HA Vodden

BIODEGRADATION

1. MICROBIAL DEGRADATION

We made laboratory studies of the effects of two specific biphenyl-degrading organisms on a range of PCB compounds and commercial mixtures. Results showed that many low chlorine compounds were degraded quite readily. (Slide 1 or Transparency).

The degradation of many of these compounds was even more pronounced when they were present as components in commercial mixtures like Aroclors 1242 and 1016. Slides 2 and 3 show curves depicting the rates of degradation of groups of trichloro- and tetrachloro-biphenyls which together account for more than 90% of the composition of Aroclor 1242 and more than 95% of Aroclor 1016. From curves of this type we estimate that dichlorobiphenyls degrade to half concentration in less than two days, trichlorobiphenyls in less than five days and tetrachlorobiphenyls in less than 20 days(at 25°C). For more highly chlorinated biphenyls we could not obtain meaningful rates, but in favourable circumstances some pentachloro- and hexachloro-biphenyls could be degraded.

Microbial degradation may contribute significantly to the degradation of PCB in a natural system, but other forms of biological action will also have significant effect. To get some idea of the behaviour of PCBs in natural systems, we have studied two other types of experiment. These have been called the Ruabon Pond Experiment and the Inveresk Studies.

2. RUABON POND EXPERIMENT

The objective of this experiment was to study the relative degrees of accumulation of different PCB in fish kept in open-air ponds.

Five self-supporting fish ponds were set up at Ruabon, North Wales. Each had a surface area of about 6(metres)^2 and contained about 1000 litres of water. After being stocked with plants and water-snails they were allowed to equilibrate for about two months.
About 100 goldfish and tench were introduced to each pond and, after a settling-in period, about 2g. each of Aroclors 1242, 1254 and 1016 were introduced to three of the ponds.

After a few weeks, measurements showed that the levels of PCB in the fish were around 20 ppm and that the water contained about 20 µg/litre Aroclors 1242 and 1016 and about 15 µg/litre of Aroclor 1254. Unfortunately, most of the fish in all five ponds became infected by a fungus disease and most of them died, so the experiment was abandoned. The results, however, indicated that at these relatively high levels of PCB the fish rapidly acquired a fairly high level of PCB, probably by a physical absorption process from pumping a lot of water through the gills.
We have therefore repeated the experiment with much lower levels of PCB. After emptying the ponds and refilling with water a few times we found levels 0.1 µg/litre of Aroclor 1254 and around 1.0 µg/litre of Aroclors 1242 and 1016. The ponds were restocked with goldfish and the effects of these

levels of PCB on the accumulations have been studied over a period of more than one year. (Slide for Transparency.)

A preliminary interpretation of the results to date suggests that the PCB in the fish at any time consists of a level arising from physical-type absorption and that superimposed on this is a more permanent residue arising from a true accumulation. For Aroclor 1242 there is a rapid rise to about 1 ppm in the fish (wet weight-whole fish) which is followed by a slow rise to about 2 ppm. For Aroclor 1254 the short term level appeared to be <1 ppm and this increased to about 5 ppm after one year.

The accumulation factors thus seem to be as follows:

	Short term	Long term
Aroclor 1242	1000	2000
Aroclor 1254	$<10\,000$	50 000

These data have been derived from packed column g.c. We are currently studying capillary column chromatograms of fish residues and these are showing very interesting pattern changes indicating substantial selective degradation of Aroclor 1242, but only minor changes in Aroclor 1254.

3. INVERESK STUDIES

In these experiments we studied the consumption of PCB in model ecosystems.

Six self-supporting model ecosystems were established (at Inveresk Research International) and, after sufficient equilibration, two had Aroclor 1242 and two had Aroclor 1254 introduced to produce theoretical concentrations of 40 µg/litre of the respective Aroclors in the systems.

The tanks measured 120x30x30 cm, and contained 67.5 litres of water; sediment and detritus covered the base to average depth of 1cm. Clumps of weed were placed at either end of the tanks to provide shelter for the crustacea, molluscs and fish (3-spined sticklebacks (Gasterosteus aculaetur)). The water temperature during the eight week period involved was between 14°C and 16°C.

At the end of the eight week period 10 litres of water were taken from each tank and PCB was extracted into hexane. The tanks were drained and the contents including fish, molluscs, weed, crustacea, mud, algae and tank wall washings were kept for analysis. Thus, estimates were made of the total PCB content of each tank at the end of the period.

The results of g.l.c. analyses using packed columns are shown in the histograms. (Slide for Transparency)

Capillary column chromatograms show considerable pattern changes in all samples from the tanks containing Aroclor 1242 whilst those from the tanks containing Aroclor 1254 show relatively little change.

