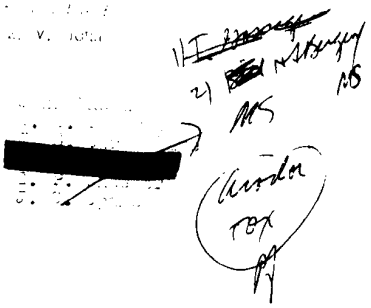

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feature

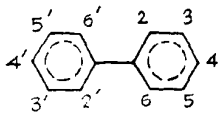
PCB's—prevalent and persistent

Intensified research is needed to minimize their dangers

Carl G. Gustafson, *Federal Water Quality Administration, Athens, Ga.*

During the past three years, a special class of compounds, called polychlorinated biphenyls (PCB's), has claimed the attention of ecologists and pesticide analysts in this country. These compounds were not discovered in the environment until 1966 in Sweden and 1967 in the U.S., despite the fact that they have been available commercially for 40 years. Interest in PCB's has arisen because they are frequently found in fish, bird, water, sediment, and other environmental samples when such samples are examined for chlorinated pesticide residues. That a wide variety of samples containing PCB's has been collected from England, Scandinavia, The Netherlands, Antarctica, Central America, and many different parts of the U.S. makes them truly ubiquitous pollutants.

Polychlorobiphenyls are made by substituting chlorine atoms for one or more of the hydrogen atoms at the numbered positions of the biphenyl structure.



In the process of replacing hydrogen atoms with chlorine atoms, a large number of substitution combinations arise. For example, three monochlorobiphenyl isomers are possible, 12 dichlorobiphenyl isomers, 21 trichlorobiphenyl isomers, and so on. Theoretically, 210 compounds can be prepared by this substitution process; a typical example would be 2,4,6,2′4′-pentachlorobiphenyl.

Whenever aromatic hydrocarbons such as biphenyls are chlorinated, the product is a mixture of compounds, including isomers. It is quite difficult to synthesize single, specific chlorobiphenyl compounds in the laboratory unless involved procedures are employed. Consequently few of the individual compounds have been prepared in the pure [illegible] for study.

In the commercial process [illegible] manufacture, biphenyl is chlorinated with anhydrous chlorine in tall cylindrical towers with either iron filings or ferric chloride as the catalyst. The by-product is hydrogen chloride; the product is [illegible] mixture of several PCB's. The degree of chlorination is determined by measuring the specific gravity of the mixture or, when the product is more viscous, the ball-and-ring softening-point test is used. The whole process takes from 12 to 36 hours.

[illegible] U.S., the sole manufacturer [illegible] is the Monsanto Co., which markets them under the trade name Aroclor. PCB's are also manufactured in Europe and Japan, under trade names such as Phenochlor and Clophen. The various Aroclors are differentiated by a four-digit number, with the last two digits indicating the percentage of chlorine in the mixture.

Properties

The three most important physical properties of the PCB's are low vapor pressures (they have high boiling points), low water solubility, and high dielectric constants. They are miscible with most organic solvents and compatible with many types of polymers. Although some individual polychlorobiphenyl compounds are crystalline, the Aroclor mixtures are either liquids or resins.

The chemical properties that make PCB's desirable industrial materials are their excellent thermal stability, their strong resistance to both acidic and basic hydrolysis, and their general inertness. They are quite resistant to oxidation. Monsanto reports, in a technical bulletin on PCB's, that they can be heated to 140° C under [illegible] of oxygen pressure "without showing any evidence of oxidation as judged by development of [illegible] or formation of sludge."

The physiological properties of the PCB's make them potentially significant contaminants of the environment. For any pollutant, two factors are involved: acute toxicity, which is immediately evident because of a high dose or other maiming effect, and [illegible] toxicity, which is the [illegible] of [illegible] accumulation of the poison in the body and is a subtlethal effect. [illegible] acute toxicity is high, a poison will be readily recognized and [illegible] remedial actions will be introduced. If, on the other hand, acute toxicity is low,

The Monsanto Co. stated recently in a letter to Congressman William F. Ryan of New York that as of August 30, it would no longer [illegible] PCB's to customers for use in general plasticizer operations [illegible] disposal of the end-products can [illegible] be controlled. After some lag [illegible] the time it takes to eventually [illegible] of [illegible] products made from [illegible] and currently in processor's inventories [illegible] quantity of PCB [illegible] into the environment may [illegible] potentially [illegible]. If Mon[illegible] customers look for PCB [illegible] rather than purchasing PCB's from [illegible] manufacturers in Japan and Europe, the project [illegible] decrease could become a reality.

