

MONTANTO CHEMICALS LIMITED

→ MS 6/5/69

PRODUCT TOXICOLOGY - PAROCLORS

toxicity *pg*

Report summarising present knowledge concerning chlorine-containing residues in wild life and visits made to organisation implicated therewith during the period April 28th - May 1st, 1969.

by: D.V.N. Hardy*

Circulate!
→ ~~1) B. B. B.~~
~~2) B. B. B.~~ / PG B
3) ~~B. B. B.~~
4) H. S. Bergen

Circulation

J.W. Barrett, London.
R.A. Baxter, Ruabon.
H.A. Vodden, Ruabon.
H.R. Newman, Newport.
A.C.W. Pemberton, Newport.
W.J.S. Budd, London.
J. Herefousse, Brussels.
D. Wood, Brussels.

R.E. Keller, St. Louis.
E.P. Wheeler, St. Louis.
R.E. Kelly, St. Louis.
W.R. Richard, St. Louis.
H.S. Bergen, St. Louis.

*Formerly Research Services Manager, MCL, and now Consultant to MCL in the area of Product Toxicology and Safety in the Use of the Company's products.

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TRAN 021762

INTRODUCTION

The wide agricultural usage of insecticides in the post-World War II period and consequent effects on wild life have led in certain circles to apprehension concerning the overall effect on man. The situation has been under study for many years and Government agencies and manufacturers of insecticides have been implicated in the various aspects, particularly in the assay of such residues in many species of wild life. Fish, fish-eating birds and mammals have been subjected to wide ranging study, and it became clear that terrestrial usage of insecticides could have far reaching and hitherto unsuspected effects on wild life, part of it making an important contribution to the diet of man and domestic animals.

The size of the wild life specimens and the minute concentrations of insecticides therein demanded highly sensitive methods of assay, which have been progressively refined. Gas liquid chromatography using electron-capture or microcoulometric detection has become established as the most suitable technique. It appears that the chromatograms of the residues showed not only the peaks corresponding to the insecticides and their known metabolites, but additional peaks of unknown chlorine-containing substances.

Towards the end of 1965 these unknown substances were identified by Sören Jensen, a research worker at the Institute for Analytical Chemistry, University of Stockholm, under the direction of Gunnar Widmark. Using a combined gas chromatograph mass spectrometer (LKB-9000) it was shown that the peaks are due to polychlorinated biphenyls (PCB's). The evidence and reasoning are available and the conclusion can hardly be in doubt.

Unfortunately the announcement was coupled with sensational statements concerning the poisonous nature of the PCB's, which were calculated to cause misgivings both to public authorities and to the general public.

Jensen and Widmark found PCB's in specimens of pike from different parts of Sweden, fish spawn, a dead eagle and in human hair, and even on fir cones! The conclusion reached was that the PCB's originated from burning industrial wastes and were washed down by the rain. Examination of feathers from museum specimens of sea birds suggested that contamination commenced in 1944.

The original work of Jensen and Widmark has been extended and generally confirmed, notably by workers at the following establishments and much of the detail has been published:-

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Great Britain

1. Laboratory of the Government Chemist,
Cornwall House,
London, S.E.1.
(Notably Mr. O'G. Tatton)
2. Freshwater Fisheries Laboratory, (Ministry of
Faskally, Agriculture, Fisheries
Pitlochry, Scotland. and Food)
(Mr. A. Holden)
3. Tunstall Laboratories,
Shell Research Limited,
Sittingbourne, Kent.
(Dr. J. Robinson and Mr. A. Richardson)
4. Monks Wood Experimental Station, (*Nature Conservancy)
Abbots Ripton,
Huntingdonshire.
(Dr. N.W. Moore)

*Established by Royal Charter to (1) provide scientific advice on the conservation and control of the natural flora and fauna of Great Britain, (2) establish, maintain and manage natural reserves in Great Britain including maintenance of physical features of scientific interest, (3) develop research and scientific services related thereto.

At 30th September, 1963 there were 144 scientifically qualified staff and in 1963-4 there was a Government grant-in-aid of £701,000.

Holland

5. University of Utrecht
(Professor H. Van Genderen)

U.S.A.

