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Pesticide residue analys s in the presence of Polychlorobiphe ıyls (PCB's)

By

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I. Introduction

Although there has been so much discussion on the pros and cons of pesticide use, it would be unthinkable to start this review without a few comments on the controversy. The recent banning of DDT by some countries and the widespread and increasing animosity towards the use of the organochlorine pesticides in general are due to a number of factors including:

a) The large annual additions of the pesticides to the environment coupled with their apparent persistence.
b) Their known acute toxicities.
c) Their widespread distribution in biological materials and their reported buildup in the food chains.

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d) Their more recent implication in the derangement of calcium metabolism (PEAKALL 1967, SIKKIS 1967, WELCH *et al.* 1969) possibly causing the decrease in eggshell thickness and the population decline of certain raptorial species of birds (RATCLIFFE 1967, HICKEY and ANDERSON 1968, STICKEL 1969).
e) Their adverse effects on fish reproduction (BURDICK *et al.* 1964) and high residue levels found in Coho salmon in Lake Michigan in 1969.
f) Certain "fears" involving chronic toxicities and sublethal doses with possible deleterious effects on man and wildlife and the ultimate survival of man.

The above factors are very compelling and certainly warrant man's concern about the threat to his environment and his very existence. Nevertheless, one cannot deny that these pesticides have been important in ensuring the supply of man's rapidly increasing food requirement and in the protection of his health, as well as the saving of millions of lives. Surely, this is a case where the benefit-risks equation as well as the alternatives to the organochlorine pesticides should be carefully studied and evaluated to avoid the possibility of getting into a worse predicament.

It was quite ironic when recently a large city publicised that, because of an impending ban on DDT, the garbage collector would pick up separately all home garden sprays and other materials which contained even traces of DDT. The material that had been used more than generously and cherished for almost 30 years had suddenly become monstrous even in trace quantities. Wasn't there much greater danger posed to the collectors, children, and animals by such collection than if the home supplies had been allowed to run out gradually with no chance of replenishment?

In fact, the announced bans on DDT so far are generally not total, and hence serve the same purpose as merely tightening the control on the uses of such pesticides. In other words, when it is necessary, and until suitable and satisfactory replacements are available, limited and judicious use will be made of these pesticides.

With regard to the use of substitutes, caution is essential to avoid premature use of any compounds. It is now known that potentiation (or antagonism) of toxicity is possible with certain combinations of pesticides and with combinations of pesticide and drugs or environmental chemicals (DUBOIS 1968). A compound might be fairly safe by itself yet harmful in the presence of others.

It is a fact that even if suitable substitutes were found and the use of the organochlorine pesticides was banned completely, a need would still exist for at least a number of years to have reliable analytical methods for the determination of their residues. The present review discusses the status of organochlorine pesticide residue analysis

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with particular reference to serious inaccuracies caused by the presence of polychlorobiphenyls (PCB's) in some samples.

As would be expected, in order to cope with the numerous new pesticides that have been put into use, pesticide residue methodology has changed drastically over the years. Zweig (1963) pointed out that until about 1940, the life of an analytical chemist working in the pesticide field was a relatively serene one in which the chemist had to be familiar only with analytical methods for arsenic, lead, fluoride, pyrethrins, rotenone, and a few others. Just about ten years back, DDT and other organochlorine compounds were estimated by colorimetric methods (Schecter *et al.* 1945) which obviously did not give precise information on the amounts and identities of the individual compounds present.

Today's residue methodology is much more complex, and in order to cope with the new pesticides being introduced, the techniques are constantly being modified and improved. The wide variations in toxicity and persistence of pesticides, new or old, dictate refinements in methods in order to differentiate and determine individual residues.

Bearing in mind the complexities mentioned above and the fact that the spray history of most samples (excluding controlled spraying experiments) is unknown to the analyst, the availability of chromatographic techniques which afford separation of a number of compounds in a mixture has made the multi-residue screening approach[1] (*U. S. Food and Drug Administration* 1969 revision) the method of choice.

The gas liquid chromatographic (GLC) separation with electron capture (EC) detection is presently the most popular analytical combination for organochlorine pesticide residues.

Multi-residue analysis involving GLC generally involves five principal steps:

a) Sampling to procure a representative aliquot of the sample.
b) Extraction of the residue with a solvent (usually organic since most of the organochlorines (OC's) and many of the organophosphates (OP's) are fat soluble).
c) Cleanup of the extract to remove interfering materials such as fats, waxes, pigments, etc.
d) Analysis of the cleaned-up extract, generally by GLC-EC technique.
e) Confirmation of the pesticide identity.

Certainly there are a great number of variations in carrying out these steps, depending on the nature of the pesticide and its substrate,

[1] Editor's note: See Burke, J. A.: Development of the Food and Drug Administration's method of analysis for multiple residues of organochlorine pesticides in foods and feeds. Residue Reviews, this volume.

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the limit of detectability required, and the laboratory staff and equipment available. It is beyond the scope of this review to discuss any of these methods in detail. Furthermore, Gunther (1962) and Samuel and Hodges (1967) have reviewed this topic adequately. Accordingly, this review will deal mainly with problems involving PCB's and related compounds. No attempt will be made to review gas chromatography for pesticide residue analysis. Burke (1965) has discussed some practical aspects of this topic, while Thompson *et al.* (1969 and 1969 a) have evaluated different gas chromatographic columns for chlorinated pesticides.

Before discussing the PCB's and their interference with pesticide residue analysis, some[1] key references in the English language on residue methodology are appropriate. These are listed alphabetically as follows:

1. Advances in pest control research, vols. 1–8. New York: Interscience (1957 *et seq.*)
2. A guide to the analysis of pesticides by gas chomatography, 2nd ed. S. T. Preston, Jr. Evanston, Ill.: Polyscience (1968).
3. Analysis of insecticides and acaricides, Gunther and Blinn. New York-London: Interscience (1955).
4. Analytical methods for pesticides, plant growth regulators and food additives, vols. I–V, Zweig. New York: Academic Press (1963).
5. Guide to the analysis of pesticide residues, vols. 1 and 2, Burchfield and Johnson. *U. S. Public Health Service*, Office of Pesticides, Washington, D. C. (1965).
6. Manual of methods for the determination of residues of Shell pesticides, *Shell Chemical Company*, Agricultural Chemicals Division, New York (1969).
7. Official methods of analysis, *Association of Official Analytical Chemists*, 10th ed. Washington, D. C. (1965).
8. Pesticide analytical manual, vols. I and II, *U. S. Department of Health, Education, and Welfare, Food and Drug Administration*, Washington, D. C. (1968).
9. Pesticide residue analysis handbook, Bonelli. *Wilkins Instrument and Research, Inc.*, Walnut Creek, Calif. (1965).
10. Residue Reviews, vols. 1–34. Gunther. New York: Springer-Verlag (1962 *et seq.*)

It should be emphasized that these references were all written prior to the knowledge that there was a possibility of PCB interference with

[1] Editor's note: There are now more than 95 books concerned with pesticide residues including 60 that discuss analytical methodology in some respects; eight countries are represented by the authors. Gunther, F. A.: Pesticide residues in the total environment-Reliable detection and determination, mitigation, and legislative control and surveillance programs. Pure and Applied Chem. **21**, 355 (1970).

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certain pesticide residue analyses. In general, the methods described in these references can be modified to cope with PCB interference.

II. Presence of PCB's in the environment

Following the development of the EC detectors and their use with GLC, most residue chemists have observed unidentified peaks on their gas chromatograms. Generally, there was no specific pattern to these peaks, but analysts concerned with pesticide residues in wildlife, especially in Europe (Roburn 1965, Harrison 1966, Holden and Marsden 1966), sometimes observed a particular series (with as many as ten or more peaks) of the unidentified peaks in their sample extracts. The materials giving rise to these unidentified responses occurred most frequently and in the largest proportions in extracts from aquatic raptorial species of birds and fishes. The general supposition was that these responses were from condensation products of the metabolites of the organochlorine pesticides, since they were generally observed when large amounts of pesticides were also present. Roburn (1965) reported them to be organochlorine compounds with fairly high chlorine contents, which no doubt accounts for their high sensitivities to the EC detector. However, Jensen (1966) was the first to state that these unidentified peaks corresponded to PCB compounds, based on the analysis of a number of pike samples, an eagle, and human hair. Initially, the GLC and thin-layer chromatographic (TLC) patterns and chemical inertness were used to identify the unidentified peaks as PCB's (Jensen and Widmark 1967).