[illegible]

MONS 072237

the physiological effects will go unnoticed until the chronic effects make themselves evident. When this happens, the problem may have advanced beyond immediate or easy correction.

Acute toxicity

All studies of PCB's in animals indicate that acute toxicity is not a significant factor. Their acute toxicities are on the order of those of other chlorinated aromatic compounds. Monsanto has sponsored two investigations of the acute toxicities of Aroclor mixtures. In the first, at the Kettering Laboratory at the University of Cincinnati, Dr. J. F. Treon and his coworkers investigated the toxicity of Aroclor vapors for guinea pigs, mice, rabbits, and rats. All animals survived a 24-day exposure to 0.83 p.p.m. of Aroclor 1242 for 7 hours per day on 17 of those days. Even after more prolonged tests, there were no severe effects from Aroclor 1242. In the second investigation, still in process, three groups of beagles are fed Aroclor 1242, 1254, and 1260, respectively, at a rate of 100 p.p.m. in their diets. After three months no significant abnormalities have been noted.

Similar studies on fish have been performed in several laboratories. Dr. Richard Schoettger of the Sport Fisheries and Wildlife Fish-Pesticide Research Laboratory in Columbia, Mo., reports that 96 hour-TL_{50} toxicities of the Aroclors to trout range from 1.17 to 60 p.p.m. Compared to DDT, whose 96 hour-TL_{50} toxicity is 0.002 to 0.009 p.p.m. for trout, the PCB's have a relatively low acute toxicity. With the more sensitive bluegill, the 96 hour-TL_{50} for Aroclor 1248 is 0.278 p.p.m., while that of DDT is 0.008 p.p.m. Aroclor toxicities appear to be inversely proportional to the chlorine content of the mixture.

Shellfish, oysters, and shrimp are more sensitive to PCB's. Dr. Tom Duke, at the Bureau of Commercial Fisheries Pesticide Field Station, reports 100% mortality of juvenile pink shrimp exposed to 0.10 p.p.m. of Aroclor 1254 in water for 48 hours. This concentration of Aroclor 1254 will cause a 100% decrease in shell growth of oysters after 96 hours. To achieve the same effects with DDT in these experiments, only 0.0006 p.p.m. and 0.01 p.p.m., respectively, were required.

There is very little evidence that PCB's are toxic to insects. Studies to date show that they are less toxic than dieldrin or DDT. As with fish, their toxicity appears to be inversely proportional to the chlorine content of the mixture.

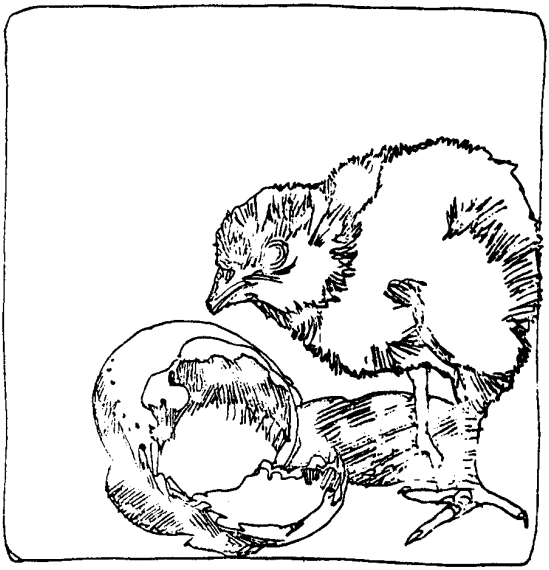
Based on the above data, it is understandable why the polychlorobiphenyls, commercially available for 40 years, have only recently attracted attention as toxic environmental contaminants.

