in their ability to bind directly with cytosolic receptor sites such as nucleic acids (Safe et al. 1982; McKinney and Singh 1981). The potency of toxic response elicited by these PCB congeners differs from one to another and is less than, but is qualitatively similar to, TCDD. Some toxic PCB congeners have been identified both in Aroclor mixtures and in environmental samples including human milk (Safe, Safe, and Mullin 1985) and the blood and liver of Yusho poisoning victims (Bandiera et al. 1984).

Enzyme induction

12. Polychlorinated biphenyl toxicities are also related to their potency and specificity as microsomal enzyme inducers. The enzymes affected are mixed function oxidases of the cytochrome P-450 and P-448 systems, whose function is biotransformation of lipid-soluble biogenic toxins, waste metabolites, and xenobiotics into more water-soluble and thus more easily excreted degradation products (Alvares 1976; Lu, Kuntzman, and Conney 1976; Cummings and Prough 1983). The TCDD-like PCBs induce both the P-450 and P-448 enzyme systems, or the P-448 system alone, and their relative potencies as toxic agents are related directly to their strength as inducers (Sawyer and Safe 1982; Trotter et al. 1982). The toxicities of chemicals, including TCDD-like PCB congeners, which induce the cytochrome P-448 enzyme aryl hydrocarbon hydroxylase (AHH), are additive (Sawyer and Safe 1985).

13. Approximately 40 PCB congeners are either demonstrated or theoretical inducers of only cytochrome P-450 enzymes (Clarke 1986). Biotransformations catalyzed by P-450 enzymes generally involve formation of reactive but unstable intermediates that are rendered soluble by hydroxylation or by conjugation with endogenous substrates such as glutathione, glucuronic acid, or sulfate (Mayer, Melmon, and Gilman 1980; Lu, Kuntzman, and Conney 1976). Induction of the P-450 system generally results in an increased tolerance of the organism to xenobiotics. The potential for toxicity exists, however, in an increased capacity to produce reactive intermediates without concomitant increased availability of conjugating enzymes or substrates that are necessary for detoxication. Fetuses and neonates, for example, have undeveloped capacity for formation of glucuronyl transferase, the enzyme required for conjugation of activated xenobiotics with glucuronic acid. The very young are thus vulnerable to an accumulation of phenolic intermediates formed by action of cytochrome P-450 oxidases on benzene ring-containing xenobiotics--including PCBs (Calabrese 1977).

14. Induction of cytochrome P-450 enzymes by PCB congeners is of lesser toxic consequence to organisms than is induction of the cytochrome P-448 oxidases. The latter group is characterized by augmented production of AHH, referred to also as benzo[a]pyrene hydroxylase, and associated enzymes that can result in biotransformation of a wide range of environmental contaminants into relatively stable toxicants. The direct toxicity characteristic of 2,3,7,8-TCDD and its isosteres is not the common case. Most toxic xenobiotics require

biotransformation into active metabolites, i.e. "bioactivation" in order for their toxicity to be manifested. For example, the polynuclear aromatic hydrocarbons (PAHs) that are known carcinogens are not active as such until they undergo a series of reactions catalyzed by enzymes of the P-448 system. It is now established that the actual carcinogen derived from benzo[a]pyrene is a diol epoxide--the parent compound being incapable of binding with nucleic acids (Thakker et al. 1985).

15. There are, then, at least two distinctly different kinds of toxicity characteristic of PCB: direct and indirect. The congeners that are directly toxic exert their effect by destructive impact on biochemical functions as, e.g., by intercalation with DNA or RNA resulting in carcinogenesis or genetic malfunctions. The PCB congeners that are directly toxic are identifiable and are few in number.

16. Indirect toxicity, if it occurs, is the result of microsomal enzyme induction, which may increase the concentrations of reactive intermediates of PCBs or of other xenobiotics beyond an organism's capacity to detoxify. The microsomal enzyme systems induced are also of at least two kinds. The cytochrome P-448 system induced by the directly toxic PCB congeners is the agent by which otherwise nontoxic PAHs, for example, may be bioactivated forming highly potent carcinogens. The cytochrome P-450 inducing PCB congeners are certainly of lesser consequence, and these, also, are largely identifiable.

17. Finally, many of the PCB congeners that are present in the environment are relatively innocuous, and not all of the potentially toxic PCB congeners have been found in environmental samples.