Other workers in Great Britain (Holmes *et al.* 1967, Holden and Marsden 1967) and the Netherlands (Koeman *et al.* 1967) also made early reports on the presence of PCB's in their fish and wildlife samples.

At the Organisation for Economic Co-operation and Development (OECD) Conference on "The Unintended Occurrence of Pesticides in the Environment," held in Scotland in September, 1967, the European chemists in particular showed much concern regarding the presence of PCB's in their wildlife samples and the possibility of interference with their organochlorine pesticide residue analysis. Up to that time, there had been no report on the occurrence of these materials in North American samples. However, in a December, 1967, report on organochlorine pesticides in seals and porpoises, Holden and Marsden included a comparison of the amounts of PCB-type materials found in Scottish and Canadian samples. They reported that the levels of these non-hydrolysable materials were generally much lower in the Canadian specimens. Since that time Risebrough *et al.* (1968) have reported that the PCB's are widely dispersed in the global ecosystem, while Reynolds (1968, 1969, and 1969 a) has found them in some Canadian wildlife samples.

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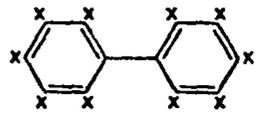
Positive confirmation of the PCB's by gas chromatography-mass spectrometry (GC-MS) has now been reported in Sweden (WIDMARK 1967), the Netherlands (KOEMAN *et al.* 1969), and in the United States (REICHEL 1969).

III. PCB interference with pesticide residue analysis

The polychlorobiphenyls (× indicates the possible chlorine positions) and related compounds (polychlorinated triphenyls, naphthalenes, terpenes, etc.) have numerous important industrial uses but are not used as pesticides. Because of their similarities in structure and properties to the DDT pesticide group, the PCB's—if present in a substrate—are carried through the usual pesticide extraction and screening procedures, and since they possess electron absorbing properties, will interfere with GLC-EC analysis of organochlorine as well as a number of the organophosphorus pesticides (REYNOLDS 1968 b).



The reported GLC patterns indicating PCB interferences have shown marked resemblances with 'Aroclor' 1254 and 1260 (JENSEN and WIDMARK 1967, HOLMES *et al.* 1967, REYNOLDS 1965 and 1969, and KOEMAN *et al.* 1969). This type of interference with pesticide residue analysis is demonstrated with a standard mixture of organochlorine pesticides and a commercial PCB mixture (Aroclor 1254) in the chromatograms of Figure 1. The results confirm that the presence of PCB's in the sample extracts will cause interference with pesticide residue analysis under these or similar operating conditions.

It should be emphasized that throughout this review when the term "PCB" is used, this includes the polychlorobiphenyls and also the other closely related compounds mentioned above. However, the polychlorobiphenyls are the most important from the point of view of interference with pesticide residue analysis. Under the GLC operating conditions, the chlorinated polyphenyls and other related compounds with molecular weights greater than the chlorinated biphenyls will generally not be separated and observed on the gas chromatograms. Modification of the operating parameters such as higher column temperatures or changes in the liquid stationary phases are usually necessary to detect the presence of such compounds.

It must be borne in mind that when high molecular weight compounds are present, their peaks can appear on subsequent chromatograms and cause "secondary interference." This occurrence can be recognised easily by the early emergence of unusually broad interfering peaks on the chromatograms. "Secondary interference" is a term used by the author to imply that the interfering peak does not have

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the same retention time as that of the compound of interest under the same operating conditions. The interfering peak often originates from a previous injection and cannot be simply repeated. Of course, if the elution time is very long, the peak might be broad enough to escape detection and in such a case would not interfere. In contrast

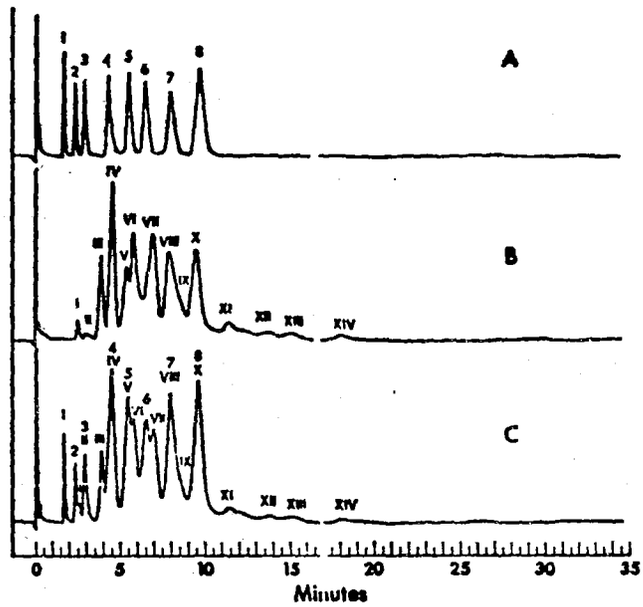

Fig. 1. PCB interference with organochlorine pesticide residue analysis on four percent SE-30/six percent QF-1 on 60/80 mesh Chromosorb W, ⅛" × 6' borosilicate column. Chromatogram *A:* standard mixture of organochlorine pesticides; peak numbers: 1 = 0.08 ng. of lindane, 2 = 0.10 ng. of heptachlor, 3 = 0.10 ng. of aldrin, 4 = 0.14 ng. of heptachlor epoxide, 5 = 0.20 ng. of DDE, 6 = 0.20 ng. of dieldrin, 7 = 0.30 ng. of DDD, and 8 = 0.50 ng. of DDT. Chromatogram *B:* 5 ng. of Aroclor 1254 (the 14 major peaks are numbered I to XIV). Chromatogram *C:* combination of above organochlorine standard pesticide mixture and Aroclor 1254. Injector 250°C., column 200°C., detector base 250°C., N_2 at 20–30 cc./minute

to this type of interference, materials which have identical retention times will cause "primary interference" which is easily repeated by reinjection of the extract. With this form of interference a single, sharp peak is obtained, and in the absence of confirmatory and other precautionary measures, misinterpretation can occur easily. PCB-type interference falls mainly in this group.

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IV. Uses and properties on PCB's

In order to understand how it is possible for PCB's to be present in wildlife and cause interference with pesticide residue analysis, it is necessary to give a brief description of some of their properties and uses. The PCB's are produced and marketed under a number of commercial trade names, e.g., 'Aroclor,' 'Clophen,' and 'Phenochlor.' KOEMAN *et al.* (1969) reported marked resemblance between Aroclor 1260, Clophen A60, and Phenochlor DP6. The 'Aroclor' plasticizers, a series of chlorinated biphenyls and chlorinated polyphenyls, are typical of these compounds. As stated by the manufacturers (*Monsanto Co.* 1967), the 'Aroclor' compounds are among the most versatile chemically produced materials available. They vary from mobile, oily liquids to white crystals and hard transparent resins. They are non-oxidizing, inert, permanently thermoplastic, of low volatility, non-corrosive to metals, insoluble in water, and resistant to alkalies, acids, and corrosive chemicals. The viscous, more highly chlorinated liquid and resin members do not support combustion and they impart fire retardance to other materials. The crystalline 'Aroclor' compounds are relatively insoluble but the liquid and resinous compounds are soluble in most of the common organic solvents, thinners, and oils.

These compounds are used in protective coatings, as placticizers and extenders, as sealers in water-proofing compounds and putty, in asphaltic materials, printing inks, waxes, and synthetic adhesives. Liquid PCB's are used as dielectrics, as hydraulic fluids, in thermostats, in cutting oils, as extreme pressure lubricants, as grinding fluids, and as heat transfer media. Solid PCB's are used to impregnate carbon resistors and as sealers in impregnating agents for electrical apparatus. The properties of many products can be varied and improved by the use of these compounds either as primary or secondary plasticizers.