Chronic toxicity

The chronic toxicities of PCB's present a more disturbing situation; several chronic effects have been observed. It was discovered, quite by accident, that PCB's have a toxic effect on chickens. Professor E. L. McCune and his coworkers at the University of Missouri found their chickens dying after they were placed in a feeding house, parts of which had been freshly painted with an epoxy paint. Careful investigation revealed that the toxic factor was Aroclor 1242, a binder in the paint. When Aroclor 1242 was fed to the chicks it produced the same characteristic effects as chick edema factor. McCune reported: "Gross pathology included hydropericardium, hydroperitonium, enlarged heart, liver, and kidneys, and hemorrhage of internal organs. Microscopically the kidneys showed marked tubular dilation and numerous casts."

Another chronic effect of PCB's is related in wildfowl. The accumulation of high concentrations of chlorinated hydrocarbons in birds resulted in disruption of normal breeding behavior and in the formation of thin-shelled eggs. A dramatic example of this effect has been observed in the case of the brown pelican. On the Anacapa Islands off the California coast, no young were hatched last year from 300 pairs of nesting birds. The shells of most eggs laid were so thin that a dent occurred when the egg was picked up.

There are two possible causes for the laying of thin-shelled eggs by wildfowl. One is a low calcium reserve in the bird; the other is the inability of the bird to deliver the needed calcium to its oviduct, where the eggshell is forming. The calcium level in the avian biosystem and the calcium reserve in the secondary bone structure or medullary bone, found only in female birds when they are breeding, are controlled by the hormone estrogen. A high estrogen level is associated with the formation of this calcium reserve. Chlorinated hydrocarbons, such as DDT,



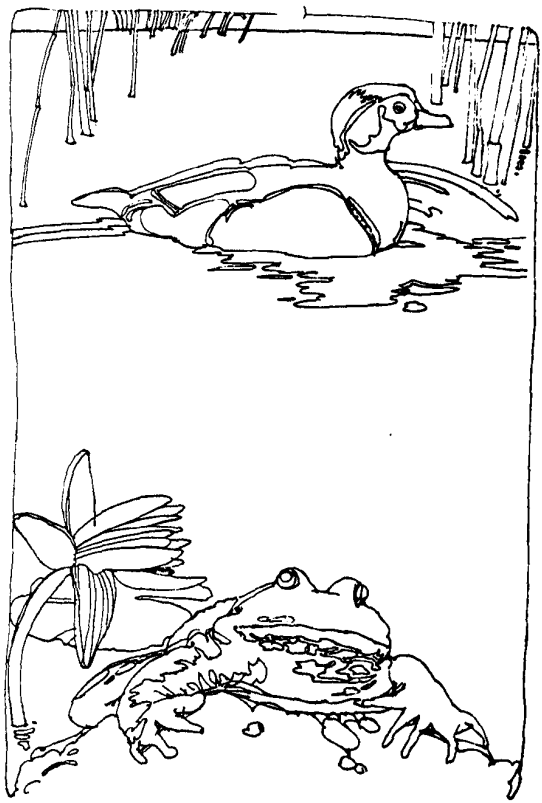
MONS 072238

chlordane, dieldrin, and PCB's, activ[illegible] enzymes in the liver which transform estrogen into a more water-soluble compound that is readily eliminated from the bird's body. This means that when estrogen levels are low, calcium reserves will also be low, and therefore very little calcium will be available for strong eggshell production. Dieldrin and PCB's are more effective than DDT in this type of enzyme-induction activity. Aroclor 1262 has an estradiol degrading potential four to five times that of *p,p'*-DDE or technical grade DDT.

The ability of the female bird to deliver calcium to her oviduct during the last 20 hours, when the eggshell is being formed, is related to the functioning of the enzyme carbonic anhydrase. When birds that have exhibited the ability to lay normal eggs are injected with a metabolite of DDT (DDE) just prior to the formation of the eggshell, they will lay thin-shelled eggs. This indicates that DDT also inhibits the activity of carbonic anhydrase, the enzyme that controls the flow of calcium from the blood stream of the bird into its oviduct.

Since dieldrin seems to have no effect on carbonic anhydrase, we may assume that neither do the PCB's. However, these compounds delay breeding time significantly. Many ornithologists feel that late breeding has a stronger influence on the reduction of bird populations than does the laying of thin-shelled eggs. If this is true, PCB's are a more potent threat than DDT to our declining bird populations, especially for predatory birds that accumulate fairly high levels of PCB's because they eat smaller animals that already have concentrated PCB's in their own tissues.

