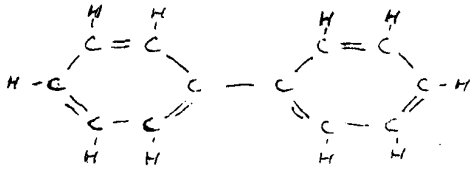
P.C.B.

Biphenyl is an aromatic hydrocarbon consisting of twelve carbon atoms and ten hydrogen atoms. The carbon atoms are arranged in two rings of six each, joined by alternate single and double bonds. The two rings being joined by a bond from a carbon atom of one to a carbon atom of the other. Each of the remaining ten carbon atoms is bonded to a hydrogen atom. The structural formula is:



One or more hydrogen atoms may be substituted by chlorine to form a polychlorinated biphenyl or PCB. Since from one to ten chlorine atoms may be substituted, there are ten homologs possible and for each homolog, of given chlorine number, several different arrangements, or isomers, of the molecule are pos-

MONS 059925

The following table shows the number of isomers theoretically possible for each homolog group, making a total of 210 isomers.

Homologs No. of Cl atoms per biphenyl molecule	0	1	2	3	4	5	6	7	8	9	10
Theoretical number of isomers	1	3	12	24	42	46	42	24	12	3	1

Commercial PCB products, of which Aroclors are examples, are produced by direct chlorination of biphenyl, the degree of chlorination being chosen to provide desired properties. As the degree of chlorination is increased the products vary from mobile ~~liquids~~ to more viscous liquids and finally to waxes and solids. Lubricity ~~fire~~ boiling-point and fire resistance ~~or~~ also increase with increasing chlorination. In all cases, however, the products consist of mixtures of homologs and isomers; ~~and it is~~ indeed many of the desirable functional properties of ~~the materials~~ arise because

they are mixtures. These materials are inert, chemically-resistant and readily soluble in most common organic solvents. They distill in the range 275°C to 450°C and are, in the classical sense, water insoluble.

~~The~~

The most widely used of the series have average chlorine contents of three, five or six chlorine atoms per molecule. Because they have high dielectric strength and dielectric constant and are fire resistant and non flamable they are used to insulate capacitors and transformers. Their thermal stability leads to their use as heat transfer fluids. Good viscosity and lubricity characteristics made them useful as hydraulic fluids and ~~lubricants whilst~~ lubricants, whilst solvent power and compatibility resulted in their selection as plasticisers and solvents for carbonless copying papers.

MONS 059927

All of these uses were reasonable because we had no written

of significant toxicity to ~~[illegible]~~ man or animals except in rare instances of massive & prolonged exposure.

Other fluids have been substituted for PCBs for heat transfer, hydraulics, lubrication and ~~[illegible]~~ plasticizer applications, as solvents in capping and carbonless ~~[illegible]~~ papers ~~[illegible]~~ However, the PCBs have a unique combination of properties which satisfy our needs as capacitor insulating fluids and for transformers where risk of fire must be minimized. No other known materials fill our needs in these areas.

Our present way of ~~[illegible]~~ living depends for its existence on the efficient transmission, ~~[illegible]~~ distribution and use of electrical power. Transformers and capacitors are essential for the last three of these.

MONS 059928

Because large electrical generators are rotating machines, they must operate in a gaseous environment. This limits their output to relatively low voltages, whereas ~~economic~~ efficient transmission over long distances requires high voltages. Electrical step-up transformers are required for this service, but are usually oil-filled since they can be located out-doors and away from people. In some cases, to further improve the efficiency the power is converted to direct current for transmission. This requires the use of large banks of capacitors. Near the point of use the power is converted from direct to alternating current requiring more capacitors.

For local distribution, the power is stepped down to lower voltages at substations which again use oil-filled transformers since they too are ~~out of doors~~ out-doors. Since much of the power

MONS 059929

used is for electric ~~fans~~ motors, which are inductive, capacitors are used to raise the power factor to avoid high line losses. Distribution transformers are often located inside buildings and in crowded areas. Here fire resistance is necessary to minimize the hazard to people. Conversion of electrical power to mechanical power for operating appliances, such as furnace blower motors, refrigerators, air conditioners, pumps for compressed air and to supply water from wells, usually involves capacitor start-run motors. Capacitors are required in fluorescent lights and high powered mercury vapour lamps for street lighting and for many other purposes.

MONS 059930

No ~~other~~ type of fluid other than chlorinated biphenyl with as many chlorine as hydrogen atoms mixed with trichlorbenzene or mixtures of tri and tetra chlorobenzenes gives

a transformer insulating fluid which does not burn or form flammable or explosive gases when an arc is struck within it. Fluids of this type called Askarels ~~[illegible]~~ fulfil a vital safety need where transformers must be located in close ~~[illegible]~~ proximity to people.