Further details concerning the different 'Aroclor' series, the gradation of their properties, and the numerous possible applications can be found in the manufacturer's technical bulletin (*Monsanto Co.* 1967). In the system of designation for the 'Aroclors,' the first two digits indicate the type of material, while the last two digits give the approximate weight percentage of chlorine in the product. For example, 'Aroclor' 1254 indicates a chlorinated biphenyl with approximately 54 percent chlorine, while 'Aroclor' 5460 indicates a chlorinated triphenyl containing about 60 percent chlorine.

V. Possible modes of entry of PCB's into the ecosystem

The means by which PCB's enter the ecosystem to contaminate fish and wildlife are still not clearly understood. There are however,

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four most likely pathways by which PCB's enter fish and wildlife:

a) Because of their inertness and versatility and consequent numerous applications, it is quite conceivable that PCB's could be flushed as wastes into rivers, lakes, etc. to pollute fish and other wildlife.
b) There is a possibility that some contamination could proceed via the atmosphere when wastes containing these compounds are burnt.
c) Although it is unlikely, some type of Ullman reaction with condensation of aromatic halides with the aid of metallic agents such as copper to give rise to the formation of biaryls, cannot be completely ruled out.
d) Lastly, but not necessarily the least likely, there is the possibility that some companies are using PCB's in some insecticide formulations to increase the kill-life.

The idea of increasing the residual persistence of insecticides has been investigated for some time and a brief résumé on the more important background work is in order.

The early investigations by LINDQUIST *et al.* (1945) and BLOCK (1948) indicated that the residual effectiveness of DDT was prolonged when the DDT was applied in resins and paints. VAN TIEL (1952) continued along these lines when he increased both the effective period and the toxicity of a DDT deposit on a glass surface by the addition of a small amount of coumarone resin to a DDT solution in kerosene. Subsequently, emphasis was placed on work involving the more volatile insecticides like lindane—a very effective pesticide but one which soon loses its activity because of volatilization.

SULLIVAN and HORNSTEIN (1953) in their experiments with the American cockroach, *Periplaneta americana*, found that lindane residue remained toxic longer when it was compounded with 'Aroclor' 5460. They suggested that the chlorinated polyphenyl prevents crystallization of the lindane and lowers the vapor pressure of the lindane in the mixture, thereby preventing unsightly residues on surfaces as well as extending the effective kill-life of the insecticide. TSAO *et al.* (1953) obtained similar results against house flies, *Musca domestica* L. Continuing this work, HORNSTEIN and SULLIVAN (1953) confirmed these findings and described a general method for prolonging the residual effectiveness of volatile insecticides. The method consisted of preparing concentrated solutions of the pesticides in the film-forming polychlorinated polyphenyls. A *Monsanto Co.* Technical Bulletin (1965) states that because "'Aroclors' in formulations 'trap' and hold more volatile ingredients, they make volatile insecticides and repellents 'last longer' in residual activity."

Attempts to determine whether this idea had been put into practice have so far been unsuccessful. However, if the PCB's are being used

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in pesticide formulation, then this coupled with the numerous other uses suggested in a later *Monsanto Co.* Bulletin (1967), might certainly explain their presence in wildlife tissues and other samples.

There is an obvious need for clarification of the sources of PCB's in fish and wildlife, and this could probably be accomplished using tracer techniques.

VI. Toxicity of PCB's

The PCB's were studied as early as 1881 (SCHMIDT and SCHULTZ) and were in wide use by 1930 (PENNING 1930). Later JONES and ALDEN (1936) reported that the compounds were toxic. GREENBERG *et al.* (1939) reported that PCB's and polychlorinated naphthalenes caused the deaths of three workers. Men employed in the production and use of PCB's developed acne-type skin eruptions (SCHWARTZ and BARLOW 1942, SCHWARTZ and PECS 1943, SCHWARTZ 1943).

MILLER (1944) reported that PCB's caused pathological changes in laboratory animals. BROWN (1947) warned about the toxicity dangers of the 'Aroclors' when there was a suggestion that one of the 'Aroclors' be used as the melting point bath liquid in preference to the customary sulfuric acid. Later McLAUGHLIN *et al.* (1963) found that Aroclor 1242, besides being toxic, produced teratogenic effects in chick embryos at lower dosage levels. RISEBROUGH *et al.* (1968) reiterated that PCB's along with other chlorinated biocides, such as DDT, could account for a large part of the aberration in calcium metabolism that has been observed in many species since the second world war. With high dosage of PCB's, hydropericards have been observed in quails (KOEMAN *et al.* 1969).

It has been stated (*Monsanto Co.* 1967) that at ordinary temperatures the 'Aroclor' chlorinated polyphenyls do not present industrial toxicological problems. However, caution was advised in handling these materials. The hazard of potential toxic exposure varies with the volatility of the compounds: the lower chlorinated, more volatile ones present more of a potential problem from the standpoint of both inhalation and skin contact. At elevated temperatures, the use of PCB's requires very effective and efficient exhaust ventilation systems.

It has also been stated by the manufacturers that "tests on animals indicate that the maximum safe concentration of vapor is in the range of from 0.5 to 1.0 milligram of the lower chlorinated 'Aroclor' plasticizers per cubic meter of air. The threshold limits (maximum allowable concentration for an 8-hour working day) set by the American Conference of Government Hygienists are 1.0 milligram of the lower chlorinated 'Aroclor' compounds per cubic meter of air and 0.5 milligram of the more highly chlorinated compounds, such as 'Aroclor' 1254, per cubic meter of air."

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However, as RISEBROUGH *et al.* (1968) pointed out, only relatively small amounts of chlorinated hydrocarbons are required to cause enzyme-induced breakdown of steroids, thus making irrelevant much of the p.p.m. approach to pollutant ecology based on toxicity data alone.

There is no doubt that further research in this area is urgently needed.

VII. Analysis of pesticide residues in the presence of PCB's

PCB's are of interest to analysts for three main reasons:

a) The compounds are toxic.
b) They are widely distributed and their uses are increasing.
c) They interfere with GLC determinations of organochlorine and organophosphorus pesticide residues.

The first two reasons have been dealt with earlier and therefore need no further elaboration. Accordingly most of the remainder of this review will be concerned with the analysis of pesticide residues in the presence of PCB's. Also the present methods of estimating the amounts of PCB's will be discussed.

As mentioned earlier, it was emphasized at the 1967 OECD conference that PCB's were in fact being detected in fish and wildlife, especially in Europe. The conference among other things served to alert other chemists and scientists to the problems of PCB's and their interference with pesticide residue analysis. Since the discovery that PCB's are contaminating fish and wildlife and that they interfere with organochlorine pesticide analysis, very little has been published on how to cope with these interferences and how to differentiate the PCB's from pesticides. Based on preliminary work, JENSEN and WIDMARK (1967) suggested a nitration technique based on the inertness of the PCB's compared to the relatively easier nitration of the pesticides. RISEBROUGH *et al.* (1968) reported the use of this method, but REYNOLDS (1969 b) pointed out that nitration is not a suitable approach since some pesticides (lindane, toxapene, Strobane, etc.) apparently will not nitrate, while some of the PCB's appeared to be nitrated under the suggested conditions. In addition, there is the problem of further complication from the interference of the nitroderivatives formed, especially when the DDT-group pesticides are present in large amounts.

To avoid the above complications and at the same time facilitate the chromatographic interpretations and afford a means of estimating the PCB's and pesticides independently, REYNOLDS (1969 b) introduced a Florisil separation scheme. KOEMAN *et al.* (1969) have also reported a similar Florisil column technique to separate the PCB's from the pesticides.

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In REYNOLDS' method, the partially cleaned-up sample extract containing the pesticides and PCB's is placed on a Florisil column and the PCB's are eluted first with *n*-hexane, followed by elution of the pesticides with an ether-hexane mixture. Originally, this technique was intended to serve as the final cleanup step, as well as effecting separation of the PCB's from the pesticides. As will be explained, the method has since been slightly modified (miniaturized) to serve mainly as a separation technique. Of the many pesticides investigated, only heptachlor, aldrin, and the DDT metabolite *p,p'*-DDE are eluted with the PCB's. With the exception of *p,p'*-DDE, these do not present difficult problems since chemical reactions (epoxidation, hydrobromination, etc.) can be used to differentiate heptachlor and aldrin from the PCB's. Furthermore, these two pesticides are more frequently found as the more stable epoxy products which are separable from the PCB's by this scheme.

p,p'-DDE on the other hand presents a more difficult problem on account of its chemical inertness. Its greater stability resembles that of the PCB's, and the compound is not amenable to any simple and convenient method of structure modification to give a product which is readily detected within the usual GLC-EC operating parameters.

