Silo Sealents as a Source of Polychlorobiphenyl (PCB) Contamination of Animal Feed

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The physical and chemical properties of polychlorinated biphenyls (PCB's) are ideal for use in a wide range of industrial and commercial materials such as plastics, polymer films, water-proofing compounds and putty, asphaltic materials, printing inks, waxes and synthetic adhesive (1,2). Because of the numerous applications of PCB's, they are widely distributed in the environment and have reportedly contaminated a number of wildlife species (3,4,5). It has been pointed out that residues of PCB's may interfere with the detection and analysis of certain organochlorine pesticides (5). Recently, Armour and Burke (6) have successfully dealt with this problem and described a silicic acid column method for separating PCB's from DDT and its analogs. The extensive distribution of PCB residues in the environment and their potential hazards have stimulated increased interest in these compounds.

Polychlorinated biphenyls were used in the formulation of some paints and sealents which are used on silo walls. Since there is no level of PCB's considered safe in milk at the present time, it is important to have information on the potential contamination of silage by contact with silo walls sealed with materials containing PCB's. Several dairy farmers in Kentucky were recently prevented from shipping milk because of significant levels of PCB residues in their milk. In addition, several other dairy farmers were notified that samples of their milk contained trace levels of PCB's and they would be prevented from shipping their milk if the levels were not maintained or reduced. One of the silos involved in the above mentioned actions had been coated 9 years earlier with a sealent containing PCB's.

Our study was initiated to determine the level and

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distribution of PCB contamination in corn silage from several silos thought to be coated with sealents containing PCB's. Samples of silo wall chips also were examined for PCB residues, and limited laboratory tests were conducted on the solubility of PCB's in water and in a water extract of silage.

Experimental

Materials. A sample of Aroclor 1254 for experimental use was obtained from the Kentucky Department of Health. A standard hexane solution of this material was prepared for gas chromatographic analysis so that 1 microliter of solution contained 1 nanogram of Aroclor 1254.

Apparatus. A Varian Aerograph series 1700 gas chromatograph equipped with an electron capture detector and a glass column, 10' x 1/8", containing 4% SE 30 and 6% QF 1 (1:1 mixture) on Anakron ABS 80/90 mesh was used for these studies. Operating conditions were as follows: nitrogen 35 ml/minute; column temperature, 195°C; injector temperature, 200°C; detector temperature, 200°C; standing current, 1.28×10^{-8} AMPS. The recorder speed was 10 inches per hour.

Extraction and Cleanup of Samples. A 25-g sample of corn silage was homogenized for 3 minutes with 300 ml of a hexane-isopropyl alcohol (2:1) mixture. The homogenate was filtered and the filtrate transferred to a separatory funnel. The alcohol was removed from this mixture by washing with 300 ml of a 2% NaCl solution. The corn silage sample was homogenized a second time with 150 ml of benzene, filtered and the benzene was added to the hexane. This mixture was concentrated to approximately 2 ml and added to a florisil column (2). The column, 22 mm I.D., was packed with 25 g of activated florisil, with approximately one inch of anhydrous sodium sulfate added to the column. The PCB's were eluted with 200 ml of hexane. The hexane was concentrated to 10 ml for gas chromatographic analysis. It was established that DDT and its analogs were not present in sufficient quantities to interfere with the quantitation of the PCB's. Therefore, separation of the 2 groups of materials on a silicic acid column was not necessary.

The extraction and cleanup of the silo wall chips were similar to that employed for silage except that a 5-g sample of silo wall chips was ground in a mortar with 25 ml of the isopropyl alcohol-hexane mixture and then a second time with 25 ml of benzene. The column cleanup was the same as above.

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Collection of Samples. Silage samples were removed from the top of silos that ranged from 12 to 16 feet in diameter. At certain distances from the silo wall, towards the center, a silage sample was collected. A sample representing each distance from the wall consisted of a composite of silage from 6 sampling sites. Small chips from each silo wall were taken from 6 points of the exposed wall. All samples were kept frozen until analyzed.