It is perhaps less essential that capacitor fluids be fire resistant, but still desirable since failure of a small capacitor could start a fire in a large building with many human occupants. In addition to being fire resistant, PCBs have a higher dielectric constant than other suitable fluids and permit manufacture of smaller capacitors for a given rating which have longer life. Conservation of electrical ~~power~~ energy, ~~through the~~ by using transformers and capacitors in its distribution and use, ~~of electrical fluids~~

MONS 059931

to decreased pollution because of more ~~efficient~~ efficient use of energy converted to electricity.

MONS 059932

In 1966, Jensen[1] demonstrated by mass spectrometry that the unknown substances, appearing with organo chlorine insecticides dau ~~causing interference~~ ~~in the~~ analyses of of environmental ~~wild life~~ specimens ~~for organochlorine insecticides by~~ by gas/liquid chromatography, were PCBs. Since then, considerable analytical evidence, including much from Monsanto Laboratories using ~~for~~ increasingly sophisticated techniques (Jepper) has accumulated in support of the view that PCBs are widespread in nature and may reach levels which are significant in many aquatic animals and ~~[illegible]~~ in some species of fish-eating birds.[2-8] The combination of chemical and physical properties necessary for accumulation through a food chain, principally ~~resistance~~ resistance to oxidation and lipid solubility, are characteristic of the chlorinated biphenyls.

MONS 059933

~~and~~ It is not too surprising that quite low levels in water, perhaps less than 1 part in 10^{10}, can be magnified to more than 1,

in 10^6 when passing through a food chain of aquatic species to predatory birds. The commercial PCB products like Aroclors are not single chemical species, but consist of quite large numbers of homologues and isomers (9), which although similar are not identical in chemical and physical properties. We might expect, therefore, to find variations in the extent to which these various components accumulate in wild-life and, indeed, many of the published data indicate a predominance of certain homologues, principally those containing 5 or 6 chlorine atoms, in wildlife residues. (5, 6, 9, 10)

Aroclors are not particularly toxic to small mammals. Acute oral LD_{50} values for rats range from about 6 to 11 g./Kg. For some marine species dietary toxicity may be more serious; LC_{50} values ranging from 0·3 to 10 p.p.m. have been reported

MONS 059934

for brown shrimp (crangon crangon) (12) and even lower concentrations have been reported to be lethal to the Gulf Shrimp (13). In the present content, where accumulation over long periods may be envisaged, the chronic toxicity of Aroclors is probably more relevant. Feeding trials over periods of two years have indicated that in small mammals (mice and dogs) significant effects are not observed at levels of 1 and 10 ppm in food. At levels of 100 ppm liver enlargement has been noted with more highly chlorinated Aroclors (14). In birds there is evidence that breeding success may be affected by PCBs and feeding trials with Aroclors have indicated the possibility of interference with calcium metabolism leading to thin-shelled eggs and poor hatchability (4, 8, 14, 15) MCNS 059935

Generally, however, direct evidence that the present levels

of PCBs in the environment are biologically harmful has not been established. There is reason for concern, though, that a continued accumulation of PCBs could, eventually generate harmful effects in many species, particularly those near the top of a food chain of aquatic origin.

There have been suggestions that some of the PCB residues have originated by biological or photo-chemical synthesis from other substances present in the environment. It is possible, for example, that DDT can be converted to PCB by such a mechanism (21, 23), although it seems probable that only the 4-4' dichloro-diphenyl would be formed in this way as this is not present in significant quantities in the environment.

MONS 059936

The fear of that unpredictable consequences ~~about~~ might follow indefinite.
accumulation of PCBS in the environment ~~at an ever increasing rate~~ has caused many ecologists to ask how this may be prevented. Some action appears to be necessary, although ~~of~~ opinion may be ~~strongly~~ divided on how drastic that action should be.

A simple solution, apparently, would be ~~to impose a ban against~~ a total withdrawal ~~the future~~ of production and use of PCB products. To be effective, such ~~a legislation~~ as this policy would need to be applied universally and experience shows that ~~international~~ multilateral ~~negotiations~~ agreements for introducing such measures can be long and protracted. Further, the complete withdrawal of these products would

MONS 059937

have serious consequences for some industries and the effects on the ~~national~~ distribution of electrical power for

example could produce serious ~~social~~ problem. It is important to balance the social benefits arising from the continued use of such products against the threats posed by the ~~environm~~ environmental pollution problem. We believe that a satisfactory solution can be achieved by a combination of actions designed to limit the extent to which accumulation can occur, whilst retaining the use of ~~such~~ these products in essential applications. The level ~~Accumulation~~ reached ~~depends~~ depends on ~~occurs because of~~ a combination of factors including resistance to degradation, lipid solubility and rate of input into the ecosystem. The present situation has arisen because the

MONS 059938

rate of degradation of residues is lower than the corresponding rate of input; ~~which~~ the high rate of input was ~~largely~~ due ~~to~~ largely ~~[illegible]~~ to the numerous applications ~~from which supplies have been withdrawn~~ previously discussed & which are not ~~[illegible]~~ regarded as essential.

