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Aqueous Solubility, Adsorption, and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254

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■ The water solubility, adsorption from aqueous solution, and the vapor behavior of the polychlorinated biphenyl Aroclor 1254 have been determined. The aqueous solubility of Aroclor 1254 has been found to be ~56 ppb. The extent of adsorption of the PCB's is highly dependent on the nature of the adsorbent. Del Monte sand adsorbs very little as compared to a Woodburn soil. The vapor loss of Aroclor is significant from the sand but negligible from the soil. The vapor loss increases with increasing temperature. In general, the isomers containing fewer chlorine atoms show greater loss as compared to other isomers having more chlorine atoms.

The occurrence of polychlorinated biphenyls (PCB's) in the environment and their consequence on environmental quality have been well emphasized in recent years (Nelson, 1972; Gustafson, 1970, 1972; Peakall and Lincer, 1970). Data describing PCB residues in water and animal tissue and their toxicological effects are accumulating at a rapid rate (Nelson, 1972; Gustafson, 1972). However, little is known about the mechanism of transport of PCB's in the environment. The question of how PCB's are transported in the biosphere still remains. To answer this, one must know the basic properties of PCB's. In the present manuscript, we shall describe the behavior of the PCB, Aroclor 1254, in some laboratory water, soil, and air systems. The chemical properties discussed are the water solubility, vapor loss, and adsorption.

Experimental

The PCB, Aroclor 1254, was a sample from Monsanto Chemical Co. and was used without further purification. The clay, sand, silica gel, and soil samples used in this study and their sources are given in Table I. All adsorbents were used as received, aside from screening (60/80 mesh), except Ottawa send (20/30 mesh), which was used as received. Woodburn soil was determined to have 3.1% organic matter and 16.2% clays. The distilled water used throughout the studies was extracted with hexane and boiled for 1 hr to remove the residual hexane. This procedure was necessary to be sure test water was free from dissolved organic materials. The procedure for each experiment is outlined as follows:

Solubility Studies. Approximately 5 grams of the chemical was placed in a large Erlenmeyer flask (6-liter), stoppered, and equilibrated with water. To prevent dispersion of PCB, the sample was slowly stirred with a magnetic stirrer. To eliminate heat transfer, the stirrer and flask were separated by a ½-in. polystyrene sheet. An aliquot of aqueous sample was removed, centrifuged at 3000 rpm for 10 min, extracted with hexane, and analyzed for the PCB. The analysis was carried out at 1-week intervals and was continued until it was determined that the concentration had reached the saturation point.

A typical gas-liquid chromatogram of a standard and a water extract is shown in Figure 1. The individual peaks in the chromatogram corresponding to different numbers of chlorine substitutions were identified by mass spectrometry. The distribution of chlorine components in the mixture was established initially by microcoulometric gas chromatography. The gas chromatogram shape changed owing to the differential rates of solubilization of the vari-

Table I. Sources of Materials Under Investigation

Surface	Source
Illite clay	Illite #35—Fithian, Ill., Wards Natural Science Establishment Inc., Rochester, N.Y.
Kaolinite clay	Kaolinite #4—Oneal Pit, Macon, Ga., Wards Natural Science Establishment Inc., Rochester, N.Y.
Montmorillonite clay	Montmorillonite #26—Clay Spur, Wyo., Wards Natural Science Establishment Inc., Rochester, N.Y.
Silica gel	Silica Gel, Powder #3405, J. T. Baker Chemical Co., Phillipsburg, N.J.
Del Monte sand	Del Monte Sand, EL-30, Del Monte Properties Co., San Francisco, Calif.
Woodburn soil	Woodburn Silt Loam, 0-4 in., Hyslop Farm, Corvallis, Ore.
Ottawa sand	Scientific Supplies Co., Seattle, Wash.