Solubility Experiments. An attempt was made to determine the amount of PCB's that would dissolve in water or in a water extract of silage. For this purpose 5 g of the silo wall chips obtained from farm C were placed in flasks with 45 ml of water or with 45 ml of a water extract of silage in the other. The silage extract was prepared by homogenizing 50 g of a silage sample, previously shown to be free of PCB residues, with 200 ml of water. The filtered water from the silage had a pH of 4.3. The flasks were incubated at 37°C with shaking for intervals up to 72 hours. For analysis, 15-ml aliquots were filtered through Whatman No. 5 filter paper to remove the suspended particles. The samples were extracted with hexane, passed through a bed of anhydrous sodium sulfate and concentrated to 10 ml.

Determination of PCB Residues. Aroclor 1254 is a mixture of chlorinated biphenyls which produced 17 peaks when analyzed by gas chromatography (Fig. 1). Since pure standards of each peak were not available, a problem relative to how to quantify the residues of PCB's in silage and silo wall samples existed. However, this problem was not too great in this particular study because the relative peak heights were the same in Aroclor 1254, in silo wall chippings and in the silage (Fig. 1, Table 1). Because of this, only peaks J and M were used for quantification. The standards were injected frequently into the gas chromatograph during the analysis and in amounts which approximated the levels of residues in the samples. Owing to interferring materials, peaks A, B, C and O, P, Q (Fig. 1) were not always evident in the silage samples.

Results and Discussion

Gas chromatographic analysis of silo wall chips from the farms included in this study demonstrated that they did contain Aroclor 1254 residues (Fig. 1). Scan II in Fig. 1 is representative of the results obtained from the silo chips and is identical to scan I which is a technical sample of Aroclor 1254. The data shown in Fig. 1 were obtained using a 10 ft column. However, a

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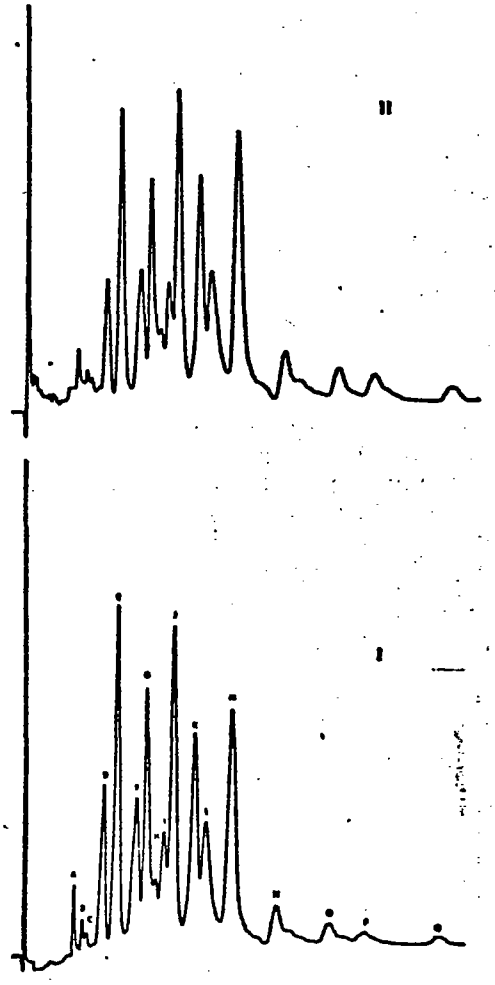

Figure 1. Gas chromatographic analysis of (I) a technical sample of Aroclor 1254 and (II) of an extract of silo wall chips from farm B. See methods section for operating parameters.

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6 ft column yielded identical results except that peaks B, C and H, I were not resolved completely. The farm A silo contained very small amounts of PCB residues, having an average concentration of only 10 ppm. Farm B contained 10,000 ppm residues of PCB and farm C approximately 2,000 ppm.