Degradation may occur in many ways, but the principal

mechanisms affecting the ~~[illegible]~~ environmental situation are probably biological and photo-chemical. Evidence for photo-chemical breakdown of PCBs is scanty, but U.V. photolysis of some highly chlorinated PCBs has been reported. (16). Evidence for the biodegradation of PCBs through enzyme catalysed hydroxylation is, however, ~~[illegible]~~ substantial. Studies of biological degradation arising from exposure of single isomers and commercial mixtures to micro-organism cultures are discussed later & detailed in Appendix. These studies show that biodegradable PCB ~~[illegible]~~ products are feasible & ~~[illegible]~~ and that virtually complete degradation can be achieved in selected products. ~~[illegible]~~ show very substantial degradation. Several authors report the results of feeding PCB products to various animals, coupled with tissue analyses (5, 14, 17, 18) These show substantial metabolism of many of the PCB isomers

MCNS 059939

especially those with 2 and 3 chlorine atoms per molecule. ~~[illegible]~~

The use of products which contain only these less intractable isomers, by increasing the rate of degradation, should reduce the level of residues arising from a given rate of input to the environment. If the rate of input ~~[illegible]~~ is also ~~[illegible]~~ reduced by restricting the applications ~~of~~ to those such as in the Electrical Industry, where tight control can be exercised, there is every prospect that the trend to increasing residues can be reversed and that the level of residues in ~~[illegible]~~ the environment ~~should~~ will fall. Monsanto has already restricted sales of ~~its~~ products to ~~of~~ those applications which are controllable and is (~~planning to supply~~ supplying) more degradable products where they are functionally acceptable. These actions seem appropriate to meet the situation and it is interesting to note that this

MONS 059940

is regarded as ~~very~~ satisfactory and realistic by Government representatives United States (19) and ~~United States~~ in the United Kingdom ~~Government~~ (~~£~~220) [For such a policy to be successful, co-operation between the industries involved is important to ensure that pollution arising ~~etc~~ from manufacturing processes and disposal of wastes is minimised. Some of the steps taken to ensure this are ~~detailed in Appendix~~ discussed in the next section.]

In Sweden, where legislation to control the use of PCBs has been introduced, it is important to realise that although indiscriminate use has been banned, a licensing system permits use in well controlled applications such as ~~the~~ in electrical capacitors. Similar policies are expected to be adopted in Finland, the Netherlands & other countries.

Part of the overall policy for controlling the ~~entry~~ level of PCB in the environment is to establish a system which effectively limits the rate of entry. It has been emphasized that many of the applications for which PCB products were used formerly were, by their nature, allowing most of the product to find its way into the environment, through ~~open~~ effluent, inadequate incineration, and generally, indiscriminate disposal methods. For many of these applications substitute products are now available. For example in plastics, resin adhesives, carbonless papers, hydraulic ~~fluids~~ & heat transfer ~~fluid~~ systems and miscellaneous smaller uses, these products, although desirable, are not essential since alternatives ~~products~~ can be used, sometimes admittedly at some ~~cost~~ penalty in cost/performance and fire hazard. ~~In~~ In some applications effective control over the

MONS 059942

route of leakage to the environment is feasible. Electrical transformers ~~are~~ ~~can~~ ~~example~~, for example, are constructed so that the dielectric/cooling fluid is contained in a steel tank and in operation there is no reason for leakage to occur. In fact, in order to prevent the ingress of water, which ~~would~~ could impair the ~~dielectric~~ electrical properties of the system, they are designed to make leakage very unlikely. They also have a very long life, 20 years or more, and at the end of this period, it is possible to dispose of the fluid ~~can be removed and safely~~ safely. ~~disposed~~ In the event of the fluid becoming damaged through electrical faults in the system the fluid can be removed, reclaimed and re-used in a similar system. The ~~electric~~ application of the product in electrical transformers also happens to be a very essential one, as explosive carbon

MONS 059943

and we see no reason why this application should not continue satisfactorily using relatively intractable PCB fluids, which are necessary to provide the functional & fire resistance properties.