The results indicate that there appears to be substantial loss of both Aroclors in these model ecosystems. The fact that the Aroclor 1254 is relatively unchanged in composition suggests that ~~relative~~ selective degradation is not responsible for the loss in this case. We do not know the reason for this - it may be inefficient recovery, although the two separate experiments gave very similar percentage recoveries.

For Aroclor 1242, however, the evidence suggests that the loss is due at least in part to biodegradation in the system.

The results also indicate the way in which the two Aroclors are partitioned in the system. The bulk of the residue resides on the mud/sand with weed accounting for most of the remainder. Relatively small amounts remain in the water phase.

Accumulation into the fish seems to be much greater for Aroclor 1254 than for Aroclor 1242.

From measurements of the concentrations in water and fish the accumulation factors are approximately

1 500	for	Aroclor 1242
25 000	for	Aroclor 1254

GENERAL

As a result of these studies and of many reports in the literature we conclude that substantial degradation of low chlorine PCBs occurs even in relatively low temperature aquatic environments.

If PCBs enter the food chain of warm-blooded animals further selective degradation becomes likely.

I would like to conclude with a simple example, presented earlier this year at a conference in the UK.
In this we assume that an animal eats food containing PCB at a level of w ppm and calculate the accumulation.

We assume that the degradation mechanism is a first order reaction - i.e. the rate of degradation is proportional to the quantity. (Slide 6)
If D is the rate constant and R the rate of input, the amount A at equilibrium will be

$$A = R/D$$

(Slide 7) Simple calculation shows that if the animal eats its own weight of food in time T the level of accumulation, neglecting direct excretions will be

$$A = \frac{W}{T}\frac{M}{D} \times 10^{-6}$$

The maximum concentration in the animal will therefore be

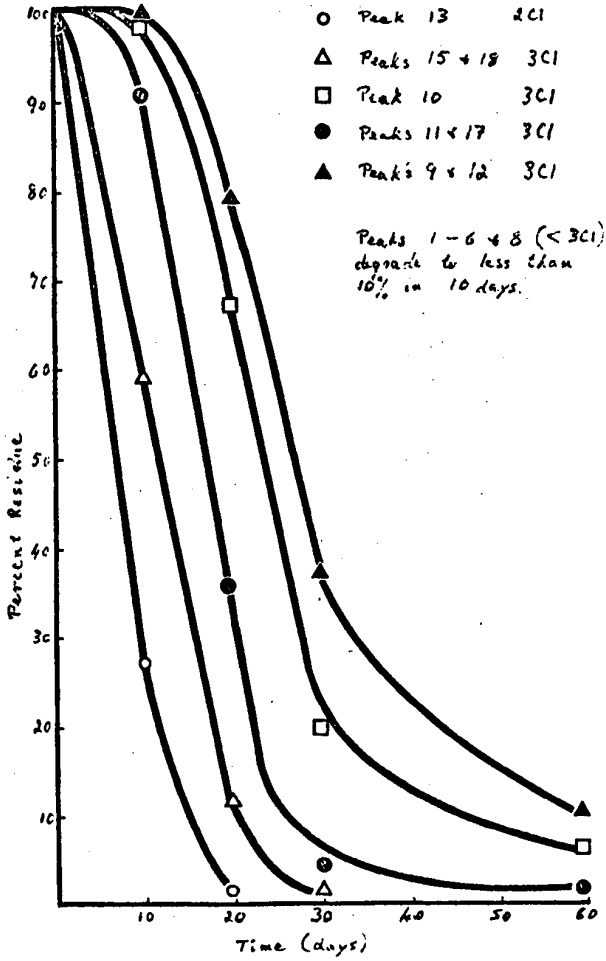
$$C = \frac{W}{TD} \text{ ppm}$$

Using this expression and values of D estimated from our experimental work for the various PCB components in commercial products, I have compared the effects of Aroclor 1242 and 1254 (Slide 9)

Notice particularly that on balance the Aroclor 1242 does not accumulate, in the sense that its concentration in the animal is lower than in the food, and also the trend towards accumulation of the more highly chlorinated components.

If Aroclor 1016 was the contaminant, the 5 and 6 chlorine homologues would be very much lower.

SLIDE 2


Percent Residue
Time (days)
10
20
30
40
50
60
Peak 13 2Cl
Peaks 15 + 18 3Cl
Peak 10 3Cl
Peaks 11 + 17 3Cl
Peak's 9 + 12 3Cl
Peaks 1 – 6 + 8 (< 3Cl) degrade to less than 10% in 10 days.