In the silage, the greatest amounts of residues were in material collected within the first 6 inches of the wall (Table 2). The relative peak heights given in Table 1 show that the PCB's in the silage were similar to Aroclor and that the number of peaks were identical. The residue declined rapidly as the distance from the wall increased and none were detected in samples taken 4 to 6 ft from the silo wall. Silage samples taken at 0 to 2 inches from the wall contained extremely high residues and may have resulted, in part, from small flakes of the sealent in the silage. One sample collected 0-1 inch from the wall of silo C, for example, contained 60 ppm residues of PCB's. However, samples taken at the 2-to 4-inch distance also contained high levels of PCB residues which indicated that the contamination of the silage was not caused entirely by mechanical means.

A decrease in residues was noted in silage samples taken from farm C after a 6 month period. Perhaps the lower levels of PCB residues detected in the second sampling reflect a loss of the PCB as a result of their movement with the liquids which had drained from the sampling area.

It was clear from the laboratory experiments that PCB's from the silo wall chips would contaminate distilled water and a silage extract in which they were placed. The silage extract contained 0.42 ppm after 72 hours (Table 3). These data suggest that the PCB's contaminate silage by being dissolved in the silage liquor which, in turn, moves from the wall, and downward, spreading the PCB's over a wide area. This contamination may be enhanced by the action of automatic feeding devices working inside the silo which mix highly contaminated silage near the wall with that near the center.

In some top feeding silos a layer of silage 3 to 6 inches thick sometimes remains against the walls of the silo and does not mix with the rest of the silage. As shown in this study, the silage nearest the walls contained the greatest residues of PCB's and if that portion of silage was discarded, it is very unlikely that contamination of the silage would be sufficient to cause contamination of the milk and meat of animals.

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TABLE 1

Relative GLC Peak Heights of the Major Components in Aroclor 1254, in Sealents from Silo Walls and in Contaminated Silage

	Peak height relative to Peak E[a]										
Sample	A	D	E	F	G	H	I	J	K	L	M
Aroclor	.21	.49	1.00	.45	.76	.22	.35	.93	.63	.37	.70
Sealent	.20	.43	1.00	.50	.77	.27	.42	1.07	.78	.45	.92
Silage	.30	.64	1.00	.67	.87	.20	.34	1.19	.89	.56	1.02

[a]See Figure 1.

TABLE 2

Levels of PCB Residues in Corn Silage and Silo Wall Chips taken from Dairy Farms where PCB Residues in the Milk had been Reported[a]

		PCB Residues, PPM[b]					
		Inches from silo wall					
Farm	Silo wall chips	0-2	2-4	6-12	12-24	36-48	48-72
A	10	0.00	0.00	0.00	0.00	0.00	0.00
B	10,000	24.31	4.02	.27	.15	.13	0
C	2,000	31.43	.07	.10	.10	0	0
C[c]	2,000	15.04	3.40	.13	0	0	0

[a]Samples collected 3 months after corn was placed in silo.
[b]Limit of sensitivity = 0.02 ppm.
[c]Samples collected 6 months after corn was placed in silo.

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TABLE 3

Level of PCB Residues in Distilled Water and in an Aqueous Extract of Corn Silage at Various Intervals after the Addition of Silo Wall Chips from Farm C

Hours of Incubation[a]	PPM Residues in Distilled water	PPM Residues in Silage extract
24	0.02	0.16
48	.03	.25
72	.06	.42

[a]Silo chips incubated, with shaking, at 37°C.

Unlike farms B and C, the silo wall chips from farm A contained only small amounts of PCB's and the silage was free of these residues. Since PCB residues had been reported in the milk of cows on farm A, it was obvious that there was another source of contamination. Further search for the PCB source on farm A revealed that the feed troughs were the contributing sources. These troughs had been coated with a sealent containing Aroclor 1254, and chips from the bottom of the troughs contained 8,000 ppm of residues. Care will be required to prevent accidental contamination of animal feed due to the large number of materials that contain PCB's and the potential of silage and other feed to pickup PCB residues.