A similar argument can be applied to the application of fluids in large power correction capacitors which are large sealed units which can be kept well controlled. For small capacitors, ~~which~~ some difficulties may be experienced in establishing absolute control since their numbers are relatively large and ~~life~~ average lives much shorter. For such applications ~~the use of~~ we insist that less intractable fluids ~~is~~ like ~~Arodor~~ 1016 ~~is being~~ must be used, so that ~~a~~ ~~[illegible]~~ some leakage can be accepted without the levels of residue building up significantly. Coupled with good

MONS 059944

capacitor manufacturing plant-keeping and reasonably

effective control over the disposal of waste capacitors we consider that the use of PCBs for this application can be allowed to continue.

An important feature of this type of controlled application is that a relatively small number of responsible manufacturers is involved, and this is in fact the case with these two electrical applications.

The concept that an ecologically acceptable PCB product is feasible stemmed originally from the observation that, whereas the case pattern of PCB products covered a very broad spectrum of homologs, the analytical evidence from the literature (5,6,9,10) & Monsanto work indicated that most wild-life PCB residues were concentrated in the penta / hexachloro region. This certainly implied that many of the other dominant isomers in the parent materials were not accumulating.

As part of a broad Monsanto study to elucidate the reasons for this, we have investigated the effects of micro-organisms on PCBs under aerobic conditions.

MONS 059946

Initially our studies were undertaken using activated sludge, taken from one of our biological effluent treatment

isolants, and pre-adapted to degrade (Culture C_1) biphenyl. Although some evidence of degradation of certain single isomers and mixtures was obtained, difficulties were experienced in achieving reproducible results. We were aware that workers at University College, Bangor, N. Wales, had isolated from soil a biphenyl-degrading pure culture, reported to be a nocardioform of the order actinomycetes. (Culture C2) The Bangor workers had studied the breakdown mechanism for biphenyl, using this culture and had demonstrated the metabolic pathway (21). Details of this have been included in Appendix 2.

Using this culture for degrading single isomers of chloro-biphenyls, we were able to establish a pattern of degradation broadly agreeing with the metabolic mechanism proposed by the Bangor workers for biphenyl.

Subsequently the Bangor workers isolated another biphenyl degrading pure culture from a canal mud. (Culture C3) This was reported as being of the

MONS 059947

pseudonomas family. The metabolic route for ~~this~~ degradation by ~~this~~ organism was ~~found~~ shown to be different from that of the ~~to~~ earlier culture. Subsequent studies of the degradation of chlorobiphenyl isomers ~~were~~ ~~showed~~ showed broadly ~~in~~ agreement with ~~this~~ proposed metabolic pathway and it was ~~[illegible]~~ demonstrated ~~[illegible]~~ that ~~a~~ ~~great~~ most ~~[illegible]~~ of the lower chlorine isomers of PCBS (< hexa) were susceptible ~~could~~ to degradation by ~~either~~ one or other of these micro-organism culture.

~~[illegible]~~ When commercial mixtures of isomers were subjected to attack by these pure cultures ~~it was established that~~ the analytical results indicated ~~that a~~ a different pattern of degradation ~~was emerging~~ than ~~[illegible]~~ ~~that~~ might have been predicted from the studies of single isomers. For example, the isomer

MONS 059948

44' dichlorobiphenyl was not degraded by culture C3 although it was degraded by culture B3 in agreement with the

proposed pathways. In admixture with other isomers, as in Aroclor 1242, however, the 4-4' dichlorobiphenyl was degraded by both cultures independently. This implied that in the presence of suitable levels of ~~[illegible]~~ ~~[illegible]~~ degradable isomers the organism could adapt to utilise some at least of the more intractable isomers as carbon sources. Certain isomer mixtures, of practical significance, such as Aroclor 1016, were prime targets of this study and the results indicated virtually complete degradation of this particular product with these two organisms. For Aroclor 1242, very substantial degradation of the significant isomers has been demonstrated and the evidence ~~[illegible]~~ suggests that ~~[illegible]~~ some of the more highly chlorinated penta + hexa chloro isomers in 1242 can also be degraded ~~in Aroclor 1242~~ through adaptation. More evidence for ~~this~~ is being sought in current experiments

MONS 059949

in which the more highly chlorinated components are being accentuated to establish better data.

In the work on single isomers it was established that the rates of degradation could be accelerated by including biphenyl itself with the isomer under test. The reasons for this have not been established, but one suggestion is that a mechanism of co-oxidation may be responsible (24). Most of the work done so far has therefore included biphenyl in the study and this does raise the question whether the conditions are too artificial for extrapolation to the natural environment. For single isomers, this probably would be a valid criticism, although nature is well endowed with organic chemical structures not unlike that of biphenyl (25), which could induce similar mechanisms for degradation.