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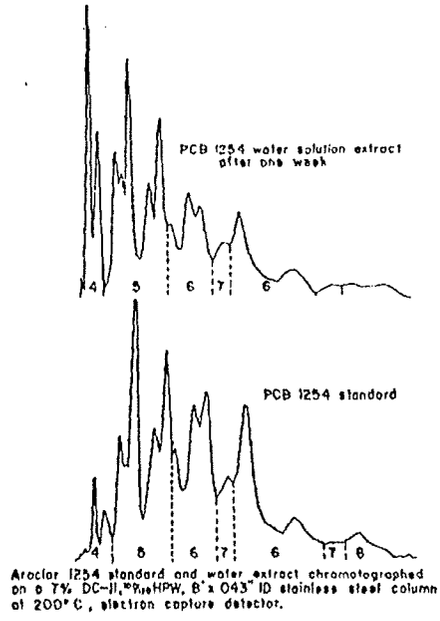

Figure 1. Typical gas chromatograms of standard and a water extract Aroclor 1254 in hexane

ous isomers before equilibrium. The envelope was divided into 4, 5, 6, and 7 chlorine components by drawing a line perpendicular to the baseline at the minimum of the trace between various chlorinated portions. Further division was not attempted owing to insufficient separation of individual isomers. Since many of the peaks were not sharp, the cut and weigh method was used to determine peak areas. Isomers having different numbers of chlorine atoms possess varying electron-capture detector response, thus a correction was needed to quantitize the data. The differential response for various chlorine containing isomers was referenced relative to *p,p'*-DDE. The final concentration of the PCB was determined by comparing with a known standard.

Adsorption Studies. The adsorption studies were carried out by equilibrating a saturated aqueous solution of PCB with a known amount of the adsorbent material. The saturated aqueous solution was previously equilibrated as described for approximately 6½ months. Since the solubility of Aroclor 1254 is in the ppb range, the equilibrium experiments were performed with the concentration of PCB constant and the amount of adsorbent material varied rather than vice versa. A known quantity of adsorbent material was weighed in a 250-ml centrifuge bottle, and a saturated solution of the PCB (125 ml) was added and kept on a shaker for 24 hr. Earlier studies showed that this period of time was sufficient to reach equilibrium for the adsorption of other pesticides on surfaces from aqueous solution (Haque and Sexton, 1968; Haque and Coshow, 1971). The samples were then centrifuged at 3000 rpm, and 100 ml of the supernatant liquid were extracted with three 15-ml portions of hexane.

The extract was blown down to approximately 3 ml under a nitrogen stream and the sample made up to 5 ml in a volumetric flask. The concentration of PCB remaining in solution was determined on an Aerograph 550 gas chromatograph, equipped with an electron capture detector. The adsorption of Aroclor 1254 on the surface of the container was accounted for by running a blank through the analysis. We have determined the adsorption of Aroclor 1254 on surfaces by taking into account the sum of all the gas chromatographic peaks. No attempt was made to determine the adsorption of each constituent on individual materials. The amount of chemical adsorbed, x, was calculated by the formula:

$$x = V(C_2 - C_1) \qquad (1)$$

where V is the volume of the adsorbate, C_2 and C_1 are the original and final concentrations of adsorbate (ppb).

Vapor Loss Studies. Two different kinds of investigations were carried out to observe the vapor loss of PCB. In one experiment the loss was studied from Aroclor 1254 itself, whereas in the other case the vapor loss was monitored from Ottawa sand and Woodburn soil. In the first set a known quantity (~0.6 gram) of the chemical was placed in planchets (exposed area 5.07 cm^2) and the vapor loss was monitored gravimetrically as a function of time. The experiments were carried out in duplicates and at two different temperatures (26° and 60°C). The second experiment was performed as follows:

Sand and the soil surfaces were treated with the PCB. An ether solution of Aroclor 1254 of known concentration was mixed with sand or soil and dried on a rotary evaporator for 2.5 hr. Ottawa sand (130 grams) containing PCB was placed in petri dishes. Entire samples were taken at 0-, 1- and 4-week intervals and extracted in Soxhlet extractors. The chemical was extracted with 250 ml of acetone for 24 hr and the volume of acetone was reduced to 100 ml by evaporating under nitrogen stream, partitioned into hexane by adding 200 ml of 2% Na_2SO_4 and extracted three times with hexane. The sample was concentrated and analyzed on a Tracor gas chromatograph equipped with Ni^{63} detector.