6. University of California
(Drs. R.W. Riseborough, P. Rieche and S.G. Herman)
7. Cornell University
(D.B. Peakall)
8. San Diego Natural History Museum
(M.N. Kirven)

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This report is written following discussions with staff from Establishments 1, 2 and 3 in which Dr. R.E. Keller and Dr. E.P. Wheeler (1 and 3 only) were associated. Drs. Keller and Wheeler are proceeding to visit 5, University of Stockholm, to see Jensen and Widmark. They are also visiting Bayer to ascertain its reactions as manufacturers of PCB's (Clophens).

SUMMARY

1. There can be no doubt that traces of PCB's (Aroclors) are to be found in wild life, fish and certain items of human diet.
2. There is little evidence to show how serious this minor contamination will prove to be, but what evidence there is is reassuring.
3. There is little evidence to show how the PCB contamination arises. It may be by run off of wastes into rivers, or by burning of industrial wastes with consequent washing down by rain. It is remotely possible that the PCB's might arise by biochemical action on insecticides and other chlorine-containing materials which are similarly discharged into the rivers, seas and oceans. It could be that among the vast quantities of materials destroyed on land and at sea during the 1939-45 war, significant quantities of Aroclors and Aroclor-containing materials found their way into the rivers, seas, etc., and are being slowly released by corrosion, extraction, etc. (see footnote at end of report).
4. A considerable Monsanto effort will be necessary to obtain the necessary analytical and toxicological information for dealing with this threat to our commercial operations.

A. Visit to Freshwater Fisheries Laboratory, Pitlochry* Monday, April 28th, 1969.

Mr. A.V. Holden - Officer in Charge.
Dr. R.E. Keller - MC
Dr. D.V.N. Hardy - MCL

This visit was made not so much on account of contributions made to the subject but because Mr. Holden acts as Co-ordinator

*Dr. E.P. Wheeler was prevented from taking part in this visit due to the sudden indisposition of Mrs. Wheeler.

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toxicological interest might be transferred from insecticides to PCB's, there has been no attempt to do so. In fact papers by Robinson do not refer to PCB's but make a very sound approach to the insecticides problem and to its true perspective. Nevertheless they had collected some information on possible usage of Aroclors, for example, they had noted that the Coal Board disposes of 1,000,000 gals. of high pressure lubricant each year. Did this contain Aroclor? We thought it unlikely but questions concerning safety in use of Aroclors had certainly been referred to MCL by the Coal Board and it was therefore likely that some minor uses have been developed. There might conceivably be a small content of Aroclors in the high pressure lubricant. Usage of insecticides was of a high order, and in Kent alone 1000 tons of DDT had been consumed since its introduction after the 1939-45 war. Reference was also made to usage of Aroclors in cutting oils; the Government Laboratory had suggested that this was a possible source of contamination. Cutting oils are normally sold as proprietary formulations and it would be difficult to estimate how much Aroclor is consumed in this form.

Shell would much prefer to have a direct method for estimating insecticides. Now, owing to the stability of PCB's, it was necessary to estimate insecticides and PCB's, then PCB's by destroying or removing the insecticides and getting the insecticides by difference.

Aroclor 1254 had been fed to chicken at 100 parts per million of the diet and no adverse effect observed over a period of 12 months. The Nature Conservancy has carried out feeding tests on Bengalese Finches with DDT and found no adverse effects, and similar results have been with chicken and quail fed on 10 and 20 parts per million of Dieldrin. Other workers found some effect on mallards and chicken. At the Government Laboratory it has been shown that human fat (from mothers' milk) may contain PCB. Reference was also made to the work of Mr. Alabaster, Ministry of Agriculture, Fisheries and Food, on toxicological levels with fish.

It was agreed that many of the specimens submitted for analysis were not representative of the total population, e.g. predators were heavily weighted, and of the sick and dead birds, were most frequently collected. There must be large numbers of each predator much less contaminated than those submitted for analysis.

Samples of fish oils and margarine (supplied by Unilever) have been examined, and while PCB's can be found in the oils, they disappear during the hardening process so that margarine is free.

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C. Discussions with Representatives of the Government
Laboratory at Monsanto House
Thursday, May 1st, 1969.