Toward a Meaningful Analytical Method

18. There is an emerging understanding of the true importance of PCBs as environmental pollutants. At center is a recognition of the fact that these compounds are individuals with widely differing physical and biological behaviors; "PCB" is not a single entity. The remainder of this paper describes investigations conducted recently in the Ecosystem Research and Simulation Division of the US Army Engineer Waterways Experiment Station. The investigations were intended to determine the extent and nature of PCB composition alteration as aquatic organisms exposed to contaminated sediments bioaccumulated these compounds. The results have been presented in symposium

(McFarland et al. 1985) and a more formal report is in preparation.

19. Sediments were collected at seven sites in the Upper Hudson River below Ft. Edwards, N. Y., and were deposited in the bottom of the aquaria as illustrated in Figure 3. Three replicates of each sediment exposure (treatment) were established concurrently with washed gravel controls. Water flowed through the aquaria at a constant replacement rate and temperature was maintained at a constant 23° C. Freshwater clams, *Corbicula fluminea*, and fathead minnows, *Pimephales promelas*, were exposed to the experimental conditions simultaneously, and tissue and water samples were taken periodically over an interval of 18 days. Steady-state residues of PCB quantitated by isomer groups in clams and fish were projected from the time-sequence sampled whole organism residue data using a first-order kinetic model (Blau, Neely, and Branson 1975). This gave the calculated concentration of PCB that would have been expected to occur in the fish had the exposure been continued for a sufficiently long period.

20. All PCB analyses were performed on an HP 5880 GC/ECD equipped with a 30-m DB-5 fused silica WCOT glass capillary column. The instrument was standardized with dilutions of a mixture composed of 78 pure single-congener standards representing all 10 PCB isomer groups. Results obtained by analysis of Aroclor standards and sediment, water, and biota using this procedure were expressed as percentage composition by isomer group. Grouping by isomer was chosen as the simplest means of expressing relative compositional differences for these complex mixtures. Monochlorobiphenyls (monoCBP) were excluded from these calculations because the chromatographic response by ECD of the three monoCBP congeners is on the order of 50 times poorer than that for any of the more chlorinated congeners, and because monoCBP congeners are of low environmental concern.

21. Nine chromatographic Aroclor standards were obtained from the US Environmental Protection Agency, Research Triangle Park, N. C., and are representative of the standard PCB mixtures against which environmental samples are routinely analyzed in this country. Table 1 shows the percentage of di-through decachlorobiphenyl contained in each of the Aroclors analyzed using the method described above. The table is arranged in order of increasing percentage chlorination of the Aroclor mixtures, i.e., from A1221 with approximately 21-percent chlorine by mass to A1268 with a nominal 68-percent chlorine. Aroclors 1016 and 1242 were both designed by the manufacturer to

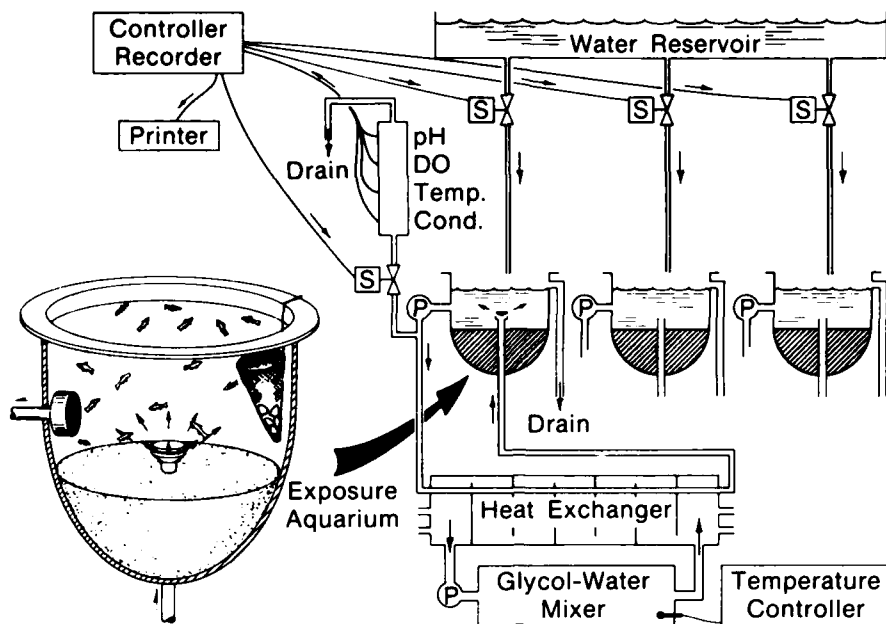


Figure 3. Flow-through exposure system. Clams were suspended in conical mesh baskets and fish were allowed to swim freely in the water column. Rate of water flow-through and water quality sampling were automated by computer programs. The system consisted of 24 identical aquaria

have about 42-percent total chlorine. As total chlorine content increases, the mixtures contain proportionately more of the highly chlorinated isomer groups. Aroclors 1242 through 1262 have the greatest abundance of the isomer groups potentially containing toxic congeners, i.e., tetra- through hexachlorobiphenyls.