MONS 059950

For mixtures like Aroclor 1016, however, the adaptive mechanism which has been observed for both cultures C_2 and C_3 would probably ensure that ~~the composition~~ adequate nutrient could be derived from the PCB products. Experimentation to confirm this point is currently in progress. It ~~is~~ should be understood that degradation has clearly been demonstrated even in the absence of biphenyl; under the laboratory conditions, lag times are observed with biphenyl present.

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MONS 059952

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MONS 059953

Appendix C.

The ~~study~~

Degradation of Polychlorinated Biphenyls by Micro-organisms.

The fate of PCBs in the environment is of considerable ~~importance~~ interest to ecologists. Among the various natural mechanisms for degrading organic materials, a significant contribution may be expected from the many micro-organisms which abound. As part of a broad study designed to investigate the probable causes for the apparent distribution of PCBs in ~~the~~ the environment we have studied the effects of selected micro-organism cultures on both single isomers and commercial mixtures of PCBs.

The basic experimental procedure consists of shaking prepared substrates comprising PCBs, mineral solution ~~as~~

MONS 059954

inocula, inhibitors, etc for varying periods of time and then determining the loss of PCB by GLC analysis of extracts. In this work only primary degradation of PCBs has been measured and we have not attempted to identify many of the products of the metabolic processes involved. Most of this work was done with PCB compounds or mixtures present at a level of 5 p.p.m. Solutions were prepared in diethyl ether at 100 p.p.m and 5 ml aliquots were introduced into 250 ml culture flasks (B24 Quickfit Erlenmeyer flasks) and the ether evaporated by a stream of dry nitrogen without external heating. For each flask 100 ml of Since preliminary experiments indicated that the rates of degradation could be

MCNS 059955

increased by the addition of biphenyl, most of the experiments described have included this. 5 ml aliquots of ~~100 ppm~~ di-ethyl ether containing 1000 p.p.m biphenyl were added to the ~~flasks~~ flasks with the PCB before evaporation. To each flask was then added 100 ml of appropriate culture solution. ~~containing nutrient~~ We have demonstrated that mercuric chloride was an effective inhibitor for the micro organisms used and this was included at 100 ppm in a number of experiments for control purposes. ~~After stocking~~ at Flasks were shaken at 100 to 120 c.p.m for periods up to 100 days. During this time the flasks were stoppered, but vented at 3-4 day intervals to ensure aerobic conditions.

MONS 059956

Since experiments had shown that sampling of aliquots led to inaccurate results, probably due to absorption effects, the total contents of each flask were used for analysis. Residual PCBs were extracted with n-Heptane following a set procedure to avoid losses. ~~This procedure is~~ 20 ml of n-Heptane shaken with liquid in culture flask, transfer to 200 ml separating funnel, wash stopper and flask ~~mouth~~ mouth with n-Heptane. Allow layers to separate, ~~run~~ run aqueous layer back to culture flask and solvent layer to 100 ml ~~measuring cylinder~~ volumetric flask. Repeat to give four x 20 ml. extracts and make ~~up~~ volumetric flask to mark with n-Heptane. This is then submitted for GLC analysis, details of which have been described separately (2,5).

MONS 059957

Some early experiments were made using activated sludge inoculum, from the biological effluent treatment plant at Ruabon N. Wales, pre-adapted to degrade biphenyl. The experimental procedures were developed during this work and some degradation of PCBs was observed, but most of the results discussed here were from experiments using specific biphenyl degrading cultures isolated by Evans & Leant (21). Two such cultures have been investigated for the degradation of PCBs. These are a mycobacterium of the order actinomycetes isolated from a soil sample from the Ruabon (Culture C_2) and are isolated from canal mud sample (U.K.) and reported to be of the pseudomonas family (Culture C_3)

MONS 059958

Evans and Hunt have described studies of the microbial attack by these cultures on biphenyl and have suggested the ~~following~~ metabolic routes shown in fig 1. ~~[illegible]~~

Stocks of active ~~age~~ organisms (C_2 and C_3), received from Professor Evans, have been prepared and maintained according to his recommendations. A proposed growth medium (Table 1) was inoculated with the culture and the mixture aerated continuously in the dark at a temperature of 25°C using scrubbed & filtered air. Inocula for subsequent experimental substrates were withdrawn after stopping the air flow for a brief time to allow excess biphenyl to settle. ~~When~~ The media were prepared in 15 litre quantities, as prepared the pH was ~~the~~ about 5·8, but was brought to

7 by addition of NaOH solution before introducing the inoculum. When only relatively small volumes of stock culture (one or two litres) were removed for experiments, the bottle was replenished by addition of an equal volume of solution containing the inorganic constituents of the growth medium. For larger quantities the practice was adopted of starting a fresh culture.