Of course the ideal situation would be a convenient addition of one mole of hydrochloric acid to the *p,p'*-DDE to form *p,p'*-DDT while the PCB's are not affected. This would afford confirmation and quantitative estimation of *p,p'*-DDE in the presence of PCB's. Generally under such circumstances it would not be necessary to do an additional Florisil separation. The amount of *p,p'*-DDE present could be estimated indirectly from the *p,p'*-DDT produced since, as will be discussed later, the *p,p'*-DDT (and *p,p'*-DDD) can be separated from the PCB's by the use of highly polar liquid phases.

It should be emphasized that although *p,p'*-DDD and *p,p'*-DDT are mostly separated by the polar phase columns, without introducing a Florisil separation the earlier emerging pesticides are superimposed on the PCB's and hence a separation is necessary to identify and to quantify these latter pesticides.

After the Florisil separations of PCB's and pesticides are made, the two eluates are chromatographed separately on the SE-30/QF-1 column and compared with appropriate standards for quantitation. This is normally followed by confirmation of the identities of the pesticides.

VIII. Confirmation of pesticide identity

Despite the separation of the PCB's and their elimination as sources of interference, the non-specific nature of the EC detector

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makes it necessary to confirm the identity of the pesticides by additional techniques.

The sequence usually followed by our laboratory is:

a) Injection of the pesticide eluate onto a more polar liquid phase column (e.g., polyester such as DEGA or DEGS). Typical

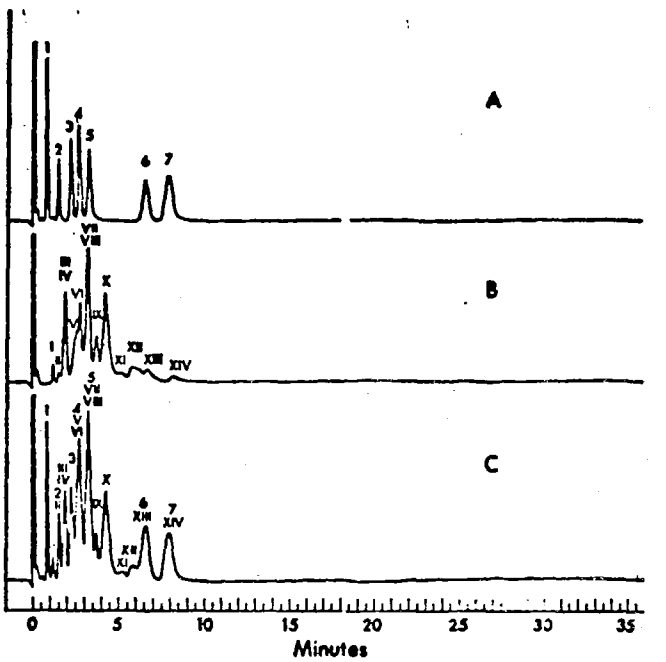

Fig. 2. Separation of PCB's and organochlorine pesticides on polar phase column (five percent DEGS/two percent H_3PO_4). Chromatogram *A*: standard mixture of organochlorine pesticides with same amounts as in Figure 1; peak numbers: 1 = heptachlor and aldrin, 2 = lindane, 3 = heptachlor epoxide, 4 = DDE, 5 = dieldrin, 6 = DDT, 7 = DDD. Chromatogram *B*: 5 ng. of Aroclor 1254 (the 14 major peaks are numbered I to XIV as in chromatogram *B* of Figure 1, assuming that the order of elution is unchanged). Chromatogram *C*: combination of organochlorine standard pesticide mixture and Aroclor 1254. Other GLC parameters as in Figure 1

separations of pesticides, PCB's, and a mixture of the two groups are shown in Figure 2. The reversal of *p,p'*-DDD and *p,p'*-DDT and their separation from most of the PCB's is noteworthy and quite useful. One drawback is that peak No. 13 of Aroclor 1260 interferes partially with *p,p'*-DDT. Other useful information can be obtained by study of the retention times

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of individual pesticides For example, this approach affords separation of the three main BHC isomers. The technique is especially useful for ruling out the presence of pesticides indicated as possibly present by the SE-30/QF-1 column. However, the retention times on two or more stationary phases cannot be regarded as independent parameters of identity (Robinson 1967).

b) Derivatization and use of characteristic GLC retention times of the derivatives. As reported earlier (Reynolds 1969 a), our laboratory has increasingly utilized chemical reactions for confirmations of pesticide residues because the samples to be analysed are generally small and the amount of residue is insufficient to allow effective application of infrared, mass, and other spectroscopic methods.

The derivatization technique has been used by a number of workers (Gunther 1962, Klein *et al.* 1964, Hammence *et al.* 1965, Sans 1967, Duffy and Wong 1967, Csadchuk and Wanless 1968, Cochrane and Chau 1968, Chau 1969, Chau and Cochrane 1969, Wiencke and Burke 1969) and is gaining in popularity. Success of the technique usually depends on the specific derivative remaining lipophilic and therefore extractable with the organic solvent (usually hexane) for direct analysis by the usual GLC-EC method.

A number of chemical reactions is available, but two of the more broad-spectrum types that are quite useful for the pesticides generally found in wildlife are:

(i) Reaction with ethanolic potassium hydroxide (mainly dehydrochlorination) to give products with shorter retention times. This is effective for DDT, DDD, and their isomers, as well as α- and γ-BHC; the β-isomer is not affected.

(ii) Reaction with hydrogen bromide/acetic anhydride reagent to give bromohydrin or bromoacetoxy derivatives with longer retention times. This reaction has been found useful for heptachlor, aldrin, heptachlor epoxide, dieldrin, and endrin.

c) Thin-layer chromatography. In spite of certain drawbacks with TLC for confirmation of small amounts of pesticide residues (Reynolds 1969 a) the technique is still valuable for the confirmation of DDE. TLC can be quite useful also for some group separation, as an ancillary cleanup technique, and for semiquantitative estimation of some pesticide residues.

IX. Identification of PCB's in samples

Data obtained by our laboratory in the course of work conducted for The Canadian Wildlife Service have demonstrated that PCB's are present in some but not all species of Canadian wildlife. Undoubt-

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edly the presence of PCB's has complicated the pesticide residue methodology, but this complication cannot be avoided if meaningful results are to be obtained. Since not all samples contain PCBs, it would be unwise to do a Florisil separation on all extracts before having some indication whether or not the separation is necessary. Accordingly our laboratory uses the approach described below.

The sample to be analysed is extracted, cleaned-up, and assayed using the SE-30/QF-1 column. Depending on the EC results, a decision is made whether or not to make a Florisil separation and check further for the presence of PCB's. This decision is based on the assumption that if there are no apparent *p,p'*-DDD and *p,p'*-DDT peaks, then the presence of PCB's would not be expected. The DDD-DDT combination is chosen as the criterion because peaks eight and ten, two of the larger peaks in Aroclor 1254 and 1260 have identical retention times with *p,p'*-DDD and *o,p'*-DDT, respectively. Also, the PCB components giving rise to peaks eight and ten are less likely to be metabolized than the earlier emerging compounds. Hence, if PCB's (1254 or 1260 pattern) are present, peaks should show up giving apparent *p,p'*-DDD and *p,p'*-DDT values with the EC detection system.

Other useful information regarding the presence of PCB's can be obtained from the initial gas chromatography. If the GLC pattern (prior to PCB separation on Florisil) shows high "apparent" *p,p'*-DDE with little or no *p,p'*-DDD and *p,p'*-DDT present, then all or most of the "apparent" DDE is probably "true" DDE. This is because peak five (the peak which interferes with *p,p'*-DDE) in the common PCB commercial mixtures (Aroclor 1254 and 1260) is relatively small compared to the DDD- and DDT-interfering peaks (eight and ten) as shown in Figure 1. This rule has been borne out by TLC confirmation of DDE in a number of such cases.