22. Comparison of the isomer group composition of PCB in the Hudson River sediments shown in Table 2 with the data of Table 1 reveals no correspondence between these environmental samples and any Aroclor standard. The sediments contain a high proportion (>50 percent) of dichlorobiphenyls, which would put them between the relatively low chlorination Aroclors 1221 and 1232 in this respect. The sediment trichlorobiphenyl content is similar to that of A1232. However, the sediment content of the bioaccumulating (and possibly toxic) tetrachlorobiphenyls is similar to that of A1254, the pentachlorobiphenyls relate to A1221 and the hexachlorobiphenyls are nearest in proportion to A1260. Small amounts of hepta- through nonachlorobiphenyl are also present in the sediments but are not found in the low-chlorination Aroclors. The same situation is evident in the results shown in Table 2 for unfiltered water

samples and for organisms. The compositions of the environmental matrices are related graphically to each other and to Aroclors 1221 and 1242 in Figure 4.

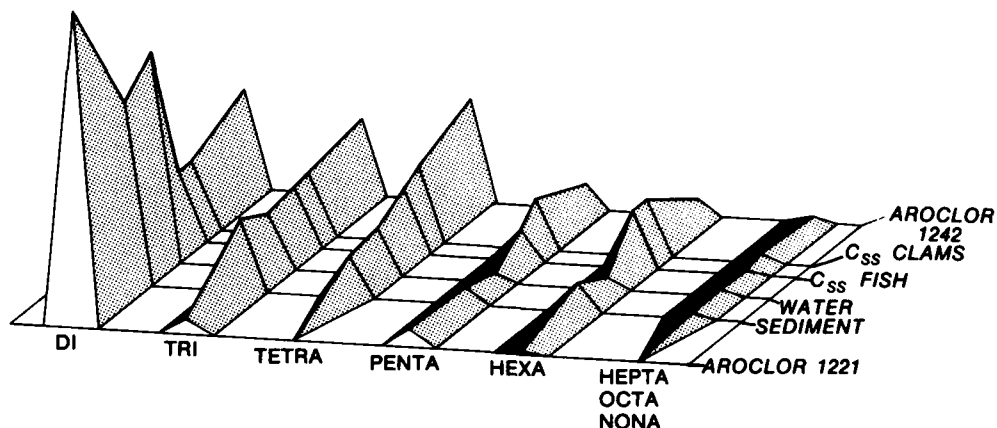
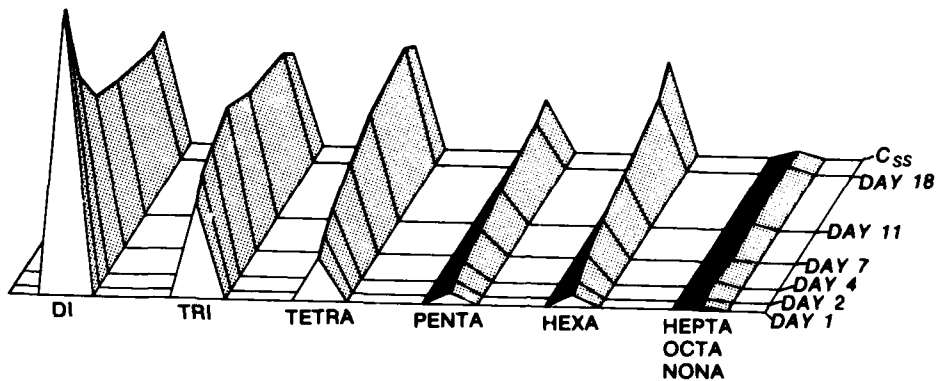


Figure 4. Relative composition (percent means over all treatments) by isomer group of two standard PCB mixtures, Aroclors 1221 and 1242 (foreground and background, respectively), and the environmental matrices sediment, water, fish, and clams