Table 1 Media for Culture of Biphenyl-Degrading Organisms

Constituent	Gm. per litre
$(NH_4)_2 SO_4$	1.0
$KH_2 PO_4$	1.0
$Mg SO_4 . 7 H_2 O$	0.5
$Fe SO_4$	0.05
Biphenyl	1.0

MONS 059960

Results.

A number of single isomers and simple mixtures have been studied in contact with cultures C_2 and C_3, mostly with C_2. Packed column GLC (26) has been used to measure the loss of P.C.B. The results are summarised in Table 2.

~~following table 2.~~ TABLE 2

Isomer	Culture	With or without Biphenyl	Approximate Time for Disappearance to 50%.
2,4'-dichloro-	C_2	With	5 days
	C_2	Without	2 days
4,4'-dichloro	C_2	with	> 50 days
	C_2	without	> 50 days
	C_3	with	< 20 days
	C_3	without	< 15 days
2,3-dichloro-	C_2	with	4 days
		without	4 days
3,4-dichloro	C_2	with	2 days
		without	3 days

MONS 059961

2,3,2'- trichloro-	C_2	with	3 days.
		without	7 days
2,3',4'- trichloro-	C_2	with	< 2 days
		without	3 days
3,3',4'- trichloro-	C_2	with	5 days
		without	6 days
2,4,6 - trichloro	C_2	with	> 50 da
		without	> 50 d
2,2',4,4'- tetrachloro-	C_2	with	> 50 day
		without	> 50 day
2,2',4,6,- tetrachloro-	C_2	with	> 50 da
		without	> 50 day
2,3',4',5',2,6 - hexachloro-*	C_2	with	< 1 da
		without	> 50 day

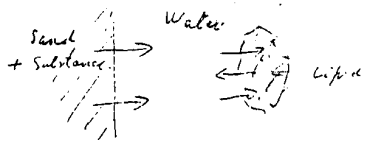
* Mixed with 2,3,2' and 2,3',4',- trichloro-biphenyls to improve solubility.

MONS 059962

PCB

Several commercial mixtures have also been studied in contrast with cultures C_2 and C_3. Since only a few single isomers were available for this study it was hoped that investigations of the commercial mixtures, employed with high resolution GLC, would extend the range of our knowledge very considerably. In order to obtain adequate resolution, capillary column [200 feet S/S 0.030" bore (ex Phase Sep.) coated with Apiezon L] / Electron Capture detection was employed. Identification of many of the isomers separated by the capillary column was possible using the methods developed by Sissons & Welti (9). Results for two commercial mixtures Aroclor 1242 and Aroclor 1016 are summarized in Table 3.

MONS 059963



Let C_{W_0} & C_{L_0} be saturation concentrations in water
& C_W & C_L " concentration at time t

$$\frac{dC_W}{dt} = \alpha(C_{W_0} - C_W) + \beta\left(C_L - \frac{C_{L_0}}{C_{W_0}} C_W\right)$$

$$\frac{dC_L}{dt} = \gamma(C_{L_0} - C_L) + \delta\left(\frac{C_{L_0}}{C_{W_0}} C_W - C_L\right) - \varphi C_L$$

where α = coeff of desorption from sand.
& β γ & δ are coeffs for lipid/water exchange
& φ = rate constant for degradation in lipid
Let C_F be concentration in fish.

$$\frac{dC_F}{dt} = R C_L - \psi C_F$$

where R = rate of consumption of lipid
ψ = rate constant for degradation in fish.

MONS 059964

Further Work

One of the lessons ~~learnt~~ learnt from the PCB problem is that ~~it may not always be possible to~~ assessment ~~the~~ is difficult and time consuming. There would be obvious advantages in being able to assess quickly the probable effects of introducing chemicals into the environment ~~either~~ whether by intent or by accident. In the case of PCB products then it still a need for a good method of assessing the probable outcome of the actions indicated by Monsanto; ~~for~~ for new products it still more doing need exists.

~~Whether~~ Whether a chemical leaves an environmental problem depends on many factors including water and lipid

solubilities, volatility, ~~oxidation~~ oxidation stability, and toxicity... Whilst all these factors can be studied independently, the final interpretation of the effect of ~~disp~~ disposal into the environment is difficult and some integrated measure of effect would be much more valuable. For many chemicals, including PCBs, the aquatic environment is finally the ultimate accumulation sink. A study of accumulation in an aquatic system therefore be a useful indicator. Metcalf et al. ( ) have described such a system using a small aquarium as model ecosystem to study the fate of radiolabelled pesticides. ~~Such~~ This alternative approach would be to use a small pond in which fish at the tip of the food chain ~~were~~ used as indicators of accumulation

MONS 059966

of residues. In practice a series of ponds could be used to compare the effects of different compounds. For example, ~~the effect of~~ ~~new Aroclor products~~ Aroclor 1016 could be compared with ~~existing~~ Aroclors 1242 and 1254 and the results used to predict more accurately their behaviour in the natural environment. It should also be possible to set up mathematical models ~~of~~ for the experimental ~~system~~ and natural systems and to predict the private changes in the environment to be expected from the actions initiated by Monsanto.