Mr. J.O'G. Tatton - Laboratory of the Government
Chemist

Mr. G.B. Collins - " " " "

Dr. R.E. Keller - MC

Dr. E.P. Wheeler - MC

Dr. D.V.N. Hardy - MCL

Mr. Tatton said that the possible danger of Aroclors used as plasticizer (in food packaging and in lacquers for cans) had been considered quite early on and reference is made thereto in the Annual Report of the Government Chemist 1953-4. He will send me a photostat copy. As regards residues in wild life peaks not due to pesticides were observed in 1963-4 and this caused trouble in view of the complicating effect on insecticide determination. Attempts to identify the disturbing material failed until Jensen showed their nature. Jensen's work has been fully confirmed and extended and PCB's have been found in eggs, predatory birds, rarely in human food, and traces in cod liver oil. Human fat seems to be free from PCB but there may be 2 - 12 parts/ 10^6 of insecticide. Some PCB found in human lung samples. Work has been carried out on air and on circumstantial evidence PCB must be present. 1 part DDT compounds/ 10^{12} parts of air has been found. The analysis is complicated by the presence of hydrocarbons. Tatton will supply references to this work which was carried out on sample of about 1200 litres. The content of insecticides in air and water is variable, generally higher in London due to soot particles acting as absorbent, and also depending on when spraying is in progress. Dr. Kroll (Water Research Association) has failed to find PCB in river waters at parts per 10^9 .

Many samples are sent to the Government Laboratory by the Nature Conservancy, but having carried out the analysis nothing more can be done as the source and significance of the sample are known only to the Nature Conservancy.

The peaks seen in the chromatogram represent only part of those observed in commercial samples of Aroclor 1254. Probably the middle components are favoured by the analytical procedure: certainly peaks due to higher boiling material can be obtained by raising the operating temperature of the column.

Recently high PCB figures have been found on herons (several hundred parts per million in the liver), kestrels, owls

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and kingfishers. Dr. N.W. Moore (Monkswood Experimental Station) might be prepared to discuss their significance and the geographical factor. Tatton considers that Jensen's peaks are more in line with Bayer's Clophen. He thinks that some of the bird samples are representative as they were taken from colonies.

Tatton also referred to possible traces of PCB nature in occasional food samples, e.g. milk, mutton and beef fat. He will supply me with copies of all relevant papers, including a report on some new detectors for VPC analysis. Dr. Keller will reciprocate by sending chromatographic curves for the various Aroclors.

I referred to MCL work now starting on the biodegradation of Aroclors and suggested that our workers should contact him on the analytical techniques. He would be most happy to do so.

D. Discussion with Representatives of Cremer & Warner,
Consultants, 140 Buckingham Palace Road, London, S.W.1.
Thursday, May 1st, 1969.

Sir Frederick Warner	-	Cremer & Warner
Dr. David Train	-	" "
Dr. R.E. Keller	-	MC
Dr. E.P. Wheeler	-	MC
Dr. D.V.N. Hardy	-	MCL

This was a lunch discussion arranged to determine the possible value of this firm of consultants in the assessment of the PCB problem.

Cremer & Warner have contracted with the Port of London Authority (and possibly with others too) to study the effect of certain contaminants in the Thames. They are concerned specifically with detergents and Mr. Cremer is Chairman of the Government Committee which has been advising on the problem due to hard detergents. Cremer & Warner are also advising on atmospheric pollution due to sulphur dioxide and smoke, and on the design and interpretation of data from the recording stations.

They have also acted as consultants for the new potash project in relation to the effluent disposal problem. They have advised that the effluent should be discharged 1 mile from the shore at a minimum depth of 75 feet.

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They were interested broadly in our problem and fully appreciated that after all the analytical work had been done it would be necessary to interpret the data and to correlate it to safety standards in a way which would carry conviction with the authorities. They seemed confident that this area was one of their strong suits, but it is far too early to assess their ability to contribute to the present problem.

D.V.N. HARDY

JWB/HMH
6.5.69.

Footnote (See p.4 - Summary, Item 3)

Compare Jensen's findings that no contamination was observed prior to 1944.

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