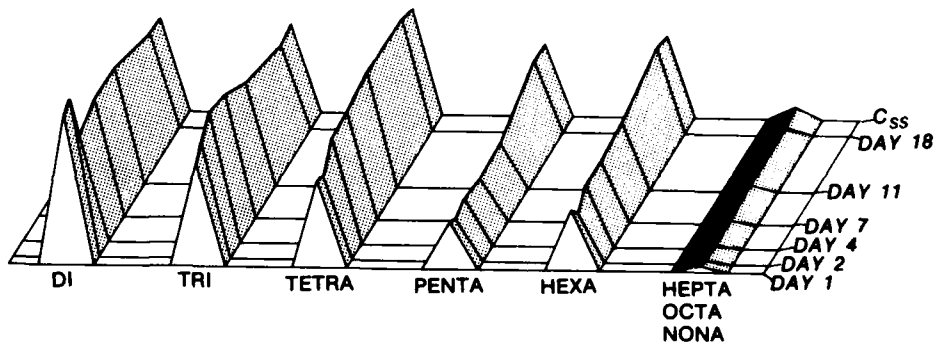
23. The increase in percentage composition of the dichlorobiphenyls in water as compared with sediment is explainable on the basis of solubility. For example, the water solubility of 2,4'-dichlorobiphenyl (congener No. 8, Appendix A) has been reported as 637 ppb while that of 2,2',5-trichlorobiphenyl (congener No. 18, Appendix A) was given as 248 ppb (Haque and Schmedding 1975). Solubilities of single tetra-, penta-, and hexachlorobiphenyl congeners ranged from one to two orders of magnitude less than the solubility of 2,2',5-trichlorobiphenyl in the same study. The relatively high percentages of tetra-, penta-, and hexachlorobiphenyl in the water samples of this investigation are probably due mainly to particulate-bound and to soluble organic carbon-bound PCB rather than to true solution since the exposures included ambient suspended material caused by interaction of the fish with deposited sediment in the aquaria.

24. Still further alteration in PCB composition is evident in the projected steady-state tissue distributions (C_{SS}) by isomer group (Figure 4). The clams and fish responded quite similarly, both showing substantial enrichment of PCB in the tetra-, penta-, and hexachlorobiphenyl groups as compared with the exposure matrices, sediment, and water. Again, there is no correspondence with any Aroclor standard.

25. Isomer group distribution of tissue PCB residues showed high initial levels of dichlorobiphenyl. The less soluble, and also less readily eliminated, more highly chlorinated groups gradually bioaccumulated to levels comparable to the dichlorobiphenyls. These effects can be seen in Figure 5.



a. Fish



b. Clams

Figure 5. Alteration in percentage composition over all treatments of PCB by isomer group in fish and in clams as a function of time of exposure to contaminated sediment and water

Conclusions

26. Although monochlorobiphenyls were not included in the results discussed here, they were present in abundance in the sediments, and in the water and tissue samples as well. Had we reported our results as "total PCB" the monochlorobiphenyls would have contributed perhaps one third to the total.

Since monochlorobiphenyls can be considered relatively inconsequential in a toxicological sense, an environmental sample that contains a substantial portion of monochlorobiphenyl, if reported as total PCB, would be considered potentially more toxic than warranted.

27. Because of the differences in relative abundance of congeners that occur as PCBs distribute themselves among the many compartments of the environment, it is erroneous and misleading to continue to characterize PCBs in environmental samples as Aroclors. Somewhat more interpretable data would be obtained by reporting the totals present in isomer groups, as was done here, in that the proportionate contributions represented by the potentially most toxic congener-containing groups of isomers would be recognized. This would still fall short of the ideal from the standpoint of toxicological interpretability: congener-specific analysis.

28. With the recent synthesis by Mullin and co-workers (1984) of all 209 PCB congeners and the separation of nearly all of them into individual chromatographic peaks using high resolution glass capillary column methods, it is rapidly becoming feasible to create a "standardization cocktail" of PCB congeners chosen for their importance on the basis of toxicity, persistence, and prevalence. It should be possible to develop a chromatographic program and to find the most efficient column length and coating for cost-effective single-congener peak resolution. These developments are anticipated in the near future. It should become possible to routinely analyze environmental samples containing PCBs for specific congeners of interest. Doing so will enable scientists and engineers to assess the environmental effects of various dredged material disposal options more accurately than is presently the case.

References

Alvares, A. P. 1976. "Stimulating Effects of Polychlorinated Biphenyls (PCB) on Cytochromes P-450 and P-448 Mediated Microsomal Oxidations," Microsomes and Drug Oxidations, Proceedings of the 3rd International Symposium, Berlin, July 1976, Pergamon Press, New York, pp 476-483.

Ballschmiter, K., and Zell, M. 1980. "Analysis of Polychlorinated Biphenyls (PCB's) by Glass Capillary Gas Chromatography, Composition of Technical Aroclor- and Clophen-PCB Mixtures," Fresenius Zeitschrift fuer Analytische Chemie, Vol 302, pp 20-31.