Other investigators have produced evidence to show that PCB's are similar to DDT in their activity. Dr. Joseph Street at Utah State University has shown that when PCB's accumulate in the liver, they induce microsomal enzyme activity by bringing about more rapid metabolism of drugs, insecticides, and other foreign compounds. He fed rats a diet containing 50 p.p.m. of Aroclor 1254 or Aroclor 1260. After 10 days on this diet, the test animals were administered hexobarbitol at a dose of 100 p.p.m. to induce sleep. In comparison with a control group, the sleeping time for these rats was reduced by 65 to 80%. Street also found that Aroclor, when fed [illegible] the same level, will reduce dieldrin storage in adipose tissue by 90 to 95%; increase aniline oxidation by 200 to 300%; and increase EPN detoxication by 430 to 470%. In addition, the PCB's cause activation of organothiophosphate compounds, which adversely affect the system. This latter effect counterbalances the detoxification of dieldrin.



Normally, when a substrate activates an enzyme, it is converted to a water-soluble form that will be eliminated from the system; however, this is not the case with PCB's. Because they remain in the system for prolonged periods of time, their enzyme induction activity is always present. In this way the normal concentration of important body chemicals may be lowered to the point of bringing about malfunctions in the system. For example, Street believes that the PCB's bring about steroid degradation, which can lead to altered endocrine relationships.

The chronic toxicity to man is as follows:

> Like the chlorinated naphth[illegible]nes, the chlorinated diphenyls have two distinct actions on the body, namely, a skin effect and a toxic action on the liver. The lesion produced in the liver is an acute yellow atrophy. This hepa[illegible]xic action of the chlorinated diphenyls appears to be increased if there is exposure to carbon tetrachloride at the same time. The higher the chlorine co[illegible] of the diphenyl compound, the more toxic it is liable to be. Ox[illegible] of chlorinated diphenyls are more

MONS 072239

toxic than the unoxidized materials.

The skin lesion is known as chloracne, and consists of small pimples and dark pigmentation of the exposed areas, initially. Later, comedones and pustules develop. In persons who have suffered systemic intoxication, the usual signs and symptoms are nausea, vomiting, loss of weight, jaundice, edema, and abdominal pain. Where the liver damage has been severe, the patient may pass into coma and die.

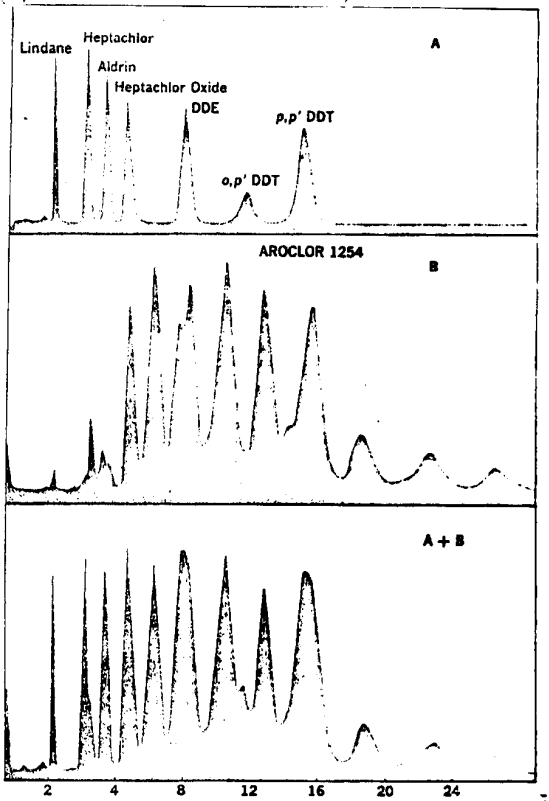
Sax, N. Irving, "Dangerous Properties of Industrial Materials," 3rd ed., Van Nostrand-Reinhold, New York, 1968.

The ubiquity of PCB's is related to the wide spectrum of applications that have been found for them. The largest single use of PCB's is related to their electrical properties—as coolant-insulation fluids in transformers. For this purpose the Aroclors are also sold under such trade names as Chlorextol (Allis-Chalmers Mfg. Co.), Dykanol (Federal Pacific Electric Co.), Inerteen (Westinghouse Electric Co.), Noflamol (Wagner Electric Co.), Pyranol (General Electric Co.), and Therminol (Monsanto Co.).