In all samples analyzed, except one, the various components of the Aroclor 1254 mixture appeared to move into and contaminate the silage in an equal manner. This indicated that there was little or no selectivity in solubility of movement of the compounds that make up the Aroclor material in the silo walls. With the one exception mentioned above, peaks E, G and L (Fig. 1) were present at twice the amount of the rest. This occurred in the sample from farm B taken 36-48 inches from the silo wall and the total residues levels were very small. It is possible that the mobility of the components of Aroclor 1254 may vary to some degree. Obviously, more information concerning the compounds in the Aroclor mixture, and other PCB-containing products, must be obtained before their toxicological significances as residues in milk and other food products can be completely assessed.

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A New Idea

But another possibility for putting the U.S.D.A. discovery to work has lain dormant until recently; this is the possibility of using to good advantage the ability of "Aroclor" resins to make the lindane adhere to smooth hard surfaces like metal, glass, painted areas, etc. This would consist of painting or spraying "Aroclor"/lindane formulations on such areas as the inside of garbage can lids, on window screens, doorsills, the painted walls of outbuildings, dairy plants, storage areas, etc., in order to obtain lasting control of flies, ants, roaches, silverfish and other troublesome pests. Suitable formulations can be readily packaged in shoe-polish type "dauber" bottles, aerosol spray cans, and bulk packages for mechanical spray application. Development of this idea is based on the following:

Advantages of Using "Aroclor" Resins in Insecticide Formulations

* A suitable "Aroclor" (Monsanto makes seven) can remarkably extend the effective life of lindane and other chlorinated insecticides as much as ten times (up to 2 and 3 months).

* "Aroclor" resins are very low in cost (around 20¢/lb.).

* Small quantities are sufficient (5 to 25 parts per hundred, by weight).

* Formulation is extremely simple -- the resin is dissolved in a suitable solvent compatible with the insecticide.

* Stable in inventory and in insecticide formulation. "Aroclor" resins are fire-resistant, non-oxidizable, non-corrosive, withstand weather extremely well.

* Non-staining "Aroclor"/insecticide films formed when the solutions dry are practically invisible. "Aroclor" 5460 has a pale yellow color as supplied. Other suitable "Aroclor" products are nearly colorless.

* "Aroclor" resins are odorless -- won't impart "chemical" odors.

* "Aroclor" resins are safe to handle as long as they are not volatilized and inhaled. They are practically non-volatile at ordinary temperatures, do not irritate or sensitize normal skin.

* The nature of the residue can be varied. Monsanto supplies a variety of "Aroclor" resins. These are chlorinated to various degrees and vary in physical properties as follows:

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Chlorinated Terphenyls

Aroclor 5460 - Yellow, transparent, friable solid (dries hard)
Aroclor 5442 - Yellow, transparent, sticky semi-solid (dries tack
Aroclor 4465 - Yellow, transparent, brittle resin (dries sticky)

Chlorinated Biphenyls

Aroclor 1262 - Light yellow, sticky, viscous semi-solid (dries sti
Aroclor 1260 - Pale yellow, soft, sticky semi-solid (dries sticky)
Aroclor 1254 - Pale yellow, viscous oil (dries "wet")

Experimental Work and Formulations

The following information was derived from preliminary reports on work done by U.S.D.A. research groups. These data are not to be construed as recommendations by either the U.S.D.A. or Monsanto, but rather are intended to serve as a guide or starting point for the development of private formulations.

Fifty to 200 milligrams of lindane per square foot of surface has given good insect control on nonporous surfaces. The ratio of lindane to "Aroclor" 5460 has been varied from 1:1 to 1:4. For most purposes a 1:1 or a 1:2 mixture is satisfactory.

Formulations as used in the U.S.D.A. experiments are:

1) For application as a solution.

Lindane	5 parts by weight
"Aroclor" 5460	5 parts by weight
Carbon Tetrachloride	750 parts by weight

(Carbon tetrachloride is toxic and should be handled with extreme caution. Less toxic solvents are easily obtained.)

2) For application as an emulsion.