Ballschmiter, K., Zell, M., and Neu, H. J. 1978. "Persistence of PCB's in the Ecosphere: Will Some PCB Compounds 'Never' Degrade?" Chemosphere, Vol 2, pp 173-176.

- Bandiera, S., Farrell, K., Mason, G., Kelley, M., Romkes, M., Bannister, R., and Safe, S. 1984. "Comparative Toxicities of the Polychlorinated Dibenzofuran (PCDF) and Biphenyl (PCB) Mixtures Which Persist in Yusho Victims," Chemosphere, Vol 13, No. 4, pp 507-512.
- Blau, G. E., Neely, W. B., and Branson, D. R. 1975. "Ecokinetics: A Study of the Fate and Distribution of Chemicals in Laboratory Ecosystems," American Institute of Chemical Engineers Journal, Vol 21, pp 854-861.
- Bruggeman, W. A., Martron, L. B. J. M., Kooiman, D., and Hutzinger, O. 1981. "Accumulation and Elimination Kinetics of Di-, Tri- and Tetrachlorobiphenyls by Goldfish After Dietary and Aqueous Exposure," Chemosphere, Vol 10, No. 8, pp 811-832.
- Bunyan, P. J., and Page, J. M. J. 1978. "Polychlorinated Biphenyls, The Effect of Structure on the Induction of Quail Hepatic Microsomal Enzymes," Toxicology and Applied Pharmacology, Vol 45, pp 507-518.
- Bush, B., Simpson, K. W., Shane, L., and Koblinz, R. R. "PCB Congener Analysis of Water and Caddisfly Larvae (Insecta: Trichoptera) in the Upper Hudson River by Glass Capillary Chromatography," Bulletin of Environmental Contamination and Toxicology, Vol 34, pp 96-105.
- Calabrese, E. J. 1977. "Insufficient Conjugate Glucuronidation Activity: A Possible Factor in Polychlorinated Biphenyl (PCB) Toxicity," Medical Hypotheses, Vol 3, No. 4, pp 162-165.
- Clarke, J. U. 1986. "Structure-Activity Relationships in PCBs: Use of Principal Components Analysis to Predict Inducers of Mixed-Function Oxidase Activity," Chemosphere, Vol 15, No. 3, pp 275-287.
- Cummings, S. W., and Prough, R. A. 1983. "Metabolic Formation of Toxic Metabolites," Biological Basis of Detoxication, J. Caldwell and W. B. Jakoby, eds., Academic Press, New York, pp 2-30.
- Duinker, J. C., and Hillebrand, M. T. J. 1983. "Composition of PCB Mixtures in Biotic and Abiotic Marine Compartments (Dutch Wadden Sea)," Bulletin of Environmental Contamination and Toxicology, Vol 31, pp 25-32.
- Duinker, J. C., Hillebrand, M. T. J., and Boon, J. P. 1983. "Organochlorines in Benthic Invertebrates and Sediments from the Dutch Wadden Seas; Identification of Individual PCB Components," Netherlands Journal of Sea Research, Vol 17, No. 1, pp 19-38.
- Goldstein, J. A., Hickman, P., Bergman, H., McKinney, J. D., and Walker, M. P. 1977. "Separation of Pure Polychlorinated Biphenyl Isomers into Two Types of Inducers on the Basis of Induction of Cytochrome P-450 or P-448," Chemical-Biological Interactions, Vol 17, pp 69-87.
- Haque, R., and Schmedding, D. 1975. "A Method of Measuring the Water Solubility of Hydrophobic Chemicals: Solubility of Five Polychlorinated Biphenyls," Bulletin of Environmental Contamination and Toxicology, Vol 14, No. 1, pp 13-18.
- Hutzinger, O., Safe, S., and Zitko, V. 1974. The Chemistry of PCBs, CRC Press, Cleveland, Ohio.
- Lu, A. Y., Kuntzman, R., and Conney, A. H. 1976. "The Liver Microsomal Hydroxylation Enzyme System," Frontiers of Gastrointestinal Research, Vol 2, pp 1-31.

Mayer, S. E., Melmon, K. L., and Gilman, A. G. 1980. "Introduction: The Dynamics of Drug Absorption, Distribution and Elimination," Goodman and Gilman's The Pharmacological Basis of Therapeutics, 6th ed., A. G. Gilman, L. S. Goodman, and A. Gilman, eds., Macmillan Publishing, New York.

McFarland, V. A., Clarke, J. U., Gibson, A. B., and Neal, B. S. 1985. "Polychlorinated Biphenyl Isomeric Composition Alteration in Transfer from Sediment to Biota," Aquatic Toxicology and Environmental Fate: 9th Symposium. Presentation to: American Society for Testing and Materials, ASTM Committee E-47 on Biological Effects and Environmental Fate, 14-16 April, Philadelphia, Pa.