Other uses of PCB's include formulation into ballasts for fluorescent fixtures; impregnation of cotton and asbestos for braided insulation of electrical wiring; a plasticizer in wire and cable coatings; capacitors and askarel-type transformers; and plasticizers of vinyl chloride polymer films. Because of their thermal stability and fire resistance, the PCB's also find application in high-pressure hydraulic fluids, specialized lubricants and gasket sealers, heat transfer agents, and machine tool cutting oils. Miscellaneous uses include: formulation into some epoxy paints; protective coatings for wood, metal, and concrete; adhesives; and in carbonless reproducing paper. One of the primary manufacturers of carbonless reproducing paper also sells Aroclors in an encapsulated form.

Generally the kinds of applications described above mean that the PCB's will be in many types of products that eventually find their way to the domestic market. When used in manufacture of ballasts for fluorescent fixtures they will be found in kitchens, bathrooms, stores, and offices throughout the country. Wherever office forms are used that do not use carbon paper, one may find PCB's formulated into the microcapsules of dye that comprise the reproducing layer of the business form. PCB's have also been found on the transparent receipts used in credit card charge forms. As plasticizers they can be expected to appear in many consumer plastics.

Since the chronic toxicities are so significant, it becomes important to know just how extensively the PCB's are distributed in the ecosystem, and just how they find their way into the environment. Rainwater in England, brown seals off the coast of Scotland, white-tailed eagles in Sweden, cod in the Baltic Sea, mussels in The Netherlands, adelie penguin eggs in the Antarctica, brown pelican eggs in Panama, Arctic terns, shrimp in Florida, river water in Japan, waters in the Great Lakes, human hair, and human adipose tissue—samples of all these have been found to contain PCB's.



Gas chromatogram A is of a standard pesticide mixture, B is typical of Aroclor 1254, and A + B is the chromatogram of a 50 : 50 mixture of both. The concentration of Aroclor 1254 is approximately 10 times those of the pesticides in A, hence it is understandable why PCB's were not readily recognized in pesticide chromatograms. Gas chromatograph (Packard 7620) conditions: gas flow 80 ml./min. nitrogen; temperatures—oven, 210° C., inlet, 230° C., detector, 218° C.; Ni^{63} electron capture detector; 5' × ⅛" glass column packed with 8% SE-30 on Chromosorb Q 80–90 mesh.

MONS 072240

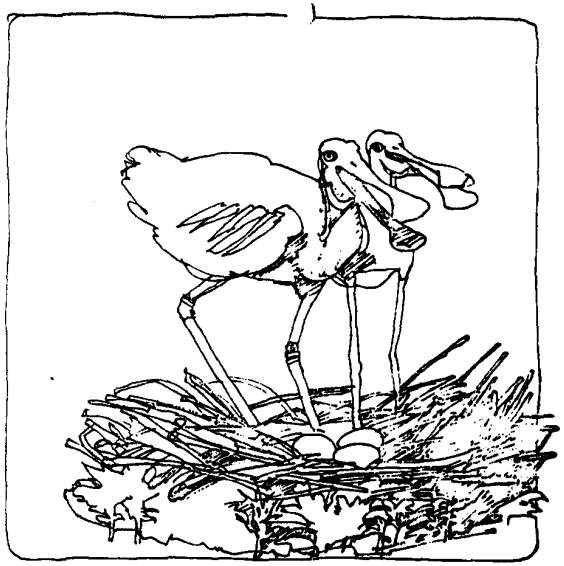
thus making them a class of wide dispersed pollutants.

Readily absorbed

The properties of PCB's that make them industrially useful are the same properties that cause them to persist in the environment. These include thermal stability, resistance to oxidation and hydrolysis, solubility in a wide range of organic solvents, water insolubility, high dielectric constant, and compatibility with many types of macromolecules. Their resistance to oxidation and hydrolysis also makes PCB's more stable and persistent than DDT. Consequently, they could eventually accumulate to a higher concentration than DDT, especially if the use of DDT is sharply curtailed in the U.S.

