A Review of Chlorinated Biphenyl Contamination in Natural Waters

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Abstract

A review of the present state of knowledge concerning environmental contamination by organochlorine compounds indicates that the chlorinated biphenyls may be one of the more widespread contaminants. The significance of this contamination has not yet been evaluated due, in part, to the lack of systematic analytical procedures for the quantitative and qualitative determinations of the components of chlorinated biphenyl mixtures. The possibility of the chlorinated biphenyls producing serious errors in chlorinated pesticide analyses is emphasized.

Introduction

Chemical determinations of the types and concentrations of chlorinated pesticides in natural waters have become increasingly important to fish management, wildlife ecology, and water pollution control. Based on gas chromatographic (GLC) analyses of environmental samples, pp' DDE is generally considered to be one of the more widespread contaminants. However, implicit in every GLC analysis is the possibility that unresolved and/or unidentified components which have specific retention volumes similar to that of the sought-for substance may introduce serious errors in the interpretation of the chromatogram. Increasing numbers of investigators have reported the presence of organochlorine compounds in environmental samples which cannot be identified as the common chlorinated pesticides. Although the unidentified compounds have been attributed from presumptive evidence to the metabolites of common pesticides, plasticizers, or chlorinated biphenyls, proper chemical identifications have not been reported. Therefore, when studying natural water systems which receive industrial wastes, it may be more correct to consider unidentified compounds as chlorinated organic contaminants until confirmation techniques

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are developed.

Within the last three years, the chlorinated biphenyls (or polychlorinated biphenyls--PCB) have received considerable study. The preliminary evidence indicates that this group of organochlorine compounds may be widespread in the environment. For example, Widmark (1967) reported that mass-spectrum analyses of compounds eluting from GLC of fish and bird extracts indicated that unknown organochlorine compounds were present which behaved as chlorinated biphenyls of higher chlorine content. More recently, mass numbers and chlorine numbers per molecule for each peak in the chromatograph of commercial chlorinated biphenyls were reported (Jensen, Nucci et al., 1968). However, to our knowledge, no spectral data or other confirmatory data for positive structural identification of these compounds have ever been published.

With this improper basis of identification, a number of other publications have followed which identify unknown compounds as chlorinated biphenyls. Since mixtures of chlorinated biphenyls may contain greater than 20 compounds which can only be resolved by GLC with great difficulty, assignment of unidentified peaks to one of the chlorinated biphenyls has been accomplished by comparison of a chlorinated biphenyl with the nearest relative retention time. For example, Holden and Marsden (1967), who had earlier reported the presence of unknown compounds in fish (Holden, 1966), reported the presence of chlorinated biphenyls in seals with no supporting data other than relative retention data from GLC columns.

Robinson, Richardson et al. (1967) reported compounds of unknown identity in marine organisms which gave GLC retention times longer than pp'DDE and microcoulometric response. The authors indicated that the chromatographic characteristics of the unknowns suggested that they were not metabolites of the "cyclodiene-type" pesticides as has been proposed by Poburn (1965).

Holmes, Simmons et al. (1967) attributed unknown peaks from GLC to the chlorinated biphenyls and noted that the substances seemed to accumulate in organisms associated

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with natural waters (seals, fish and birds) to a greater extent than in domestic animals. This work reported relative retention data with no supporting data.

Risebrough, Huggett et al. (1968) and Risebrough, Riechc et al. (1968) reported organochlorine compounds in fish, birds and bird eggs which were attributed to the chlorinated biphenyls. With no supporting data and despite the absence of structural confirmations for the chlorinated biphenyls, the investigators reported concentrations of the unknowns (as chlorinated biphenyls) as well as ratios of DDT to chlorinated biphenyls. From these ratios, it was concluded that a chlorinated biphenyl fallout pattern existed around industrial centers and that air transport of the contaminants was significant.

Koeman, De Brauw et al. (1969) presented GLC chromatograms of extracts from environmental samples as well as mass numbers and numbers of chlorine atoms per molecule for each peak of the chromatogram. Although no spectral data were presented, the mass number data strongly suggested that chlorinated biphenyls were present. This paper also presented the results of the analyses for each unknown as being "present" or "absent" in a particular sample, rather than attempting to quantitate the amount of material present.

The Chlorinated Biphenyls

Since contamination of the environment by chlorinated biphenyls has been implicated in the brief review presented, the need for the environmental scientist to become familiar with the present state of knowledge concerning these molecules is apparent. Mixtures of chlorinated biphenyls have been manufactured since 1929, and present registered trademarks for commercial brands include: Arochlor (Monsanto), Chlorextol (Allis-Chalmers), Dykanol (Cornell-Dubilier Division, Fed. Pacific Electric), Inerteen (Westinghouse), Noflamol (Wagner Electric), Pyranol (G. E.), Therminol (Monsanto) in the U. S.; and Clophen (I. G. Farbenindustrie A. G., Germany), Fenclor (Caffaro, Italy), Kannechlor (Kanegafuchi Chemical Co., Japan), Pyralene (Prodelec, France), and Soval (Russia) (Hubbard, 1964). The chlorinated biphenyls have been used as plasticizers for adhesives,

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polyvinyl acetates, acrylic resins, in sealing compounds, pipe joint compounds, printing ink, rubber manufacturing, high pressure-high temperature lubricants, fungicidal insulations, anti-corrosion, nail coatings, water proofings, diffusion pump fluid, stabilization of polymers, dielectrics, heat transfer media, coax-cable insulations, paints and varnishes, ice-preventing coatings, and is an evaporation retardant for pesticide applications (Monsanto O/PL-306; Hubbard, 1964; Hopkins and Hoffman, 1955; Sullivan, Hornstein et al., 1955).