Lindane	20 parts by weight
"Aroclor" 5460	20 parts by weight
Xylene	100 parts by weight
"Triton" X-100 (available from Rohm & Haas)	3 parts by weight

To obtain a stable 1% lindane emulsion, mix 1 part by weight of the above concentrate to 13 parts by weight of water.

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3) For use as a pressurized (aerosol type) spray.

a)	Lindane	5 parts by weight
	"Aroclor" 5460	5 parts by weight
	Methylene chloride	40 parts by weight
	"Freon" 12 (DuPont)	50 parts by weight
b)	Lindane	5 parts by weight
	"Aroclor" 5460	5 parts by weight
	Cyclohexanone	10 parts by weight
	Ortho-dichlorobenzene	35 parts by weight
	"Freon" 12 (DuPont)	45 parts by weight

Experimental Results - American Roaches

Using Formula 3a or 3b, the toxicant was applied onto a painted wall, depositing about 200 mg./sq. ft. of lindane and a like amount of "Aroclor" 5460.

When the toxicant coat was one month old, it gave 90-100% kill of American roaches when the roaches contained in a petri dish were placed against the surface of the treated wall for two hours.

The U.S.D.A. research team found that the lindane-"Aroclor" 5460 mixture (used at the rate of 50 mg. of actual lindane per sq. ft.) would kill 80% of all cockroaches exposed for 2 hours to a 60-day-old treated surface. It remained lethal to 66% of the roaches after 90 days. Regular lindane sprays used at the same rate killed only 4% of the roaches after 60 days.

Results with Houseflies

Deposits of 25 mg. of lindane plus 25 mg. of "Aroclor" 5460 applied from carbon tetrachloride onto glass and aluminum (hard surfaces) gave 100% kill of normal houseflies exposed for 2 hours to these treated surfaces after they had aged 18 weeks, the duration of the test.

Without the "Aroclor" the hard surfaces treated with lindane alone were effective only about a week.

A lindane plus "Aroclor" mixture sprayed as an aerosol onto leaves of a willow tree continued to kill houseflies after 2 months of outdoor weathering. Careful inspection of the treated leaves showed that the toxicant was held firmly to the surface and notwithstanding rain and weather, the coating remained in good condition. Also, within limits of a preliminary inspection there seemed to be no injury to the willow leaves.

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(Note: The primary purpose of this report is to provide information for the development of suitable insecticide formulations for application to "nonsensitive" surfaces such as metals, glass, paints, and other materials that will not be damaged by the application. Development of formulations for living plants requires sufficient test work to insure that the formulations will not be injurious to the plants or their products.)

Another Formulation Reported

A more recent development in these experiments is the following simple formulation:

"Aroclor" 5460	25%
Lindane	25%
Methylethyl Ketone (MEK)	50%

Work on this was reported in the August 14, 1954 issue of Chemical Week magazine.

This simple formulation appears to be most suitable for "painted on" formulations packaged in bottles but should be used with caution in mechanical spray equipment since the MEK solvent will soften rubber and certain plastics. The formulation could also be modified easily for aerosol packaging.

Since MEK evaporates rapidly, it should not seriously affect painted areas unless too heavy applications are made. The package label should include a caution to this effect. Also, MEK is flammable. Possible substitutes that are less flammable are methylchloroform or a mixture of methylchloroform and methylene chloride.

Formulating Other Insecticides

The beneficial effects of "Aroclor" 5460 apply generally to other chlorinated insecticides including chlordane, aldrin and dieldrin, but do not apply to phosphate type insecticides such as TEPP, parathion, methylparathion, malathion and chlorothion.

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For samples of the "Aroclor" products mentioned in this report, contact the nearest branch office (see attached list) or write to:

MONSANTO CHEMICAL COMPANY
Organic Chemicals Division
Plasticizers Department
800 North Lindbergh Boulevard
St. Louis 66, Missouri

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MONSANTO CHEMICAL COMPANY
Organic Chemicals Division
District Sales Offices

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BOSTON: Everett Station, Boston 49, Massachusetts

CHICAGO: McGraw-Hill Building, 520 N. Michigan Ave., Chicago 11, Ill

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