The solubility of PCB's in nonpolar solvents explains why they are readily absorbed into fatty tissue and into the liver. Their resistance to oxidation or other types of chemical degradation explains their persistence in the environment and accumulation in animal tissue. The latter effect is enhanced both by their insolubility in water and solubility in organic solvents. Their chemical inertness and resistance to metabolism account for their low acute toxicity. But as they slowly build up in a living system their concentration approaches toxicity levels, at which point chronic effects make themselves evident.

It has been established that fish-eating birds will accumulate large concentrations of PCB's, as in the case of the white-tailed eagle, which has been found to have as much as 14,000 p.p.m. of PCB's. Peregrine falcons, taken off the coast of California, were found to have as much as 2000 p.p.m. in their lipid tissue. When shrimp were exposed to 10 p.p.b. of Aroclor 1254 for 48 hours, they accumulated 1300 p.p.b. of PCB's, which represents a 130-fold concentration in a very short time. Oysters, exposed to an identical concentration of Aroclor 1254 for 96 hours and then placed in PCB-free water for four days, still had a concentration of 33,000 p.p.b. of PCB's, which constitutes a 3300-fold concentration. This means that even though the concentrations of PCB's are in the parts-per-billion range in the environment, their high lipid solubility causes them to collect in fatty tissues of lower animals and marine life. Therefore, species at the top of a food chain will also accumulate PCB's in their bodies, particularly in their lipid tissue and liver, in much the same way as they accumulate DDT and other chlorinated pesticides.



Because of the low solubility of PCB's in water, when a solution or dispersion of them is discharged into a river or lake, they will accumulate on the sediment in relatively high concentrations. Subsequently, they will redissolve very slowly in the water as conditions change. Therefore, it will usually take a long time to flush out a contaminated area.

Accidental occurrence

The reason that PCB's have not been found in the ecosystem as extensively as DDT, and are not present in environmental samples at as high a concentration as DDT, is that PCB's find their way into the environment accidentally. DDT is deliberately spread because this is the only way its insecticidal properties can be utilized. PCB's are not intended to get into the environment, but they do because their unique chemical properties prevent them from being destroyed by our usual waste disposal methods. Thus, they inadvertently escape and become widely dispersed.

In Sweden, where the use of DDT has been banned, and where the main power source is hydroelectric, investigators find that the concentration of PCB's in the environment is as high as that of DDT.

There are several ways by which PCB's get into the ecosystem. One of these is by incineration. Products containing PCB's, such as carbonless reproducing paper in business forms, plastics (especially polymer film and sheeting that contain PCB's as plasticizers), spent ballasts from fluorescent light fixtures, and objects coated with PCB-formulated coatings, all find their way to the city dump or incinerator for burning. The PCB's do not burn but are vaporized. They are then carried into the atmosphere, where they collect on particulate matter and are subsequently returned to the surface of the earth, into the rivers, lakes, and oceans. In this way they become widely distributed throughout the global environment. Another source is probably land run-off from industrial wastes and dumps. A third source is the point of manufacture and the plants where PCB's are processed into other products. They can escape through the plant ventilation and exhaust systems into the atmosphere and through its waste treatment system into sewers or directly into waterways.

MONS 072241

It is interesting to note that the incidence of PCB's in environmental samples is highest in industrialized and urbanized areas. Birds whose primary habitat is the San Francisco Bay area have a larger concentration of PCB's per unit of body weight than those located in Baja, Calif., which is completely rural. Aquatic life in the Archipelago of Stockholm, the most industrialized area of Sweden, were found to have a higher concentration of PCB's than fish samples taken from the western coast of Sweden, a less developed area. Sediment samples taken from southern portions of Lake Michigan have a higher concentration of PCB's than those from other parts of the lake.

Monsanto states that until a recent change in marketing policy (see inset, page 814), sales of Aroclors were increasing at the rate of 8% per year. While this increase does not seem significant, it may be important if the increased consumption was in consumer products and thus would find their way into our normal solid waste disposal systems. Such an occurrence would mean a definite increase of PCB residues in the environment, and therefore a marked increase in their chronic toxicity effects.

Detection

PCB's were not discovered in environmental samples until very recently for several reasons. First, as indicated above, they have not been deliberately distributed about the ecosystem. Secondly, because of their relatively low acute toxicities, their presence was not immediately evident. Finally, they are difficult to detect analytically.