A simple model for predicting the residue levels of ~~the~~ various PCB homologues might be set up as follows. Assume that the total quantity of a homologue present in the ~~[illegible]~~

global ecosystem ~~it~~ the nth day is C_n. ~~then~~ The amount present on the $(n-1)^{th}$ day would have been C_{n-1} and ~~then~~ $C_n = C_{n-1} + r - C_{n-1}(d)$, where r is the daily rate of input and d is the daily degradation rate. Since $C_n = C_{n-1}$ when $C_{n-1} = \frac{r}{d}$, the equilibrium level will be simply $C_n = r/d$, and as the ~~time~~ approach to ~~equilibrium~~ this level will be exponential ~~function~~ with a time constant proportional to $1/d$. For the work on degradation by micro-organisms it is possible to assign some values to d and from the annual production figures and a knowledge of the temperature distributions it is possible to put in some numbers and calculate the ~~residue~~ levels of various hydrocarbons in

MONS 059968

be expected for various situations. Thus of the total PCB residue arising from the 1969 pattern of production and sales is assumed to be 100, the distribution for homologues 2 3 4 and >5 would be as follows

Homologue:	2	3	4	>5	Total
	1.5	5	13	80	100

Whereas following the proposed pattern of production and sales for 1972 the residue pattern would level out at

Homologue:	2	3	4	>5	Total
	1.5	5	9.5	24	40

These are relative levels assuming only bacterial degradation ~~specific effects~~ and a uniform distribution of the product in the environment. For more specific environments, like fish and birds higher up the food chains, different patterns would emerge and models appropriate to such

MONS 059969

situations are being examined.

MONS 059970

The actions taken to cut introduction of PCBs into the environment to a minimum are the following:

1) Monsanto decided to sell PCB containing products only for those uses where two requirements were met:

a) There was no technically feasible substitute.

b) The use was such that the product did not escape into the environment.

Uses which met these requirements were those as an impregnant in capacitors, as a transformer insulating and cooling fluid and a small group of high temperature heat transfer fluid applications. In all instances, the fluid is contained in a closed system. In the case of the electrical uses the containers are sealed and the life of the device is expected to be about 25 years. Larger capacitors and transformers are owned by public utilities

MONS 059971

and industrial concerns who could be expected to see to it that any accidental losses from failed or broken units would be recovered and disposed of without environmental pollution.

This single action cut the total use of PCBs by 50%. However, it eliminated those uses which permitted the product to escape into the environment. The company has now restricted sales for electrical uses only and to make certain that PCBs are not used in heat transfer systems which, if accidental leakage took place, might introduce PCBs either directly or indirectly into food products. MONS 059972

2) Since there is a considerable amount of experimental evidence (Reference) showing that the five, six and higher chlorine containing biphenyls degrade much more slowly than those containing the

chlorine, Monsanto has altered the composition of the fluid it sells for capacitor impregnation to cut the concentration of these to a minimum. For many years, the standard fluid for capacitor impregnation had been Aroclor 1242. This fluid has, on the average, three chlorine atoms per molecule. However, as can be seen from the table below, it contains both higher and lower homologs. In particular, it contains nearly seven percent of five chlorine and higher homologs.

Homolog Content of Aroclors 1242 and 1016

	1242	1016
Biphenyl	0.02	0.02
Monochlorobiphenyl	0.72	0.93
Dichlorobiphenyl	15.6	19.4
Trichlorobiphenyl	54.5	64.5
Tetrachlorobiphenyl	22.5	15.0
Penta & higher	6.77	0.16

Aroclor 1016, the sole fluid now sold for capacitor impregnation, contains only a few tenths of a percent of these persistent homologs. The maximum limit has been set at four tenths percent.

MONS 059973

The amount of persistent material in fluid sold for capacitor impregnation has therefore been cut by a factor of 15 to to 30.
(Give biodegradation data in similar form and cite complete data)

3) Monsanto has instituted stringent procedures in its own plants to eliminate losses during manufacture and handling of PCBs. It has discontinued their use for heat transfer and hydraulic use. Effluent from the plant now contains less than 85 ppb.

4) The company has worked to [illegible] its customers so that they will be aware of the need to prevent escape of PCBs into the environment. Several means are being used for this purpose.