As mentioned above, the two most commonly found PCB types in wildlife samples resemble Aroclor 1254 and 1260. Although these two Aroclors are quite similar in many respects, certain differences in their GLC patterns, as shown in Figure 3, can be used to identify one from the other. With a higher chlorine content, Aroclor 1260 shows about 17 major peaks (SE-30/QF-1 column) compared to 14 with Aroclor 1254. Besides this, one other obvious major difference is the peak-height ratio of peaks ten and 13. This ratio has rough values of 9.3 and 1.0 for Aroclors 1254 and 1260, respectively.

Additional information regarding the PCB mixture present in a sample can be obtained by comparisons of other peak-height ratios of the PCB standards and the PCB's in the sample. However, it must be borne in mind that in practice one might be faced with complex mixtures of PCB's rather than a single, specific mixture. In such cases an average value seems to be the best compromise. The method of estimating PCB's described below attempts to take this into account.

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Although most of the early reports on the presence of PCB's in samples indicated the Aroclor 1254 GLC pattern, more recent work by KOEMAN *et al.* (1969) and he author's laboratory has indicated that a proportion of the specimens does contain the Aroclor 1260 GLC pattern. This apparent predominance of the Aroclor 1254 type might have been due to its availability as a standard and lack of the Aroclor 1260 type in the early developmental stages of PCB methodology. The GLC profiles of a number of commercially available PCB mixtures were determined using the SE-30/QF-1 column. These are shown in Figure 4 and indi ate that the more highly chlorinated

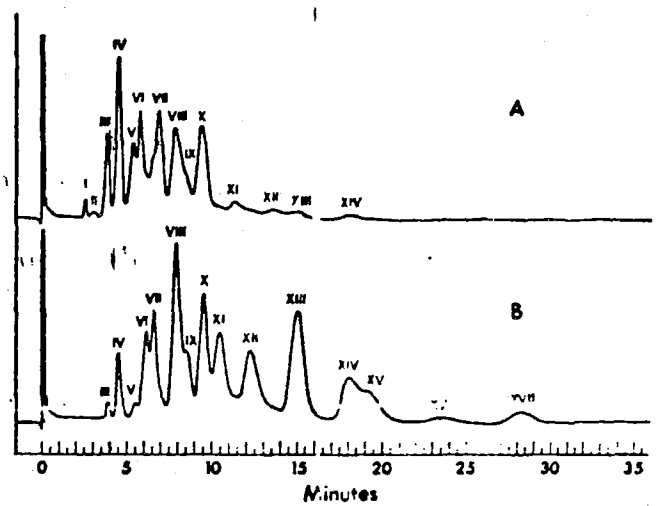

Fig. 3. Comparison of Aroclors 1254 and 1260. Chromatogram *A*: 5 ng. of Aroclor 1254; the 14 major peaks are numbered I to XIV as in chromatogram *B* of Figure 1. Chromatogram *B*: 5 ng. of Aroclor 1260; the 17 major peaks are numbered I to XVII (the early peaks correspond to those in Aroclor 1254). GLC parameters as in Figure 1

biphenyls (Aroclors 1254 and 1260) are easily detected with the usual operating parameters. On the other hand, the compounds of the lower chlorinated mixtures (Aroclors 1221, 1232, and 1242) and the higher molecular weight mixtures (e.g., Aroclor 5460) are less responsive and are, therefore, more likely to go undetected under normal operating conditions. Apparently, the lowered sensitivity is due to low chlorine content in the first group and to high molecular weight with resultant long retention times in the second group. In both cases, therefore, higher concentration would be a prerequisite to ensure detection under normal conditions. This, as well as the possibility of metabolism of the less highly chlorinated biphenyls (KOEMAN *et*

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al. 1969), might explain the genera absence or rarity of these compounds in wildlife samples.

It must not be overlooked, there ore, that in the presence of large amounts of the lower chlorinated bi)henyls (e.g., Aroclors 1221, 1232,

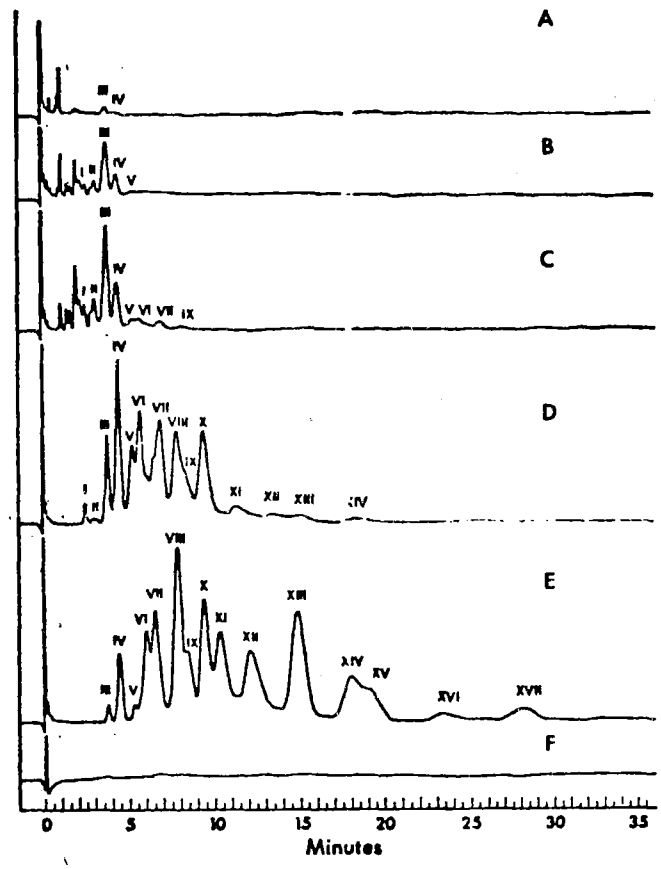

Fig. 4. GLC profiles of the more popular Aroclor mixtures under normal analytical conditions. Note: All peak numbers correspond to those of Aroclor 1254. Chomatograms: *A* = 5 ng. of Aroclor 1221, *B* = 5 ng. of Aroclor 1232, *C* = 5 ng. of Aroclor 1242, *D* = 5 ng. of Aroclor 1254, *E* = 5 ng. of Aroclor 1260, and *F* = 5 ng. of Aroclor 5460. GLC parameters as in Figure 1

and 1242) and negligible quantities of the higher chlorinated biphenyls (e.g., Aroclors 1254 and 1260), different criteria would be necessary to detect PCB interference. To date, this condition has not been encountered in Canadian wildlife samples.

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As might be expected from the complex nature of the PCB mixtures and the chemical inertness of the individual compounds, the confirmation of identities of these materials is much more difficult than with the organochlorine pesticides. Thus, in the absence of a mass spectrometer, confirmation of the PCB's is mainly by their GLC retention times and patterns on the mixed and polar phase columns in conjunction with their non-reactivities with the two general reagents used for the organochlorine pesticides.

The prior separation of the PCB's from the organochlorine pesticides by the Florisil technique also aids in the identification of the PCB's.

X. Estimation of PCB's

Since the PCB's are themselves toxic, attempts have been made to estimate the amounts present in samples. It should, however, be recognized that only rough estimates can be made since pure standards of the individual compounds in the mixtures are to date unavailable. The situation resembles that of toxaphene estimation, but is of greater complexity.

KOEMAN *et al.* (1969) based their PCB estimation on the peak of phenoclor DP6 having r_x (relative retention time with dieldrin = 1 under his operating conditions) equal to 1.45. RISEBROUGH *et al.* (1969) estimated the PCB's on the assumption that they have similar EC responses to *p,p'*-DDE and applied a factor to fit the assumed 54 percent chlorine content of the PCB's. JENSEN *et al.* (1969) reported estimates as the sum of all the PCB components.

The author's laboratory uses a method very similar to KOEMAN's with the exception that an average based on two peaks is usually employed. Should the two values before averaging vary to any extent, additional estimations are made using other peaks, and all the results are averaged. In the case of a few samples, the PCB level was obtained by averaging results from all the major peaks in the mixture; however, the use of peaks eight and ten only has been found to give equally satisfactory results. Note that results are reported as being based on Aroclor 1254 or 1260 depending on the overall GLC pattern. Peaks eight and ten were chosen because of their stability (see section on identification). In a later section the above points are illustrated by analysis of resin powder taken from a fish hatchery trough.

