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Perspective on PCBs

The discovery of polychlorinated biphenyls PCBs) in fish from the Baltic Sea attracted videspread attention among scientists. Prior to hat event in 1966 the many formulations of 'CBs—some 210 isomers are theoretically ossible—were thought to be used largely in ontrolled or closed systems. That they were resent in fish, and were later discovered in birds, dded to the concern since the inevitable last link n the food chain was man himself.

Concerns were heightened even further by the nowledge that one of the primary characteristics vhich made PCBs so useful during the past 40 ears was their extreme stability under a variety f circumstances. Furthermore, their structural esemblance to the persistent organo-chlorine esticides raised other questions about whether ll of our worries over these pesticides were ccurate or whether, as some suspected, PCBs ere the real cause of that concern.

Alert epidemiologists and other scientists in apan confirmed our expectations of the worst in 969 with their startling discovery and description f Yusho, a human disease caused by consumption f large quantities of PCB-contaminated rice oil.

A glance at the table of contents for the first issue of ***Environmental Health Perspectives*** gives the reader some idea about the quantity of research being done to specify the extent of the PCBs story. Furthermore, while the spectrum of work presented is comprehensive, it is neither all-inclusive nor definitive. Rather, our hope is that this volume will contribute a new perspective to the study of PCBs and will help as well to engender a renewed vigilance about other "inert" chemicals which are so pervasive a part of the environment of man.

The reports which follow were originally prepared for a Conference on PCBs, sponsored by NIEHS at the request of an Interdepartmental Task Force on the subject. The Conference was held at the Quail Roost Conference Center in Rougemont, North Carolina, on December 20-21, 1971. The papers presented at that meeting appear here substantially as they were presented. Your comments on them are indeed welcome.

MONS 081313

Some Chemical Aspects of Polychlorinated Biphenyls (PCBs)

by J. William Cook*

In the past few years considerable scientific information has appeared on the chemistry and biological effects of the PCBs and related materials. The amount of chemical investigation, and especially the biological effects investigation that can be done on these products, is almost limitless. Even though the PCBs show a great deal of inertness, a property very useful in their industrial applications, they certainly do change in most instances before they are inadvertently consumed by man. It is important that we learn more about the nature of these products and the changes they undergo. I believe that the choice of scientific investigation that will provide effective answers is going to be made by close cooperation between the scientists in the field of chemistry and those in the various biological disciplines. I hope that conferences like this one will help give us guidance as to the most fruitful avenues to follow in research and will assist in the interpretation of the data obtained. It is simpler to acquire data than to interpret them.

No attempt has been made to make or present a complete survey of literature on chemistry of PCBs. Instead, I have chosen to discuss in a general way some facets of the chemistry which I think are interesting and relevant to the subject of this conference. For the most part I have drawn upon illustrations from our FDA laboratories because of the easily available material.

There are a number of statements in the literature and the public press which liken PCBs to DDTs. If this were the case, we would need to do little research in chemistry of PCBs, because the chemistry of the DDTs and related compounds is well known. Even so, all the biological effects of DDTs are by no means known or fully understood even though there has been much work during the past 25 years.

In contrast to the three well known isomers of DDT—that is, the p,p′, o,p′, and o,o′-dichloro-compounds, the term polychlorobiphenyls or PCBs encompasses a very complex heterogeneous series of chemicals. When manufactured in a certain way, they form technical products which have enjoyed tremendous industrial use over the past 40 years because of the unique chemical and physical properties of the complex mixtures.

The exact chemical composition of these mixtures has not been determined. There probably was no incentive to determine the real nature of all the components as far as the industrial value of the products was concerned, but now that it has been found that there are untoward biological effects from these products and that their residues are widely distributed, there is need for more knowledge than is now available.

There are also statements in the literature which in effect assert that PCB analytical methods and limits for residues should apply to specific chemicals within the series rather than to PCB undefined. Stated differently, if the toxicity of the PCBs is mainly due to certain compounds in the mixtures, then we could be justified in developing methodology to separate, quantitate, and evaluate these toxic compounds. We will need to know more about the chemistry and biological effects before we can be so specific.

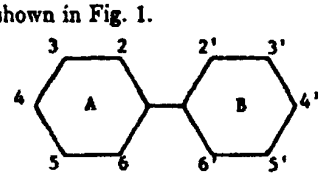
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Until we have developed data which, on the one hand, show that essentially all components have about the same biological effects or, on the other hand, show that some are greatly different from others, we have no real scientific basis on which to make a choice. Of course there is evidence that some industrial PCB products contain polychlorodibenzofurans. We need to know how and where these form. Do they form somehow in the environment, and if so, do they survive through the food chain to man? If so, are there great differences in biological effects among the large number of possible polychlorofurans as is the case among the polychlorodioxins? If these compounds are present in foods, we certainly should try to identify them soon, but if they are like the dioxins, they will be difficult to measure in food.

PCBs are manufactured in France, Germany, Great Britain, Italy, Japan, Russia and U.S.A.

Assuming that the starting raw product is only biphenyl, and assuming that no reaction takes place except chlorination of biphenyl during manufacture, 210 different chemicals are theoretically possible from the 10 positions where chlorine can add on as shown in Fig. 1.



Chlorines on B ring	Chlorines on A ring: 0	1	2	3	4	5
0	1	3	6	6	3	1
1		6	18	18	9	3
2			21	36	18	6
3				21	18	6
4					6	3
5						1

FIGURE 1. Structural formula for biphenyl and theoretically possible sites for chlorination.

It is not certain how many of these do appear in significant amounts in the technical products or in food. It is possible that a few molecules of each is present in each of the technical products.

It is important to point out that, in the industrial products, the PCBs are associated with chloroterphenyls. There are three possible terphenyls (the o, m, and p) as starting materials in contrast to one biphenyl as a starting material, and also there are 14 possible points instead of 10 at which each of the 3 isomers may be chlorinated. Therefore, these compounds could result in a considerably more complex mixture than the PCBs. The chloroterphenyls can be associated with the PCBs in the ecosystem, and they are not readily determined by the usual methods of analysis for PCBs and the pesticides. Later some gas chromatograms will be shown that illustrate some of the relationships.

The industrially important products are formed by chlorination of biphenyl to a given chlorine content. Products which contain 21, 42, 48, 54 and 60% chlorine by weight appear to be the most important ones. The end point of the desired average chlorine content is found by making specific gravity or softening point measurements on samples withdrawn during chlorination. The crude products so formed are generally purified to remove color and traces of hydrogen chloride and ferric chloride, largely by distillation. Mixing of distillate is also used to obtain uniform material of the desired composition (1).

Various factors during the manufacturing process can affect the proportion of the various isomers and the proportion of compounds of higher or lower chlorine content than the average (1). Therefore products manufactured by different processes could yield products which give somewhat different amounts of various components. If some components have different biological effects than others, then different samples would produce unequal effects.

Figure 2 shows gas chromatograms of two PCBs; A is Aroclor 1221, and B is 1232. These and the following gas chromatograms (Figs. 3-8) were made by the conditions used in FDA laboratories. The patterns generally look like those we see from other laboratories, so the products seem to be relatively uniform, except for Aroclor 1232. This appears not to have been a fully consistent product in the past.

Figure 3 shows more in the series. A is 1242, and B is 1248.

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