Similar experiments were done under wet conditions by adding approximately 30 ml of water every day. The experiments with soil were carried out by placing (25 grams) of Woodburn silt loam containing 10 ppm of Aroclor 1254 in 130-S Lilly cups. The cups were equipped with an aluminum support wrapped with 2-Kimwipes (No. 3415) and placed in the groove of the cup. The Kimwipes acted as a wick for the wet soil loss study. A filter paper (No. 42) was placed on the Kimwipe wick to act as a soil barrier. The samples were taken at 0-, 1-, 2-, 3-, and 4-week intervals and the PCB was extracted with acetone using the procedure described earlier in this paper. Similar experiments were performed under wet conditions by adding ~50 ml of water at 48-hr intervals through a small funnel inserted in the cup. All the above experiments were carried out in duplicate at room temperature (26°C).

Results and Discussion

The equilibration of Aroclor 1254 in water was achieved in approximately 2 months, the concentration at this point was approximately equal to that at 6 months. It was expected that the total solubilization process would be a slow one, although it takes only a week to achieve a major part of the equilibrium. The total solubility of Aroclor 1254 was ~56 ppb. This value is within the range reported for many chlorinated hydrocarbon insecticides (DDT-type compounds) having similar structure (Bowman et al., 1960; Bigger et al., 1967; Gunther et al., 1967). However, it is significantly lower than the values reported by Zitko (1971), who obtained solubilities in the range of 0.3–3 ppm in "fresh water." These high values may be due to the presence of foreign materials in the "fresh water."

From the intensities of various peaks in the gas chromatogram, it may be said that the water solubility of PCB isomers in general decreases with increasing chlorine atoms.

The percent decrease in the concentration of Aroclor 1254 by the addition of increasing amounts of adsorbent material is shown in Figure 2. As expected, sand and sili-

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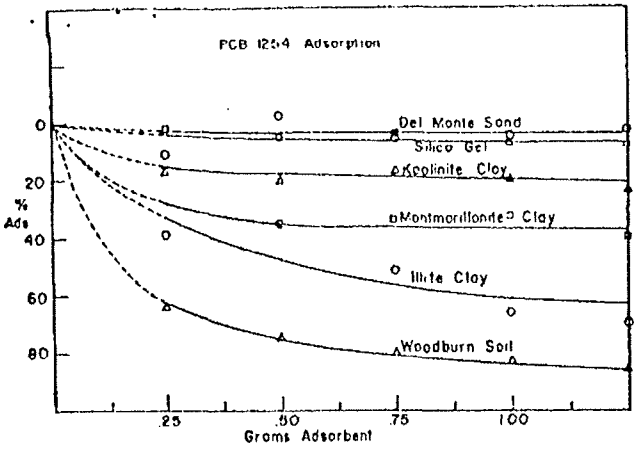

Figure 2. Percent decrease in the concentration of Aroclor 1254 by the addition of increasing amounts of adsorbent. Original concentration of Aroclor 1254, 56 ppb

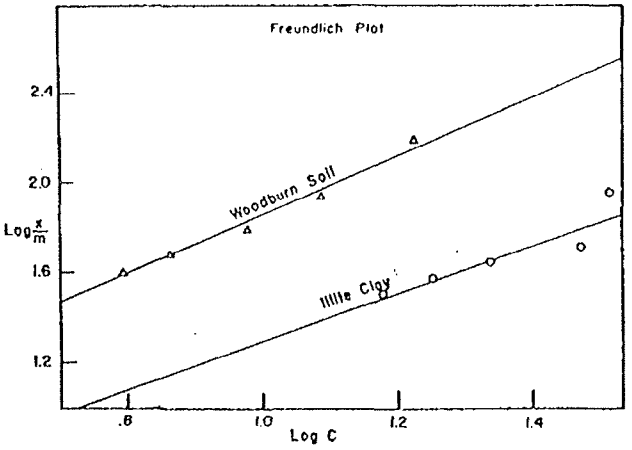

Figure 3. Freundlich isotherm showing adsorption of Aroclor 1254 on illite clay and Woodburn soil (C in ppb and x/m in ng/g)