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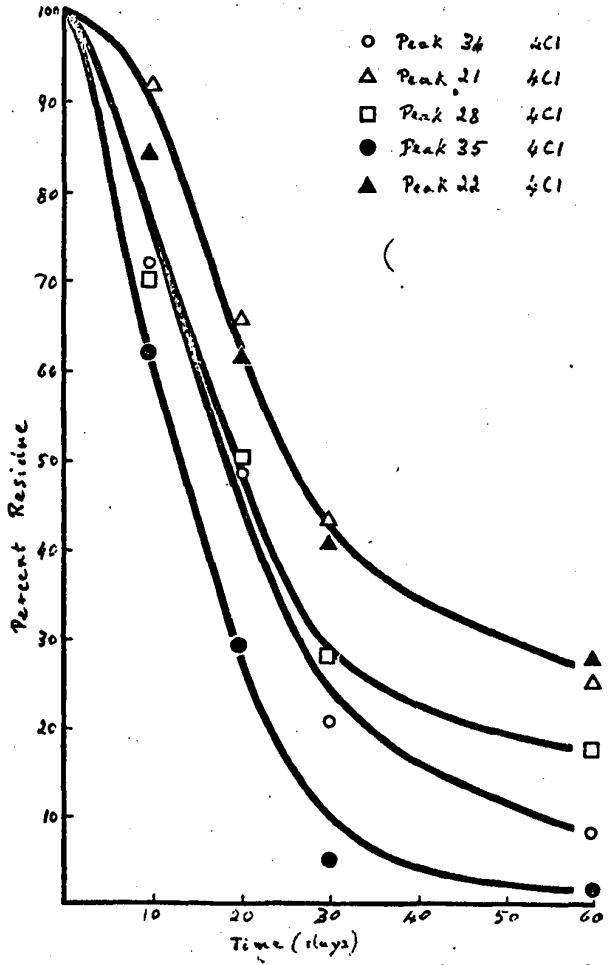
SLIDE 3

~~Fig 4~~



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slide 6

ASKARELS IN THE ENVIRONMENT

BIODEGRADATION

FIRST ORDER REACTION

D = RATE CONSTANT

R = RATE OF INPUT

A = AMOUNT AT EQUILIBRIUM

i.e. $R = DA$

or $A = R/D$

ASKARELS IN THE ENVIRONMENT

$$A = R/D$$

EFFECT OF CONTAMINATION OF FOOD

LEVEL OF CONTAMINATION = W ppm

WEIGHT OF ANIMAL = M

TIME TO CONSUME OWN WEIGHT = T

$$R = \frac{WM}{T} \times 10^{-6}$$

MAXIMUM LEVEL OF ACCUMULATION WILL BE :

$$A = \frac{WM}{TD} \times 10^{-6}$$

i.e. MAXIMUM CONCENTRATION IN ANIMAL ,

$$C = \frac{W}{TD} \text{ ppm}$$

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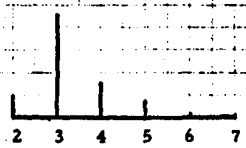
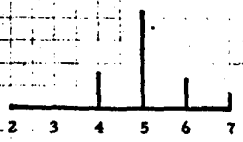
SLIDE 8.