McKinney, J. D., and Singh, P. 1981. "Structure-Activity Relationships in Halogenated Biphenyls: Unifying Hypothesis for Structural Specificity," Chemical-Biological Interactions, Vol 33, pp 271-283.

Mullin, M. D., Pochini, C. M., McCrindle, S., Romkes, M., Safe, S. H., and Safe, L. M. 1984. "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of all 209 PCB Congeners," Environmental Science and Technology, Vol 18, No. 6, pp 468-476.

Safe, S., Safe, L., and Mullin, M. 1985. "Polychlorinated Biphenyls: Congener-Specific Analysis of a Commercial Mixture and a Human Milk Extract," Journal of Agricultural and Food Chemistry, Vol 33, pp 24-29.

Safe, S., Parkinson, A., Robertson, L., Cockerline, R., Safe, L., Bandiera, S., and Okey, A. 1982. "PCBs as AHH Inducers," Chlorinated Dioxins and Related Compounds: Impact on the Environment, O. Hutzinger, R. W. Frei, E. Merian, and F. Pocchiari, eds., Pergamon Press, New York, pp 383-392.

Sawyer, T., and Safe, S. 1982. "PCB Isomers and Congeners: Induction of Aryl Hydrocarbon Hydroxylase and Ethoxyresorufin O-Deethylase Enzyme Activities in Rat Hepatoma Cells," Toxicology Letters, Vol 13, pp 87-94.

_____. 1985. "In Vitro AHH Induction by Polychlorinated Biphenyl and Dibenzofuran Mixtures: Additive Effects," Chemosphere, Vol 14, No. 1, pp 79-84.

Shaw, G. R., and Connell, D. W. 1980. "Relationships Between Steric Factors and Bioconcentration of Polychlorinated Biphenyls (PCBs) by the Sea Mullet (*Mugil cephalus* Linneaus)," Chemosphere, Vol 9, No. 12, pp 731-743.

_____. 1982. "Factors Influencing Concentrations of Polychlorinated Biphenyls in Organisms from an Estuarine Ecosystem," Australian Journal of Marine and Freshwater Research, Vol 33, pp 1057-1070.

_____. 1984. "Physicochemical Properties Controlling Polychlorinated Biphenyl (PCB) Concentrations in Aquatic Organisms," Environmental Science and Technology, Vol 18, No. 1, pp 18-23.

Smith, V. E., Spurr, J. M., Filkins, J. C., and Jones, J. J. 1985. "Organochlorine Contaminants of Wintering Ducks Foraging on Detroit River Sediments," Journal of Great Lakes Research, Vol 11, No. 3, pp 231-246.

Stalling, D. L., Huckins, J. N., Petty, J. D., Johnson, J. L., and Sanders, H. O. 1979. "An Expanded Approach to the Study and Measurement of PCBs and Selected Planar Halogenated Aromatic Environmental Pollutants," Annals of the New York Academy of Sciences, Vol 320, pp 48-59.

Thakker, D. R., Yagi, H., Levin, W., Wood, A. W., Conney, A. H., and Jerina, D. M. 1985. "Polycyclic Aromatic Hydrocarbons: Metabolic Activation to Ultimate Carcinogens," Bioactivation of Foreign Compounds, M. W. Anders, ed., Academic Press, New York, pp 177-242.

Trotter, W. J., Young, S. J. V., Casterline, J. L., Jr., Bradlaw, J. A., and Kamps, L. R. 1982. "Induction of Aryl Hydrocarbon Hydroxylase Activity in Cell Cultures by Aroclors, Residues from Yusho Oil Samples, and Polychlorinated Biphenyl Residues from Fish Samples," Journal of Association of Official Analytical Chemists, Vol 65, No. 4, pp 838-841.

Webb, R., and McCall, A. 1973. "Quantitative PCB Standards for Electron Capture Gas Chromatography," Chromatographic Science, Vol 11, p 366.

Zitko, V. 1983. "'Shorthand' Numbering of Chlorobiphenyls," Chemosphere, Vol 12, No. 6, pp 835-836.

