PCBs - The Environmental Problem.

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Introduction

The presence of polychlorinated biphenyls* (PCBs) in wild-life specimens was first demonstrated in 1966 by Jensen (1), who identified the unknown peaks, interfering with GLC chromatograms in the analysis for organo-chlorine insecticides in bird-tissues, as chlorinated biphenyls. Since then a considerable amount of analytical evidence has been accumulated to support the view that PCB's exist in the environment over extensive regions of the earth in amounts which are comparable in magnitude with those of insecticides.

Two features common to both organo-chlorine insecticides and the PCBs being found in nature are that they are persistent and accumulate in oil and fat so that the highest levels are found in fatty tissues of birds and in the blubber of certain marine animals. One noticeable difference is that, whereas insecticides are found in significant quantities in nearly all species of animal and plant life, significant amounts of PCBs are usually associated with the marine or aquatic environments. Thus the highest levels of PCBs have been found in fish-eating birds and in marine mammals. (2) (3)

Not all PCBs are found in wild-life; the chromatograms usually reported suggest that homologues containing 5 or 6 chlorine atoms are the most common. It is often claimed that the closest match for the chromatograms of wild-life extracts is that obtained from commercial products corresponding to 50-54% chlorine.

* Biphenyl is synonymous with diphenyl.

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Persistence and Toxicity

The principal cause of concern, amongst conservationists and ecologists, about polychlorinated biphenyls and organo-chlorine insecticides is that they are very stable chemical compounds. They are resistant to degradation by oxidation both chemically and biologically. Clearly, if the rate of dispersal of these materials into the environment is greater than the rate of degradation, there will be accumulation. The combination of persistence and accumulation in fat during transition through a food chain can result in considerable increases in concentration of these compounds; it is quite possible that a very low level of perhaps 1 part in 10^{11} in water can be concentrated through a food-chain of marine or aquatic species, to levels of about 1 part in 10^{5}, which are sometimes observed in the organs of fish-eating birds.

The toxicity of these compounds is relevant since the level which can be accepted will obviously depend upon this. It is perhaps worth making the point here that practically all chemical compounds are toxic to some extent so that any persistent compound would eventually become a toxic hazard. Compounds of relatively high toxicity, which are degraded in the environment, do not necessarily pose ecological hazards. The acute toxicity of polychlorinated biphenyls to rats has been determined and, for example the acute LD_{50} value for a commercial product containing 42% chlorine is about 4 ml./kg. In the present context, however, the chronic effect of continued assimilation is probably more pertinent. The difference in sensitivity of different species makes generalisation impossible, but published information suggests that the chronic toxicity of PCBs is one or two orders of magnitude less than that of DDT. For small mammals, feeding trials indicate that at levels of 1 - 10 ppm in feedstuff no significant toxic effect is observed, but at 100 ppm there are indications of some long term effects. Published work also suggests that, as with organo-chlorine insecticides, PCBs affect the breeding success of birds.(4) Some marine animals, such as shrimp, are sensitive to PCBs but again, the toxicity of insecticides is known to be much higher.(5)

Thus, although it may be argued that there is no immediate cause for alarm, sufficient evidence exists to cause disquiet amongst ecologists and conservationists. It is clear that continued accumulation of persistent compounds like PCBs and organochlorine insecticides cannot be allowed, and means must be found to check the increasing pollution of the environment.

One of the problems arising in any discussion of PCBs in the environment stems from the large number of homologues and isomers which are possible. The commercial products, in fact, contain large numbers of these in varying proportions. These different homologues and isomers may have different properties. For example, since the lower chlorinated compounds are rarely found in wild-life specimens, it is suggested that these are degraded more rapidly than the more highly chlorinated species such as the penta- and hexa-chlorinated biphenyls. The mixture of PCBs eventually found in a wild-life specimen may therefore be very different from that initially fed into the ecosystem. Thus, although claims to have detected, in wildlife, significant quantities of commercial products containing 42% chlorine are rare, it is not prudent to assume that these products are completely acceptable. On the other hand, polychlorinated biphenyls containing five and six chlorine atoms, such as are present in transformer askarels, have definitely been indicted as environmental pollutants.

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Analysis

Because of the need to measure PCBs at extremely low levels (often 1 part in 10^7 or less) the analytical method must be both specific and highly sensitive. For this reason gas chromatography using electron capture detection has been universally chosen with occasional identification and structure confirmation by gas chromatography mass spectrometry.

Analytical methods vary in detail between laboratories depending upon specific requirements, e.g. plant pollution control, analysis of wildlife samples etc. but essentially the method consists of the following steps:-

1. Sample Preparation
2. Extraction of PCBs.
3. Removal of interferences
4. Concentration
5. Gas Chromatography and Measurement

In general, it is found that wildlife samples, being more complex, require more extensive pretreatment than, for example, plant effluent and for this reason analysis of the latter will be described to illustrate the basic analytical method.

The PCBs are extracted from the aqueous sample by shaking with hexane and it is possible at this stage to introduce a concentration step by using a high ratio of sample to solvent, e.g. 500 ml. water to 100 ml. solvent. After two extractions the solvent is reduced to 2-5 ml. by evaporation on a steam bath and it is then passed through an alumina column with hexane as solvent to remove interfering non-PCB materials. The first 150 ml. of the hexane which elutes is collected from the column and this is evaporated to a small known volume. This solution is used for gas chromatography.

Separation by gas chromatography involves passing the sample in an inert carrier gas through a column packed with a material which will selectively retain components of the sample for limited periods. Components elute from the column at periodic intervals and are detected using properties which differentiate the components from the carrier gas.