ca gel adsorb very little of the chemical whereas illite clay and Woodburn soil showed greater adsorption. The adsorption behavior of montmorillonite and kaolinite clays was intermediate between those extremes. The high-adsorbing capacity of Woodburn soil is tentatively attributed to the presence of organic matter. The adsorption equilibrium of PCB on illite and Woodburn soil was treated by a Freundlich-type isotherm Equation 2:

$$\frac{x}{m} = KC_1^n \qquad (2)$$

where K and n are constants and m the mass of the adsorbent in grams. A typical Freundlich plot is shown in Figure 3. The values of K and n for illite clay and for Woodburn soil are 63.1 and 1.1 and 26.3 and 0.81, respectively. The Freundlich-type isotherm shown in Figure 3 suggests a physical-type adsorption. The Freundlich isotherm for other surfaces is not shown because of their extremely low adsorption capacity.

The loss of Aroclor 1254 from itself is shown in Figure 4. Although the loss of the chemical is rather small at 26°C, it is substantial at 60°C. It is interesting to note that the weight loss change is linear as a function of time. Mathematically, such a behavior is characteristic of diffusion in a plane sheet (Crank, 1967), and could be expressed as in Equation 3:

$$\text{Mass loss } (t) = A \cdot F \cdot t \qquad (3)$$

where A is the exposed area, t the time, and F the flux defined by Equation 4:

$$F = D\left(\frac{\partial c}{\partial x}\right)_{x=L} \qquad (4)$$

where D is the diffusion coefficient, $(\partial c/\partial x)$ is the concentration gradient, and L the thickness of the sheet. Since it is not possible to estimate the concentration gradient from the available data, it is difficult to calculate D. However, from the slope of the line (Figure 4), we can calculate the flux. The calculated value of the flux has been found to be 2.0×10^{-6} gram · day^{-1} · cm^{-2} at 26°C and $8.6 \cdot 10^{-5}$ gram · day^{-1} · cm^{-2} at 60°C.

The loss of PCB from a sand surface is shown in Figure 5. As expected, the higher chlorine-containing isomers show the least loss and vice versa. This is mainly due to the fact that the vapor pressure for PCB isomers decreases with increasing number of chlorine atoms. Vapor loss under wet conditions was similar and comparable in magnitude. Similar experiments dealing with the Woodburn