The PCB's were first detected as interfering peaks in the gas chromatographic analysis (GC) of environmental samples being analyzed for chlorinated pesticide residues. When PCB's are present in a sample they give a pattern of several GC peaks, whose retention times are similar to those of dieldrin, DDT, DDE, aldrin, and heptachlor oxide. Because the peaks were not large or sharp, investigators tended to ignore them until S. Jensen, in Sweden, and R. Risebrough, at the University of California at Berkeley, identified them as corresponding to common constituents of environmental samples being analyzed for persistent pesticides.

The problem of the interferences of PCB's with the analysis of other chlorinated pesticides has been largely overcome by prior treatment of the sample. Several investigators have used column chromatography to separate PCB's from chlorinated pesticides. At a recent meeting, sponsored by the FWQA's National Water Quality Laboratory, Duluth, Minn., a general procedure was recommended for separation of PCB's from pesticides. In this procedure for biosamples, the sample is extracted with hexane as in regular pesticide analysis. It is then partitioned with acetonitrile to remove fats, the cleaned-up extract is passed through a Fluorisil column and then through a silicic acid column. Finally, the sample is analyzed by gas chromatography, with a chloride-specific detector. In this way the pesticides are retained on the silicic acid column for later elution and identification.

Research needs

To assess fully the significance of PCB's as environmental pollutants, additional research is needed. No one really knows the extent of the chronic effects of these chlorinated hydrocarbons. Some problems that need to be considered are:

- Although PCB's are known to accumulate in human organs we do not know at what concentration they will begin to exhibit toxic effects. Will these chronic effects be similar to those shown in animals—microsomal enzyme activity, calcium metabolism inhibition, and so on? What are other possible chronic effects?
- Which of the many PCB compounds in the commercially available mixtures are responsible for their toxicity? Can commercial PCB mixtures be modified to eliminate the toxic components? Pure samples are required to answer these questions. At the present time work is continuing at the FWQA's Southeast Water Laboratory to separate each of the Aroclor mixtures into its many components, and to identify each component.
- We need to know all the uses for the PCB's. What is the annual production of PCB's? Our knowledge of these facts is limited and needs to be expanded. These facts should be known if we are to accurately determine how they get into the environment, and take steps to prevent further environmental contamination by them.
- In view of the complexity of the isolation and accurate quantitative analysis of PCB's in chlorinated residues, a straightforward, unambiguous measurement of them needs to be developed.
- What is the fate of PCB's in natural waters? More needs to be known of their partition coefficients between bottom sediments and water. This is vital if we are to estimate how long it will take for a river bed to clean itself of contamination. It will also be useful when assessing the effects of PCB's on marine life that feed on the bottoms of lakes, rivers, and estuaries. We should also learn more about PCB solubility in water of various ionic strengths.
- Are present waste treatment systems adequate to handle PCB's? Do special measures need to be taken when PCB's are part of the waste effluent being treated?

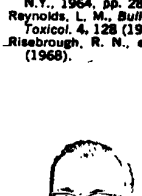
By trying to get some of these answers now, we may find that we are in a position to control the escape of PCB's into the environment before additional damage is done. So frequently, action is taken only after it is evident that massive damage has resulted from a particular pollutant. In the case of the PCB's we may have an opportunity to resolve the situation before that happens.

Additional Reading

Hubbard, H. L., "Chlorinated Biphenyl and Related Compounds," Encyclopedia of Chemical Technology, 2nd ed., 5, Interscience Publ., New York, N.Y., 1964, pp. 289–298.

Reynolds, L. M., *Bull. Environ. Contam. Toxicol.* 4, 128 (1969).

Risebrough, R. N., et. al., *Nature* 220 (1968).



Carl G. Gustafson, *chairman of the Department of Chemistry of King's College, Briarcliff Manor, N.Y., received a Ph.D. in organic chemistry from the University of Delaware in 1957. During the 1969–70 academic year, he was on leave at the* FWQA *Southeast Water Laboratory in Athens, Ga., where he studied trace organic analysis in waste effluents. As a member of the National Water Contaminants Characterization Research Program, he worked with PCB's and pulp and paper mill effluents.*

MONS 072242