One of these has been direct consultation with each user to explain the problem. Monsanto salesmen serve as consultants to our customers on methods for reducing losses. Customers with the necessary facilities to recover them out are given Monsanto analytical procedures. Samples are analyzed in the company analytical research laboratory for those not equipped to do their own analyses. Personnel of the laboratory serve as consultants for those doing their own.

Monsanto and the National Association of Electrical Manufacturers ~~[illegible]~~ joined in recommending the formation of ~~an~~ American National Standards Institute Committee C-[illegible] to standardize proper [illegible]

for handling PCB fluids in the electrical industry. The membership of the committee includes representatives from national groups concerned with the manufacturing, use and disposal of capacitors and transformers and with groups representing government and the public.

5) PCB fluids used in the electrical industry frequently become contaminated to the point that the users cannot readily reclaim them. Formerly, these would have been discarded. Now facilities are set up to reclaim several million pounds of material per year have been set up by Monsanto.

MONS 059976

4) Some of the ~~contaminated~~ fluid is so badly contaminated, that is, it is contaminated with impurities which cannot be removed by any presently available method that it must be destroyed. Monsanto has therefore installed an incinerator capable of burning ten million pounds of fluid per year. Waste products from this operation are free from unburned PCBs. To produce this result requires special equipment designed to expose the product to much higher temperatures for longer times than ordinary incineration equipment. The company accepts waste PCB fluid for incineration charging a fee which roughly covers the cost.

Experiments to determine the feasibility of incinerating solid waste containing PCBs have been run. Results indicated that it would be [illegible]. To date no such facilities have been provided.

7) For the present, it is recommended that solid waste containing PCBs be buried in sanitary land fills not adjacent to water. This recommendation is based on evidence from a long term test which shows that the rate of migration through soil is very low.

MONS 059978

We demonstrated that sampling of aliquots ~~for analysis~~ could lead to ~~inaccurate~~ inaccurate results, probably through absorption effects, and therefore used total contents of each flask for analysis. Residual PCBs were extracted with n-pentane plus small quantities of ethyl alcohol to break emulsions formed in the presence of inoculum. 4 x 20 ml pentane extractions were used to ensure total recovery and made up to 100ml ready for analysis, the details of which are described separately (26)

MONS 059979

(29)

Table 3

The results of the work reported here indicate quite clearly that most, if not all, of the lower chlorinated isomers of PCBs can be degraded by enzyme hydroxylation induced by micro-organisms. The ~~studies of~~ results with single isomers seem to support the work of Evans & Faust (21) and their suggested mechanism for biphenyl degradation with the specific organisms which they isolated. It seems reasonable to explain our findings in terms of chlorine substitution interfering with the hydroxylation steps or subsequent ring opening stages. This kind of theory would indicate that the culture C_2 would not degrade 4,4'-dichlorbiphenyl, whereas culture C_3 could. It also suggests that C_2 could degrade 2',3',4',5',2,6,-hexachlor

MONS 059981

biphenyl. These indications were supported by the experiment results obtained with single isomers and simple mixtures. The conclusion to be reached from these results, coupled with the proposed mechanisms of Evans & Dant, is that the ~~only~~ intractable low chlorine isomers (<5 cl) of PCBs would be ~~[illegible]~~ those ~~[illegible]~~ chlorinated in the 2, 6 positions on one ring, ~~chlorinated~~ and the 2, 5, 2', 5' and 3, 5, 3', 5' tetrachloro biphenyls. ~~The~~ The total number of intractable low chlorine isomers ~~[illegible]~~ would, on this basis, be 20 out of a theoretical ~~[illegible]~~ total of 82.

When commercial mixtures of PCBs are exposed to these biphenyl-degrading cultures a somewhat different pattern of degradation appears to emerge. The most noticable

feature is that many of the low chlorine isomers which appeared to be intractable when present alone, degrade comparatively readily when present in the mixture. Thus 4-4' dichlorobiphenyl degrades to 50% in approximately 2 days when ~~present~~ exposed to calcium C_2 as a component of Aroclor 1016 or Aroclor 1248. The general conclusion from the study of these commercial mixtures is that all ~~significant~~ isomers present in significant amounts in Aroclor 1016 degrade with ~~rate~~ time constants (at 25°C) ~~comparable~~ of less than 20 days and that in Aroclor 1242 a small percentage, consisting of more highly chlorinated homologs, degrades more slowly, probably with some time constants exceeding 50 days.

MONS 059983

Whilst it is not possible from our studies to give a detailed explanation of all the results, the differences between the single isomers and mixtures do suggest that ~~enantiomeric~~ adaptation of these organisms is possible when exposed to a range ~~of~~ of materials having a structurally related emulsion.

MONS 059984