The total PCB results obtained by the method described may be slightly higher than the actual values because the early emerging PCB peaks (mainly one, two, and three) are usually absent from the chromatograms of sample extracts. However, this should not affect the overall results greatly since these peaks represent minor components in the mixtures. Furthermore, there might be compensation, since no attempt has been made to apply recovery correction factors.

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The method of estimation described above appears to give a reasonable estimate of PCB contamination based on commercial PCB mixtures. For absolute measurement of PCB content it would be necessary to prepare standards for the individual PCB components, and, even if these were available, the determinations would be complex and costly. Considering our present limited knowledge of total PCB toxicity and our even greater ignorance about the toxicity of the individual components of the mixtures, it is doubtful whether such accurate determinations would be meaningful at this time. As stressed earlier, the most urgent need is for toxicological investigation in this area to indicate whether some of the PCB compounds are more toxic or have greater sublethal effect than others, as observed with the BHC isomers. At that point it would become essential to identify and estimate accurately specific individual compounds in the mixtures.

XI. Separation of PCB's from organophosphorus compounds by the Florisil technique

A limited amount of work has been carried out in our laboratory to determine whether the Florisil column technique is applicable to the separation of the PCB's from the organophosphorus compounds. Preliminary results on those tested (phorate, diazinon, ronnel, malathion, parathion, methyl Trithion, ethion) indicate that they are not eluted with the PCB's by hexane, and can therefore be separated. In comparison to the organochlorine pesticides, the organophosphorus compounds generally require larger volumes of the ether-hexane mixture for elution from the Florisil column, most likely because of their more polar nature.

As with the organochlorine pesticides, the presence of PCB's in a sample extract will interfere with some of the more common organophosphates when the EC detection system is used. However, with the use of a dual detector (EC + phosphate or thermionic) connected to a dual-pen recorder, the effluent from a single injection containing PCB's and organophosphates can be split and differentiation made as shown in Figure 5. Like the organochlorine pesticides, the PCB's are not detected on the phosphate detector. Nevertheless, in the absence of a detector which is specific for phosphorus, the Florisil column technique can be used to separate the PCB's from the organophosphates to facilitate the analyses.

XII. Residues of organochlorine pesticides and PCB's in Canadian wildlife

Following the approaches outlined, the author's laboratory has analysed a number of Canadian wildlife specimens for residues of

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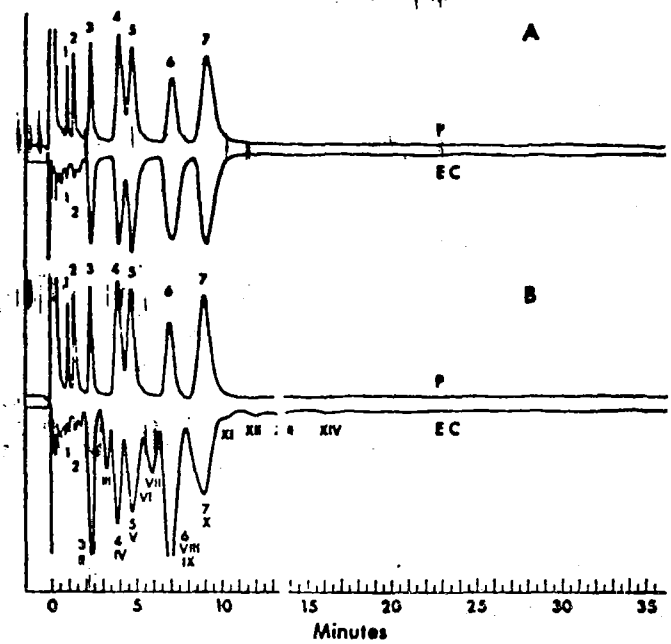

Fig. 5. Differentiation of Aroclor 1254 and organophosphorus pesticides using dual detectors and effluent split. Chromatogram *A*: organophosphorus standard pesticide mixture peak numbers 1 = 1.75 ng. of phorate, 2 = 2.0 ng. of diazinon, 3 = 5.0 ng. of Ronnel, 4 = 13.0 ng. of malathion, 5 = 5.0 ng. of parathion, 6 = 15.0 ng. of methyl Trithion, and 7 = 10.0 ng. of ethion. Chromatogram *B*: combination of organophosphorus mixture (chromatogram *A*) and 10 ng. of Aroclor 1254 numbered I to XIV as in chromatogram *B* of Figure 1 (a compromise of the E.C. response is necessary to obtain maximum response on the phosphorus detector). *P* = phosphorus detector and *EC* = electron capture detector. Column four percent OV-100/six percent OV-210 on 60/80 mesh Chromosorb W (AW); other GLC parameters as in Figure 1

organochlorine pesticides and PCB's. Some of the data on aquatic birds from Western Canada are given in Table I. The inclusion of these tabulated results, which represent only a minor portion of the total number of samples analysed, is intended to illustrate the types of analytical problems created by the presence of PCB's, and to indicate potential errors due to high levels of PCB's in samples.

Referring to Table I, some general remarks are in order:

1. The greater portion of the apparent DDE in samples is in fact DDE. This is predictable from the comparatively smaller amounts of apparent DDD and DDT, and has been verified by TLC.
2. A large proportion of the apparent DDD in the samples is due to PCB's. However, DDD is present in some samples.

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3. The effect of PCB contamination on DDT values is less marked than in the case of DDD, but it is still substantial.
4. The apparent HE values are in most cases due entirely to the pesticide. This is somewhat incongruous with the rest of the data since peak four of the commercial PCB mixtures does interfere with HE. However, this anomaly may be explained on the basis that the PCB component giving rise to peak four is degraded extensively in the bird's metabolic processes.
5. Based on all of the PCB estimates in wildlife samples noted to date, including those in Table I, the following general trends are evident:
   (a) Aquatic raptorials generally contain higher residue levels of pesticides and PCB's than other wildlife species.
   (b) High levels of PCB's are found only in the presence of high levels of organochlorine pesticides (the resin powder mentioned below is an obvious exception) but high levels of organochlorine pesticides are not necessarily accompanied by high levels of PCB's.
   (c) The most abundant PCB types detected are those which show Aroclor 1254 and 1260 patterns and, therefore, fit well with the proposed method of quantitation. However, it should not be overlooked that with the present residue methodology some other PCB-type compounds might go undetected.
6. It is important to measure moisture and fat content of samples in conjunction with residue levels. This allows for reporting on a wet-, dry-, or fat-weight basis. However, caution should be used when reporting residues in wildlife samples, for example, on a fat basis when the fat content is very low. Such figures can be inaccurate as well as highly misleading.

The gas chromatogram of a typical sample showing the presence of PCB's is given in Figure 6. It indicates the Aroclor 1260 pattern and was obtained from a duckling found dead in the Toronto area in the summer of 1969.

A good example of PCB's showing up in unexpected places occurred recently. A wildlife biologist was faced with the problem of fish dying in a hatchery for no apparent reason. He scraped some of the resin powder from the hatchery trough and found, surprisingly, that experimental fish were susceptible to even a dilute solution of the powder. He submitted a sample of the resin powder to the author's laboratory, and upon analysis a typical GLC pattern of PCB's (Aroclor 1254 type) was obtained. This is shown in Figure 7. Using the methodology described earlier in this review, the sample was found to contain PCB's but no pesticides. Based on calculations from 11 individual peaks of Aroclor 1254, the PCB concentration was estimated at 35 p.p.m (range 25 to 46). Using the average results based on peaks eight and ten only, the PCB estimate was 29 p.p.m. This is

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Table I. Organochlorine residues (p.p.m. on a wet-weight basis) in Canadian aquatic birds as measured before and after PCB Florisil separation