There are many detectors in use in gas chromatography but for PCB analysis it is only possible to use the electron capture detector. This is based upon the fact that certain compounds will abstract electrons from an artificially produced plasma (radioactive source). Reduction in electron concentration (base current) is a function of component concentration and can be measured with a suitable amplifier.

Details of the gas chromatographic system used by Monsanto are available as an appendix to the paper plus an illustrative chromatogram.

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Measurement of the PCB content from the gas chromatogram for plant effluent is generally a simple procedure - the chromatogram of the sample is compared with chromatograms of standard samples made up from known PCBs and, for accurate analysis, calibration graphs can be prepared from specific peaks in the standard samples.

In the case of environmental samples however, it is more difficult to obtain accurate measurement of PCB content because in many of these samples degradation has occurred changing the chromatogram so that measurement by peak comparison is less reliable. However, the experimental error, although greater than that in the analysis of plant samples is still acceptable for the study of PCB levels in the environment.

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Pollution Control

It is clear that, if products containing PCBs are to continue to be used in industry, positive effort must be made to control and prevent pollution by these products.

Since the most significant levels of polychlorinated biphenyls are found in species associated with the marine or aquatic environment, the highest priority should be given to preventing pollution of sewers and waterways. Atmospheric pollution must also be avoided because PCBs, washed out by rainwater, may again end up in rivers and sea.

The manufacturers of these products have a clear responsibility to prevent pollution at the manufacturing sites. Fortunately the process itself is "dry", so that aqueous effluent is not a by-product. Provided that sufficient care is taken to contain spillages and leakages during manufacturing and handling, pollution of drains and waterways can be avoided. Experience has shown, however, that it is necessary to study all aspects of the process, including drumming and tanker-loading facilities, with particular emphasis on the possibilities of leakages and spillages reaching surface-water drains. Where any chance exists of this happening, sumps or interceptor pits must be installed in the drainage system. It has also been found helpful to institute regular monitoring of plant effluent, using analytical techniques similar to those described previously, to ensure that the instructions relating to the control of pollution are being observed. Atmospheric pollution at the manufacturing site is not a serious problem, since the process is designed to avoid losses, but, again, good plant-keeping is essential to prevent accidental loss.

Close attention to detail and good plant-keeping or house-keeping practices are the main keys to pollution control and prevention at plants which use PCBs. Facilities should be provided so that spills and leakages cannot run or be washed away to surface or effluent drains. Sumps or interceptor pits should be incorporated in any areas where these products can spill or leak.

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Waste Disposal

It is clear that P.C.B. wastes should never be disposed of deliberately down effluent drains or sewers and that the utmost care should be exercised to prevent this happening accidentally.

In industry, PCBs may be present in waste materials occurring as liquids or solids. In the case of liquids, consideration should first be given to reclaiming. Some manufacturers offer a reclaim service whilst others can refer users to specialist organisations who will do this. Two basic methods of disposal of waste products exist. These are dry tipping and incineration. In the case of PCBs, incineration should only be carried out under the correct conditions. In order to break down the PCB molecules thermally a minimum temperature of 800°C is necessary. At this temperature a residence time of not less than 10 seconds will be required. At higher temperatures, shorter residence times may be acceptable. Open hearth incinerators are not suitable for this operation and their use would serve only to volatilise the material and pollute the atmosphere. With suitably designed closed tube incinerators, however, incineration provides a good method for the destruction and disposal of PCBs. Since hydrogen chloride is one of the breakdown products, the effluent gases should be scrubbed with water which can then be discharged to a lime tank. Liquid wastes can readily be handled by incineration, provided that heating is available on the feed system to achieve pumping consistency. The major problem associated with such wastes probably concerns storage, collection and transport to the incinerator site.

For solid wastes the problem is rather more complex, and, at present, it is thought that a two-stage process offers the most hopeful solution. The first stage would consist of a rotary kiln furnace, operating at below 800°C, to volatilise the PCB. This would then pass to the second stage for combustion at 1200°C or so.

Dry tipping, and subsequent covering with earth at an approved site, offers a temporary expedient for dealing with PCB wastes. Although probably not acceptable as a permanent solution it is certainly better than indiscriminate dispersal of such products into drains, waterways and the atmosphere. Owing to its low solubility in water, askarels will be leached out only very slowly from a dry site, by rainwater, so contamination of streams and rivers from such sources will be slight. Tests carried out on stagnant water in close proximity to such a site indicated very low (< 4 parts in 10^9) levels of PCB. It is also known that soil normally contains multitudes of bacteria, some of which may be active against the lower homologues of PCBs, so that over very long periods of time significant degradation may occur. In these circumstances the delay imposed on the passage of the PCB materials into the aquatic environment may in fact provide a more permanent solution to the problem than might be expected. Nevertheless dry tipping should be regardedas a temporary measure which should be abandoned when facilities for proper incineration have been organised.

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LC_{50} (PCB) = 0.3 ppm.
LC_{50} (DDT) = 0.003 ppm.

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APPENDIX

GAS CHROMATOGRAPHIC ANALYSIS OF A POLYCHLORINATED BIPHENYL CONTAINING 42% CHLORINE

Instrument	Hewlett-Packard 402 gas chromatograph
Column	6 ft. of 6 mm. O.D. glass U-Bend column containing 3% OV-225 on chromosorb W HP.
Column Temperature	195°C
Gas Flow	60 mls/min. 95% Argon + 5% Methane through column 40 mls/min. " detector purge
Detector	Ni^{63} Electron Capture
Detector Temperature	250°C
Sample Size	4 µls of a 5 ppm. hexane soln.
Chart Speed	1 cm/min.