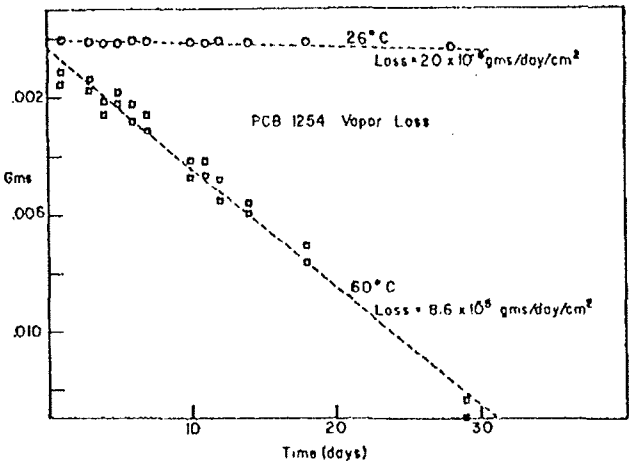

Figure 4. Loss of Aroclor 1254 from itself as a function of time

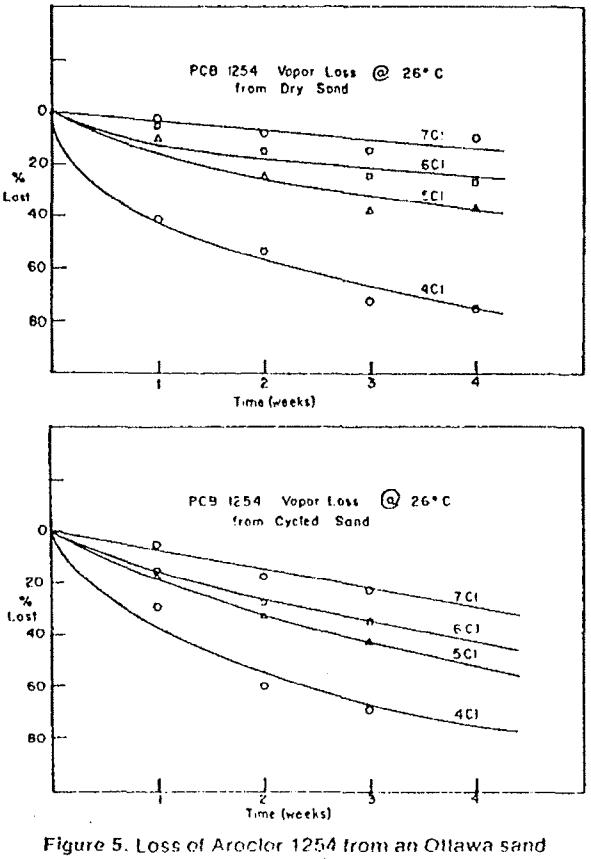

Figure 5. Loss of Aroclor 1254 from an Ottawa sand

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soils showed that vapor loss of Aroclor 1254 from the soil surface was negligible. The high loss from the sand as compared to the soil may be attributed to the marked difference in the absorbing capacity of these two surfaces. The vapor loss behavior of PCB from sand and soil surfaces is qualitatively similar to DDT (Cliath and Spencer, 1972; Guenzi and Beard, 1970).

The findings of this paper give a qualitative picture of the behavior of the PCB Aroclor 1254 in water, soil, and air. It is difficult to extend these findings directly to the field conditions. There is always a danger of drawing erroneous conclusions. However, some speculations about the environmental significance of the work could be made. In general, once PCB is introduced in the environment, the isomers will be transported in air, soil, water, and biota. The concentration in each phase will highly depend upon the partition coefficients. The water solubility will determine the distribution in water. It appears that PCB in ppb range could be transported in water. The environmental contamination of water will highly depend upon the number of chlorine atoms present in the isomer. The lower chlorine-containing isomers will show higher concentration in water and vice versa. The concentration of PCB in water will be reduced whenever the water comes in contact with a solid surface or particulate matter. The reduction in the concentration of PCB in water will depend upon the surface characteristics.

Such properties as the surface area, organic content of the material, nature of the surface (clay, sand), and pH of the medium will greatly influence the adsorption. The transport of PCB in air will be governed by temperature, vapor pressure, and the surroundings of the chemical. Significant amounts of PCB could be transported in air at higher temperatures if PCB is present in the environment where it is loosely bound or adsorbed to a surface. The loss could also be significant if PCB is evaporating from its own surface, especially at higher temperatures. The number of chlorine atoms present in the particular PCB isomer will also influence the loss to a great extent. The larger the number of chlorine atoms present in the isomer, the smaller the loss. However if PCB, on the other hand, is bound strongly to a surface, the vapor loss will be much smaller. In general, the environmental contamination and exposure of PCB to living species will be functions of the surrounding temperature, moisture, surface, and so forth.

The findings of this paper may be summarized as follows:

The solubility of Aroclor 1254 at room temperature is ~56 ppb and, although the solubilization is a slow process, the bulk of the process is achieved very rapidly. Aroclor 1254 is readily adsorbed from aqueous solution onto available surfaces. The amount of chemical adsorbed depends upon the nature of the surface. A sand surface with few sites adsorbs relatively little, whereas a soil surface with high clay and organic content adsorbs a much larger amount. The vapor loss of Aroclor 1254 from its own surface depends on the area exposed and the temperature. At room temperature it is small, but by approximately doubling the temperature, loss is enhanced by a factor of 40. The vapor loss from a sand surface is significant whereas from a more tightly bound situation on a soil surface, it is extremely small. The generally more volatile lower chlorine isomers show a greater loss than those of higher chlorine content.

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