Table 1

Percentage Composition of Dichlorobiphenyl Through Decachlorobiphenyl of Nine Aroclor Standards Using a Capillary Column GC/ECD Method of Analysis

Aroclor	Polychlorinated Biphenyl Isomer Group, percent								
	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
1221	93.0	2.4	0.0	4.0	0.8	0.0	0.0	0.0	0.0
1232	41.0	21.0	31.0	5.7	1.7	0.0	0.0	0.0	0.0
1016	40.0	29.0	29.0	1.6	0.0	0.0	0.0	0.4	0.0
1242	30.0	23.0	31.0	8.0	5.7	0.0	1.0	0.3	0.3
1248	12.0	12.0	44.0	16.0	16.0	0.0	0.4	0.0	0.0
1254	0.2	0.1	11.0	28.0	59.0	0.2	1.6	0.0	0.0
1260	0.4	0.4	3.0	9.3	59.0	14.0	14.0	1.1	0.0
1262	1.1	0.6	0.6	4.5	53.0	18.0	19.0	3.7	0.0
1268	0.0	0.0	5.3	0.2	2.8	0.4	31.0	48.0	13.0

Table 2

Mean Percentage Composition of Dichlorobiphenyl Through Nonachlorobiphenyl* in the Environmental Matrices

Matrix	Polychlorinated Biphenyl Isomer Group, percent							
	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona
Sediment	54.0	21.0	12.0	4.3	8.1	0.3	0.4	0.2
Water**	63.0	16.0	14.0	2.3	2.9	0.6	1.1	0.0
Clams†	21.0	20.0	23.0	16.0	18.0	0.6	1.8	0.3
Fish†	24.0	21.0	22.0	11.0	21.0	0.5	0.8	0.2

* Decachlorobiphenyl not detected in any sample.

** Unfiltered.

† Whole organism, fresh weight, projected at steady-state.