Description of specimen[a]	p,p'-DDE	Dieldrin	p,p'-DDD			p,p'-DDT			HE			PCB[c]
			Before (apparent)	After	%[d]	Before (apparent)	After	%[d]	Before (apparent)	After	%[d]	
California Gulls												
Abd. fat bird 1	241	1.36	3.16	ND[e]	0	3.17	ND	0	ND	ND	—	50.8
Abd. fat bird 2	138	1.02	1.02	ND	0	1.04	0.14	7	0.23	0.22	96	25.3
Abd. fat bird 3	240	1.23	2.63	ND	0	3.47	0.25	7	0.19	0.21	107	62.6
Abd. fat bird 4	246	1.91	1.59	ND	0	2.41	1.27	53	ND	ND	—	36.7
Abd. fat bird 5	169	1.78	1.71	ND	0	2.55	0.55	22	0.33	0.19	58	23.2
Abd. fat bird 6	296	1.51	3.09	ND	0	3.33	1.09	33	0.42	0.36	87	23.0
Brain bird 7	3.6	0.04	0.04	ND	0	0.04	ND	0	ND	ND	—	0.81
Liver bird 7	15.7	0.07	0.11	0.02	14	0.11	0.01	2	0.03	0.03	79	1.69
Ovary bird 7	22.9	0.12	0.17	0.04	24	0.23	0.02	8	0.05	0.04	83	2.52
Abd. fat bird 7	416	1.93	4.64	0.34	7	4.43	0.62	14	1.19	0.78	65	38.4
Egg area 1	21.8	0.19	0.20	ND	0	0.25	0.08	33	0.07	0.05	66	1.74
Egg area 2	2.9	0.09	0.11	ND	0	0.11	0.02	18	0.01	0.01	93	1.57
D.C. Cormorant Eggs												
Sample 1 area 3	3.3	0.11	0.11	ND	0	0.12	0.03	22	0.01	0.01	100	1.94
Sample 2 area 3	3.3	0.10	0.12	ND	0	0.12	0.02	13	0.03	0.03	110	2.21
10 pooled area 4	3.5	0.21	0.03	ND	0	0.07	0.03	41	0.03	0.04	106	0.67
Mallard Duck Eggs												
10 pooled area 4	0.2	0.08	0.01	0.01	80	0.15	0.15	100	0.01	0.01	100	0.09
Common Tern Eggs												
Sample 1 area 5	33.3	0.15	0.17	0.02	13	0.26	0.15	51	ND	ND	—	1.57
Sample 2 area 5	5.1	0.02	0.06	ND	0	0.16	0.15	90	ND	ND	—	0.94
Great Blue Heron Eggs												
Sample 1 area 5	78.0	0.05	0.27	0.27	100	0.41	0.42	102	0.02	0.02	94	Trace

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Table I. (continued)

Description of specimen[a]	p,p'-DDE[b]	Dieldrin[c]	p,p'-DDD			p,p'-DDT			HE			PCB[e]
			Before (apparent)	After	%[d]	Before (apparent)	After	%[d]	Before (apparent)	After	%[d]	
Sample 1 area 6	24.0	0.42	0.33	0.27	81	0.18	0.10	57	0.15	0.12	83	3.41
Sample 2 area 6	11.3	0.19	0.07	ND	0	0.30	0.23	77	0.10	Trace[g]	—	1.93
Sample 3 area 6	13.7	0.74	1.63	1.70	104	0.08	0.06	69	0.05	0.05	100	1.09
Sample 1 area 7	13.5	0.07	0.07	0.05	64	0.05	0.02	33	0.02	Trace[g]	—	0.57
Sample 2 area 7	3.7	0.06	0.12	ND	0	0.14	0.03	18	0.02	Trace[g]	—	1.38
Sample 1 area 8	6.3	0.68	0.09	0.05	49	0.04	0.01	22	0.02	0.01	52	0.53
Sample 2 area 9	9.1	0.07	0.06	0.03	52	0.07	0.05	70	0.03	0.01	44	0.33

[a] These specimens are from western Canada (VERMEER and REYNOLDS 1970).

[b] These are "Before PCB-Florisil separation" values and are likely to include PCB contributions. The "After" values (which do not change significantly from the "Before" values) are not given because the PCB peak five (the DDE-interfering peak) of Aroclor 1254 or 1260 is not separated from DDE by this method, but, as discussed earlier, the PCB contributions to the DDE values are expected to be relatively small compared to the contributions to DDD or DDT.

[c] These are "Before" values. The "After" values (not given) are not significantly different from the "Before" values since there is no direct PCB interference. However, in the presence of high levels of DDE, low levels of dieldrin will be masked. In such cases a separation (e.g., PCB-Florisil technique) is necessary, and the "After" value would be reported as the dieldrin level.

[d] $\% = \frac{\text{After value}}{\text{Before value}} \times 100$ and indicates the percentage of the total apparent pesticide level that was actually due to the pesticide.

[e] Values (p.p.m.) based on peaks eight and ten of Aroclor 1254.

[f] ND = none detected = <0.0001 p.p.m.

[g] Trace = <0.001 p.p.m.

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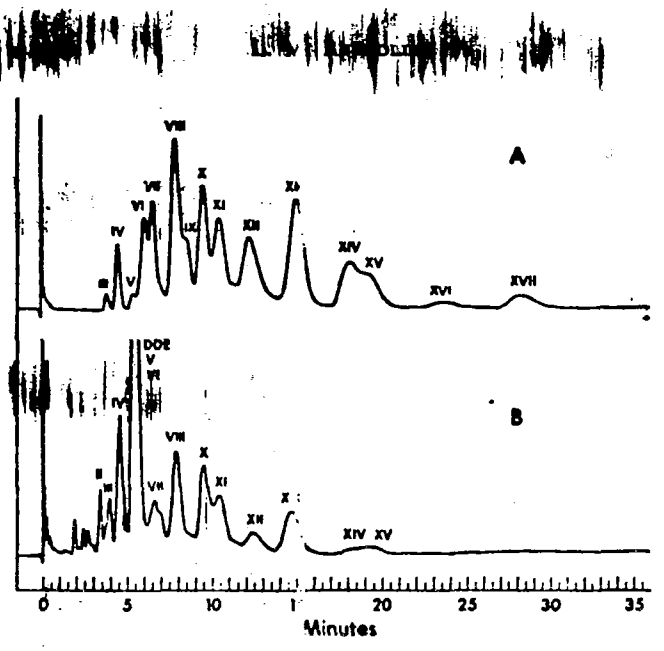

Fig. 6. Typical sample indicating the presence of PCB's of the Aroclor 1260 type in a duckling from the Toronto area. Chromatogram *A:* 5 ng. of Aroclor 1260 numbered I to XVII as in chromatogram *B* of Figure 3. Chromatogram *B:* the equivalent of 0.35 mg. of duck sample (hexane portion of Florisil split). Note the DDE contribution to PCB peak V. GLC parameters as in Figure 1

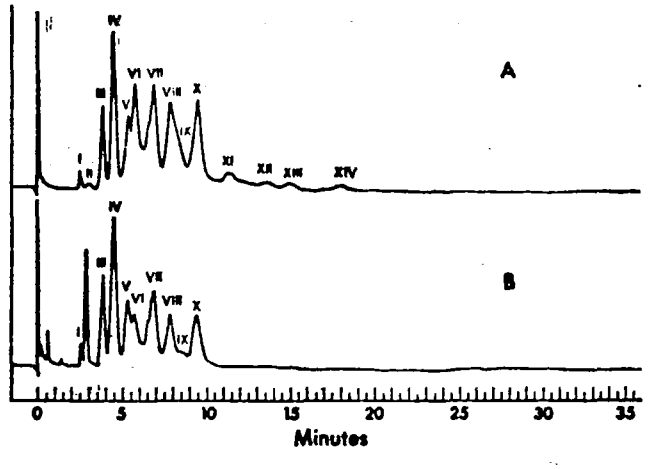

Fig. 7. Resin powder extract indicating the presence of PCB's of the Aroclor 1254 type. Chromatogram *A:* 5 ng. of Aroclor 1254 numbered I to XIV as in chromatogram *B* of Figure 1. Chromatogram *B:* The equivalent of 0.02 mg. of resin powder extract (hexane portion of Florisil split), numbered I to XIV as in Aroclor 1254. GLC parameters as in Figure 1

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an interesting example of PCB's causing contamination as a direct result of industrial application.