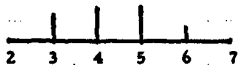
AROCLOR 1242



AROCLOR 1254

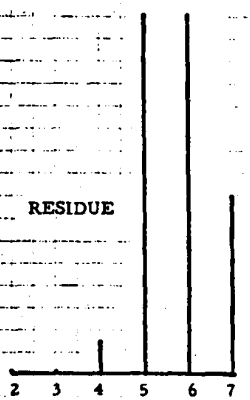


RESIDUE



HOMOLOGUE NUMBER

RESIDUE



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4 FEB 75

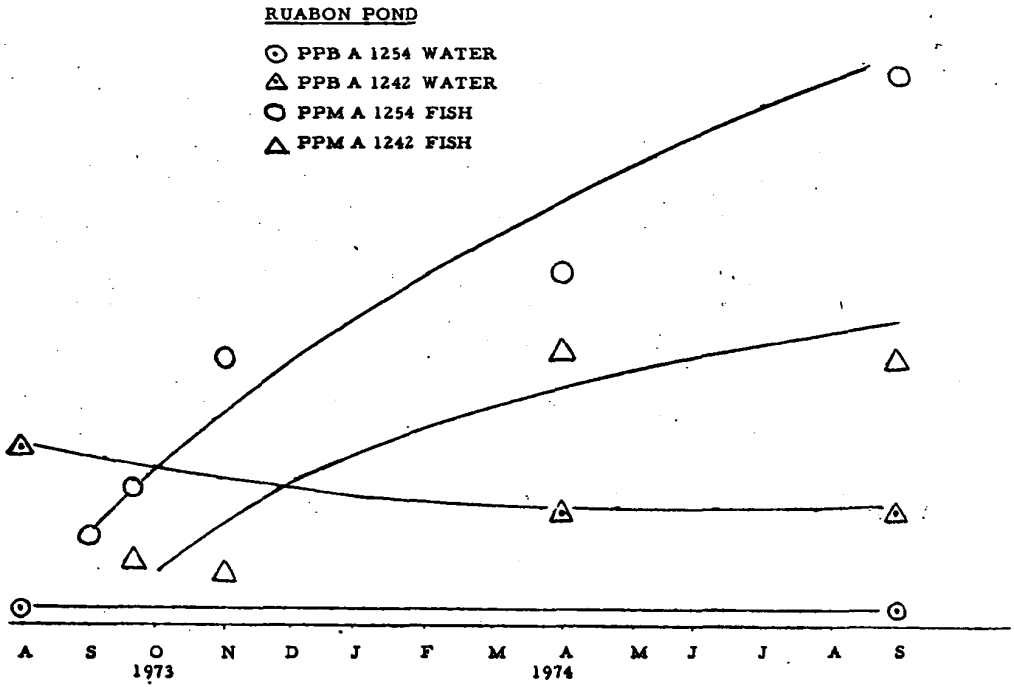

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Table II

Compound	% Degradation/ Days	
	NCIB 10603	NCIB 10643
2,4'-dichlorobiphenyl	70/7	60/73
" + biphenyl	100/7	100/73
4,4'-dichlorobiphenyl	nil /121	50/15
" + biphenyl	nil /121	50/10
2,3-dichlorobiphenyl	67/8	-
" + biphenyl	64/8	-
3,4-dichlorobiphenyl	80/8	-
" + biphenyl	100/8	-
2,3,2'-trichlorobiphenyl	50/7	-
" + biphenyl	95/7	-
2,3',4'-trichlorobiphenyl	94/7	-
" + biphenyl	100/7	-
2,5,4'-trichlorobiphenyl	nil / 73	15/73
" + biphenyl	60/73	60/73
3,4,3'-trichlorobiphenyl	76/12	-
" +biphenyl	70/12	-
2,4,6- trichlorobiphenyl	nil / 12	nil / 84
" + biphenyl	nil / 12	nil / 84
2,4,2',4-tetrachlorobiphenyl	nil / 9	-
" + biphenyl	nil / 9	-
2,4,6,2'-tetrachlorobiphenyl	nil / 9	-
" + biphenyl	nil / 9	-
2,3,4,5,2',3'-hexachlorobiphenyl	nil	-
+ 2,3,2'- and 2,3',4'-trichlorobiphenyl		
" + biphenyl	50/11	-

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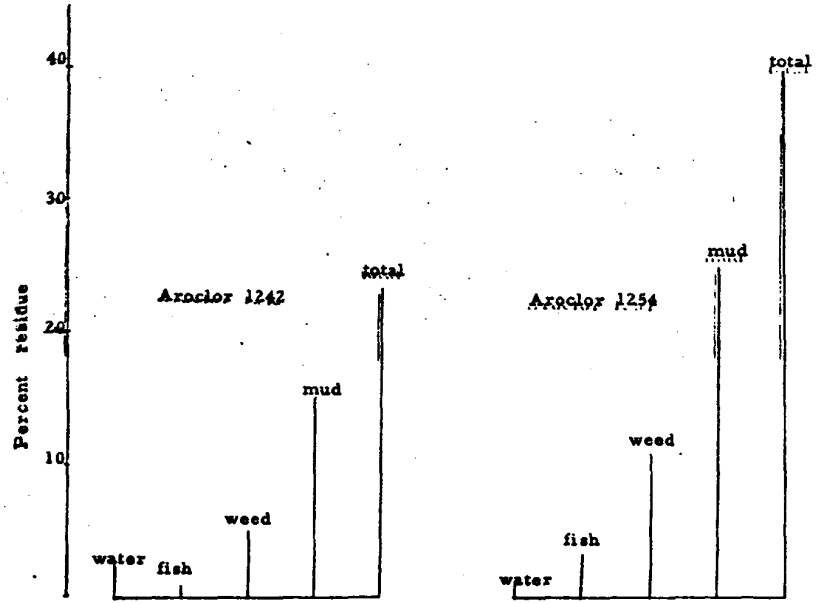
SLIDE 5.

INVERESK STUDIES



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