The toxicity and sublethal effects of the chlorinated biphenyls to biological systems has not been thoroughly evaluated (Reichel, 1969). Inhalation tests on animals indicate that maximum concentrations of chlorinated biphenyls as vapor which are "safe" is 1.0 mg/m^3 for the lower chlorinated biphenyls and 0.5 mg/m^3 for the more highly chlorinated biphenyls (Hubbard, 1964). Continuous or repeated skin contact with chlorinated biphenyls leads to a condition called "chloracne" which has been reported repeatedly with industrial workers handling products containing chlorinated biphenyls (Meige, Albou et al., 1953). Sullivan and Hornstein (1953) found no toxic effects of Arochlor 5460 on flies, but the chlorinated terphenyls were toxic (no levels cited) to the elm leaf beetle (Duda, 1957). Deonier, Jones et al. (1946) found Arochlor 5460 to be non-toxic at 0.1 ppm (24 hours) to the larvae of Anophelea quadrimaculatus.

More recently, Lichtenstein, Schulz et al. (1969) reported the toxicity of the chlorinated biphenyls to house flies (D. melanogaster) decreased with increasing degree of chlorination, and that the chlorinated biphenyls appear to be less toxic than dieldrin by a factor of 1000. The chlorinated biphenyls were found to increase the toxic effect of dieldrin and DDT on house flies.

However, in addition to investigating the sources of environmental contamination with organochlorine compounds, the environmental scientist is concerned with the possibility that these organochlorine molecules may exhibit detrimental effects on biological communities at sublethal levels. Kupfer (1967) has presented an extensive review of the

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effects of chlorinated pesticides on steroid hydroxylase induction and other metabolic systems. Also, Risebrough, Rieche et al. (1968) have demonstrated that enzyme induction by the chlorinated biphenyls (Arochlor 1262) was five times as great as pp'DDE or technical DDT as determined via oestradiol degradation. These facts make tolerance limits set by bioassay less significant since organochlorine molecules have the capacity to produce physiological effects in organisms at sublethal concentrations.

Analytical Procedures

Some controversy has been generated over the analytical procedures utilized in studies of organochlorine contaminants which have been attributed to the chlorinated biphenyl. In general, the procedures are similar to typical chlorinated pesticide analyses. However, chemical reactions such as dehydrohalogenation and nitration have been introduced prior to electron capture gas chromatography in attempts to make the procedures more selective for the chlorinated biphenyls. It is the addition of chemical treatment steps which has caused disagreement in the literature.

For example, after extract cleanup, Jensen and Widmark (1967) used a nitration step which is similar to that used in removing DDT and metabolites from toxaphene residues (Erro, Bevenue et al., 1967; Kawans, Bevenue et al., 1969). Briefly, the concentrated extract was treated with a mixture of H_2SO_4 and HNO_3 (conc. 1:1, v/v) at $0^{\circ}C$ for five minutes. It was concluded incorrectly that only PCB and BHC isomers are unaffected by the nitration step. Risebrough, Reiche et al. (1969) have reported the use of similar procedures.

To the contrary, Reynolds (1969) has been unable to repeat the nitration step reproducibly for a number of reasons. First, the reaction is not specific for the PCB and BHC isomers, since heptachlor epoxide remains unaffected by nitration. Also, the work of Bevenue (Erro, 1967; Kawans, 1969) has demonstrated that toxaphene, the reaction product of the chlorination of camphene which produces in excess of 40 unresolved peaks on GLC, is apparently unaltered by nitration. Second, Reynolds found some loss of the earlier

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eluting chlorinated biphenyls during nitration. Third, and most significant, peaks with longer retention volumes appeared in the chromatograms after nitration. These peaks resulted from the nitration of other aromatic molecules in the mixture because nitro groups reduce the vapor pressures in the gas phase (GLC) and the aromatic nitro grouping has a high affinity for the secondary electrons in the electron capture detector.

Results of studies of this laboratory (Veith and Lee, 1969) have substantiated earlier reports (Degurse, 1969) that fish and natural waters in several areas of Wisconsin contain unidentified organochlorine contaminants. Using essentially the same procedures discussed by Reynolds (1969), the resulting chromatograms contain many peaks which have retention volumes similar to those of components of several commercial chlorinated biphenyl mixtures. However, components with corresponding retention volumes were also observed in chromatograms of technical chlordane, heptachlor epoxide, benzene hexachloride, and toxaphene, as well as analytical standards of a number of the DDT family of pesticides. Accordingly, qualitative and quantitative interpretations of such chromatograms from Wisconsin fish and water await more detailed and systematic investigations of the extracts.

Conclusion

The preliminary evidence of the past several years, which has been reviewed in this communication, indicates that the environment associated with natural waters is becoming contaminated with unidentified organochlorine compounds from unknown sources. The facts that chlorinated biphenyls have been strongly implicated as contaminants, that the chlorinated biphenyls have been widely used in industry and have been prepared commercially since 1929, and that the mixtures produce GLC peaks with retention volumes similar to common chlorinated pesticides create a need for basic studies concerning analytical procedures for chlorinated hydrocarbons. Also, it is apparent that comprehensive and systematic investigations into the chemistry and the physiological effects of the contaminants as well as the degree and sources of the contamination are essential before control measures can be considered.

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