With regard to the Florisil technique for the separation of PCB's from pesticides, one important modification to the original method (REYNOLDS, 1969) is now used routinely in the wildlife studies. Originally the scheme was designed to accommodate simultaneously both the cleanup of the sample extract and the separation of PCB's. However, as pointed out earlier in this review, not all samples contain PCB's. Consequently, for general samples, to avoid unnecessary splitting of all sample extracts (each split doubles the number of eluates to be chromatographed), a normal cleanup including a Florisil column, but no differential elution, is conducted. The Florisil-PCB separation is then carried out on the cleaned-up extract, if it is required. Under these conditions smaller columns have been found to be as efficient as the larger columns used in the original method, and there is a substantial saving in the amount of reagents required. Details of the modified procedure are as follows:

> A glass column (44 cm. × 1 cm. o.d. having a 50-ml. reservoir on top) is packed with 30 cm. (~10.7 g.) of Florisil (60/100 mesh, Floridin Co., pesticide grade, stored at 130°C. until ready for use) and topped with a 2-cm. layer of anhydrous Na_2SO_4. The sample extract of about 5 ml. (*n*-hexane) is added to the column. The first elution which removes PCB's, heptachlor, aldrin, and DDE, is effected with 60 ml. of *n*-hexane (Nanograde, Mallinckrodt). The remaining pesticides are then eluted with 40 ml. of 50 percent ethyl ether in hexane.
>
> Note that in filling the columns, the Florisil is packed down by gentle tapping, and the sample extract is added to a dry column, *i.e.*, no prewetting. After the first elution the receiver is changed as soon as the last of the hexane meets the Na_2SO_4. It should be noted also that with one batch of pesticide grade Florisil, some PCB peaks (two, six, nine, 11) showed partial elution in the second eluate. These, however, are comparatively minor peaks and do not interfere with any of the common organochlorine pesticides. As there are differences in batches of Florisil, the procedure has to be checked out fully prior to application to actual samples. Modifications of volumes, etc., may be necessary to effect the desired separation. It is likely that adsorbents other than Florisil, e.g., silica gel or alumina, will give similar separation of PCB's from pesticides but these have not been investigated to date.

Acknowledgments

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Research Foundation in preparing this review for publication. The technical assistance of Terry Cooper and Sandra Takacs is gratefully acknowledged.

Table II. *Chemical designations of pesticides mentioned in text*

Pesticide	Chemical name
aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo*, *exo*-5,8-dimethanonaphthalene
p,p'-DDD (TDE)	2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane
p,p'-DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
p,p'-DDT	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane
diazinon	*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl)-phosphorothioate
dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a-5,6,7,8,8a-octahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene
ethion	*O,O,O',O'*-tetraethyl-*S,S'*-methylene bisphosphorodithioate
heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
heptachlor epoxide	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
lindane (γ-BHC)	γ-1,2,3,4,5,6-hexachlorocyclohexane
malathion	*S*-[1,2-bis(ethoxy carbonyl)ethyl]*O,O*-dimethyl phosphorodithioate
methyl Trithion	*O,O*-dimethyl *S*-(*p*-chlorophenylthio) methyl phosphorodithioate
parathion	*O,O*-diethyl *O*-*p* nitrophenyl phosphorothioate
phorate (Thimet)	*O,O*-diethyl *S*-(ethylthio) methyl phosphorodithioate
Ronnel	dimethyl 2,4,5-trichlorophenyl phosphorothionate

Summary

Since 1966, PCB's have been detected in fish and wildlife, especially in Europe and North America. Contamination from industrial wastes via the water ways appears to be the main source of PCB's in aquatic species. The PCB's have many important industrial uses but are not utilized as pesticides.

Due to their similarities in structure and properties to the organochlorine pesticides, the PCB's tend to interfere with accurate GLC-EC determination of organochlorine and many organophosphorus pesticides. In addition to their interference with pesticide residue analysis the PCB's are themselves toxic so that their quantitation is desirable.

A method for recognising the presence of PCB's in samples, separating them from pesticides, and determining the pesticide levels accurately is described. Simultaneously an estimate of total PCB content is afforded.

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The residue data of some Canadian aquatic birds indicate that high levels of PCB's are found only in the presence of correspondingly high levels of the DDT pesticide group. On the other hand, high organochlorine pesticide levels are not necessarily accompanied by high PCB content.

Further research on toxicity and sublethal effects of PCB mixtures and their individual components is required. If particular components are shown to be more toxic than others, refining of the PCB quantitation methods will be necessary

Résumé*

Analyse de résidus de pesticides en présence de diphényls polychlorés

Depuis 1966 des diphényls polychlorés (PCBs) ont été détectés dans les poissons et le gibier, particulièrement en Europe et en Amérique du Nord. Il apparait que la présence de PCBs dans la faune aquatique soit due principalement à la contamination des cours d'eau par des déchets industriels. Les PCBs sont utilisés pour un grand nombre de procédés industriels importants, mais ils ne sont pas appliqués comme pesticides.

Etant donné que la structure et les propriétés des PCBs sont semblables à celles des pesticides organochlorés, ils ont tendance à fausser la détermination exacte des substances organochlorées et organophosphorées lors d'analyses par chromatographie en phase gazeuse via capture d'électrons. En plus de leur interférence lors de l'analyse des résidus des pesticides, les PCBs sont eux-mêmes des composés toxiques dont la détermination quantitative est souhaitable.

Le présent article contient une méthode qui permet de reconnaître la présence des PCBs dans des échantillons et, en même temps, de les séparer des pesticides dont le taux de résidus peut être exactement déterminé. La méthode permet également une estimation du contenu total en PCBs.

Des résultats d'analyses portant sur des oiseaux aquatiques canadiens indiquent qu'un taux élevé de PCBs est lié à un taux élevé de résidus de pesticides du groupe DDT. D'autre part, des taux élevés de résidus de substances organochlorées ne sont pas nécéssairement accompagnés d'un taux élevé de PCBs.

Des recherches supplémentaires sur la toxicité et les effets sublétaux des mélanges de PCBs et de leurs composés individuels seront nécéssaires. Si on peut démontrer que des substances particulières sont plus toxiques que d'autres, on aura besoin d'une méthode plus spécifique permettant l'analyse individuelle des PCBs.

* Traduit par H. Geissbühler.

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Zusammenfassung*

Die Analyse von Pflanzenschutzmittel-Rückständen in Gegenwart von Polychlordiphenylen

Seit 1966 werden Polychlordiphenyle (PCB-Stoffe) in Fischen und Wildtieren, besonders in Europa und Nordamerika, nachgewiesen. Die Verschmutzung der Wasserwege durch Industrieabfälle scheint dabei die Hauptursache von PCB-Rückständen in der aquatischen Fauna zu sein. Die PCB-Stoffe werden für eine Anzahl wichtiger Industrieprozesse gebraucht, als Schädlingsbekämpfungsmittel werden sie jedoch nicht eingesetzt.

Da die PCB-Stoffe in ihrer Struktur und in ihren Eigenschaften den chlorierten Kohlenwasserstoff-Insektiziden sehr ähnlich sind, können sie die gaschromatographische Bestimmung mit Elektronen-einfang-Detektor von chlorierten Kohlenwasserstoffen und mancher Phosphorsäureester verfälschen. Die PCB-Stoffe können nicht nur Rückstandsanalysen beeinträchtigen, sondern sie sind selbst toxische Substanzen, deren Nachweis sich aufdrängt.

Im vorliegenden Artikel wird eine Methode beschrieben, die es erlaubt, das Vorhandensein von PCB-Stoffen in Proben nachzuweisen, sie von den Schädlingsbekämpfungsmitteln abzutrennen und die Rückstände der letztern genau zu bestimmen. Darüber hinaus gestattet die Methode, den Totalgehalt an PCB-Stoffen abzuschätzen.

Rückstandsdaten einiger kanadischer Wasservögel weisen darauf hin, dass hohe PCB-Konzentrationen nur in Gegenwart hoher Rückstände von Substanzen der DDT-Gruppe auftreten. Anderseits sind hohe Rückstände von chlorierten Kohlenwasserstoff-Insektiziden nicht unbedingt von hohen PCB-Konzentrationen begleitet.

Weitere Untersuchungen über die Toxizität und die sublethale Wirkung von PCB-Mischungen und ihrer individuellen Komponenten sind angezeigt. Sollte es sich dabei ergeben, dass gewisse Einzelstoffe toxischer sind als andere, wird eine Verfeinerung der Nachweis- und Bestimmungsmethoden für PCB-Stoffe notwendig.

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