Appendix A: Numbering of PCB Congeners*

No.	Structure	No.	Structure	No.	Structure	No.	Structure				
<u>Monochlorobiphenyls</u>											
1	2	52	2,2',5,5'	105	2,3,3',4,4'	161	2,3,3',4,5',6				
2	3	53	2,2',5,6'	106	2,3,3',4,5	162	2,3,3',4',5,5'				
3	4	54	2,2',6,6'	107	2,3,3',4',5	163	2,3,3',4',5,6				
<u>Dichlorobiphenyls</u>											
4	2,2'	55	2,3,3',4	108	2,3,3',4,5'	164	2,3,3',4',5',6				
5	2,3	56	2,3,3',4'	109	2,3,3',4,6	165	2,3,3',5,5',6				
6	2,3'	57	2,3,3',5	110	2,3,3',4',6	166	2,3,4,4',5,6				
7	2,4	58	2,3,3',5'	111	2,3,3',5,5'	167	2,3',4,4',5,5'				
8	2,4'	59	2,3,3',6	112	2,3,3',5,6	168	2,3',4,4',5',6				
9	2,5	60	2,3,4,4'	113	2,3,3',5',6	169	3,3',4,4',5,5'				
10	2,6	61	2,3,4,5	114	2,3,4,4',5	<u>Heptachlorobiphenyls</u>					
11	3,3'	62	2,3,4,6	115	2,3,4,4',6	170	2,2',3,3',4,4',5				
12	3,4	63	2,3,4',5	116	2,3,4,5,6	171	2,2',3,3',4,4',6				
13	3,4'	64	2,3,4',6	117	2,3,4',5,6	172	2,2',3,3',4,5,5'				
14	3,5	65	2,3,5,6	118	2,3',4,4',5	173	2,2',3,3',4,5,6				
15	4,4'	66	2,3',4,4'	119	2,3',4,4',6	174	2,2',3,3',4,5,6'				
<u>Trichlorobiphenyls</u>											
16	2,2',3	67	2,3',4,5	120	2,3',4,5,5'	175	2,2',3,3',4,5',6				
17	2,2',4	68	2,3',4,5'	121	2,3',4,5',6	176	2,2',3,3',4,6,6'				
18	2,2',5	69	2,3',4,6	122	2',3,3',4,5	177	2,2',3,3',4',5,6				
19	2,2',6	70	2,3',4',5	123	2',3,4,4',5	178	2,2',3,3',5,5',6				
20	2,3,3'	71	2,3',4',6	124	2',3,4,5,5'	179	2,2',3,3',5,6,6'				
21	2,3,4	72	2,3',5,5'	125	2',3,4,5,6'	180	2,2',3,4,4',5,5'				
22	2,3,4'	73	2,3',5',6	126	3,3',4,4',5	181	2,2',3,4,4',5,6				
23	2,3,5	74	2,4,4',5	127	3,3',4,5,5'	182	2,2',3,4,4',5,6'				
24	2,3,6	75	2,4,4',6	<u>Hexachlorobiphenyls</u>				183	2,2',3,4,4',5',6		
25	2,3',4	76	2',3,4,5	128	2,2',3,3',4,4'	184	2,2',3,4,4',6,6'				
26	2,3',5	77	3,3',4,4'	129	2,2',3,3',4,5	185	2,2',3,4,5,5',6				
27	2,3',6	78	3,3',4,5	130	2,2',3,3',4,5'	186	2,2',3,4,5,6,6'				
28	2,4,4'	79	3,3',4,5'	131	2,2',3,3',4,6	187	2,2',3,4',5,5',6				
29	2,4,5	80	3,3',5,5'	132	2,2',3,3',4,6'	188	2,2',3,4',5,6,6'				
30	2,4,6	81	3,4,4',5	133	2,2',3,3',5,5'	189	2,3,3',4,4',5,5'				
31	2,4',5	<u>Pentachlorobiphenyls</u>				134	2,2',3,3',5,6	190	2,3,3',4,4',5,6		
32	2,4',6	82	2,2',3,3',4	135	2,2',3,3',5,6'	135	2,2',3,3',5,6'	191	2,3,3',4,4',5',6		
33	2',3,4	83	2,2',3,3',5	136	2,2',3,3',6,6'	136	2,2',3,3',6,6'	192	2,3,3',4,5,5',6		
34	2',3,5	84	2,2',3,3',6	137	2,2',3,4,4',5	137	2,2',3,4,4',5	193	2,3,3',4',5,5',6		
35	3,3',4	85	2,2',3,4,4'	138	2,2',3,4,4',5'	138	2,2',3,4,4',5'	<u>Octachlorobiphenyls</u>			
36	3,3',5	86	2,2',3,4,5	139	2,2',3,4,4',6	139	2,2',3,4,4',6	194	2,2',3,3',4,4',5,5'		
37	3,4,4'	87	2,2',3,4,5'	140	2,2',3,4,4',6'	140	2,2',3,4,4',6'	195	2,2',3,3',4,4',5,6		
38	3,4,5	88	2,2',3,4,6	141	2,2',3,4,5,5'	141	2,2',3,4,5,5'	196	2,2',3,3',4,4',5,6'		
39	3,4',5	89	2,2',3,4,6'	142	2,2',3,4,5,6	142	2,2',3,4,5,6	197	2,2',3,3',4,4',6,6'		
<u>Tetrachlorobiphenyls</u>								143	2,2',3,4,5,6'	198	2,2',3,3',4,5,5',6
40	2,2',3,3'	90	2,2',3,4',5	144	2,2',3,4,5',6	144	2,2',3,4,5',6	199	2,2',3,3',4,5,6,6'		
41	2,2',3,4	91	2,2',3,4',6	145	2,2',3,4,6,6'	145	2,2',3,4,6,6'	200	2,2',3,3',4,5',6,6'		
42	2,2',3,4'	92	2,2',3,5,5'	146	2,2',3,4',5,5'	146	2,2',3,4',5,5'	201	2,2',3,3',4,5,5',6'		
43	2,2',3,5	93	2,2',3,5,6	147	2,2',3,4',5,6	147	2,2',3,4',5,6	202	2,2',3,3',5,5',6,6'		
44	2,2',3,5'	94	2,2',3,5,6'	148	2,2',3,4',5,6'	148	2,2',3,4',5,6'	203	2,2',3,4,4',5,5',6		
45	2,2',3,6	95	2,2',3,5',6	149	2,2',3,4',5',6	149	2,2',3,4',5',6	204	2,2',3,4,4',5,6,6'		
46	2,2',3,6'	96	2,2',3,6,6'	150	2,2',3,4',6,6'	150	2,2',3,4',6,6'	205	2,3,3',4,4',5,5',6		
47	2,2',4,4'	97	2,2',3',4,5	151	2,2',3,5,5',6	151	2,2',3,5,5',6	<u>Nonachlorobiphenyls</u>			
48	2,2',4,5	98	2,2',3',4,6	152	2,2',3,5,6,6'	152	2,2',3,5,6,6'	206	2,2',3,3',4,4',5,5',6		
49	2,2',4,5'	99	2,2',4,4',5	153	2,2',4,4',5,5'	153	2,2',4,4',5,5'	207	2,2',3,3',4,4',5,6,6'		
50	2,2',4,6	100	2,2',4,4',6	154	2,2',4,4',5,6'	154	2,2',4,4',5,6'	208	2,2',3,3',4,5,5',6,6'		
51	2,2',4,6'	101	2,2',4,5,5'	155	2,2',4,4',6,6'	155	2,2',4,4',6,6'	<u>Decachlorobiphenyl</u>			
								209	2,2',3,3',4,4',5,5',6,6'		

* Adopted from Ballschmiter and Zell (1980).

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