Chlorinated Organic Pesticide Residues in Fluid Milk

PAUL A. CLIFFORD, JONAS L. BASSEN, and PAUL A. MILLS

DURING the 4-month period August through November 1958, the Food and Drug Administration conducted a nationwide survey of antibiotic and pesticide residues in raw fluid milk in cooperation with many State, county, and municipal milk control officials.

A total of 936 raw milk samples from 16 Food and Drug Administration Districts were tested for residues of chlorinated organic pesticides. Twenty-three showed residues of 0.1 ppm or more. The findings on antibiotic residues have recently been published (*1*).

An earlier survey (1955) of antibiotic and pesticide residues in fluid milk by the Food and Drug Administration (*2*, *3*) revealed that 62 percent of the 800 samples tested contained pesticide residues. The samples consisted of pasteurized milk collected at dairies in retail cartons or bottles; thus it was not possible to correlate samples which bore residues with a specific group of producers and thereby to pinpoint the source of contamination.

The results of the 1955 survey were made available to milk control officials, milk industry associations, and the Federal Extension Service of the U.S. Department of Agriculture. The Food and Drug Administration encouraged each group to conduct an educational campaign to promote the safe use of pesticides on dairy farms.

Cooperation was excellent. The four regional committees of State Extension Dairymen, meeting with State Extension Directors and representatives of the U.S. Department of Agriculture in the spring of 1957, adopted a series of recommendations for eliminating antibiotic and pesticide residues from the milk supply. One of the recommendations was that the Food and Drug Administration continue its surveys.

County agents were encouraged to hold meetings with dairymen. The American Butter Institute, with the assistance of the Food and Drug Administration, prepared a leaflet entitled "Safe Use of Pesticides on Dairy Farms." The leaflet received wide distribution and its message was reprinted in several national farm journals. Other milk industry associations and local national farm organizations conducted an educational campaign among their members.

In planning the present survey the Food and Drug Administration had the active cooperation of State, county, or municipal milk control officials in those areas selected as sampling stations. The Food and Drug Administration supplied the methods of analysis used in the survey for pesticide residues to interested milk control officials and dairy plant managers (*4*, *5*).

Objectives and Plan of the Survey

This survey extended beyond the determination of the incidence and range of pesticide residues in fluid milk. A main objective was to find the source of pesticide residues in all samples containing substantial amounts of any chlorinated organic pesticide. "Substantial"

The authors are with the Food and Drug Administration, Mr. Clifford serving as assistant to the director of the Bureau of Biological and Physical Sciences, Mr. Bassen as food and drug officer in the Bureau of Program Planning and Appraisal, and Mr. Mills as chemist in the Division of Food.

amounts, for this survey, were fixed at 0.1 ppm or more of pesticide residues. We were also anxious to test the value of another chemical screening procedure, namely, paper chromatography, as a control method for the average laboratory. We hoped to detect any seasonal differences in the occurrence of pesticide residues by conducting the survey over a 4-month period; thus from August through November there would be a change in the cow's diet from predominantly pasture to bulk and solid feeds. By including all 16 Food and Drug Administration Districts in the survey, the results might reveal differences in the incidence of pesticide residues in various parts of the United States.

Each Food and Drug Administration District, with the assistance of State and local milk control officials, selected one city in its territory in which to conduct the survey. The cities surveyed and the headquarters of the Food and Drug Administration District in which they are located were: Atlanta, Ga. (Atlanta); Washington, D.C. (Baltimore); Providence, R.I. (Boston); Buffalo, N.Y. (Buffalo); Chicago, Ill. (Chicago); Cincinnati, Ohio (Cincinnati); Denver, Colo. (Denver); Wichita, Kans. (Kansas City); Minneapolis, Minn. (Minneapolis); Los Angeles, Calif. (Los Angeles); New Orleans, La. (New Orleans); Metropolitan New York City (New York); Trenton and Camden, N.J. (Philadelphia); St. Louis, Mo. (St. Louis); San Francisco, Calif. (San Francisco); Seattle, Wash. (Seattle).

In each of these cities, three dairy plants were selected as monthly sampling stations. Thus, 48 sampling stations were included in the survey. Criteria used in selection were (*a*) an interest and desire on the part of management to cooperate in the survey; (*b*) a minimum of five milk pickup routes; and (*c*) feasibility of identifying each producer on each pickup route.

The survey was divided into three phases; phase A, the collection of fluid milk samples from bulk farm tank trucks (a few samples were composites from can routes) at each dairy; phase B, the collection of milk samples from individual producers from the pickup route found to contain "substantial" pesticide residues; and phase C, a visit to the farm producer whose milk collected under phase B contained "substantial" residues.

Under phase A, starting in August, 1-quart samples of milk from five milk pickup routes were collected monthly at each dairy. In subsequent months, five additional routes were to be sampled, so that over the 4-month survey period all or nearly all routes were sampled at least once. Among the selected dairy plants the number of routes varied from 5 with an average of 8 producers to 54 with an average of 20 producers. Thus, more intensive testing of the milk supply was possible at those plants with a small number of milk routes. For example, one dairy plant in San Francisco had only five routes and each route was resampled every month for 100 percent coverage of the milk supply. On the other hand, at a dairy plant in Cincinnati with 54 routes, only 20 routes were sampled during the survey period.

Analytical Methods

The samples were initally analyzed by paper chromatography (*4,5*) for residues of DDT, DDE, DDD, lindane, BHC, dieldrin, chlordane, methoxychlor, toxaphene, and heptachlor. Samples with substantial residues, that is, an estimated 0.1 ppm or more, were analyzed by more exact quantitative methods. Where available, official quantitative methods of the Association of Official Agricultural Chemists were used. Paper chromatography gives only semiquantitative results which are not directly comparable with the results obtained by specific quantitative methods.

Successful application of paper chromatography to milk fat demands a rigorous sample "cleanup" which involves the isolation of microgram quantities of pesticide from all but traces of fatty residues. The cleanup requires steps in which losses of pesticide are almost certainly bound to occur, namely, the acetonitrile partition, the chromatography through adsorbent columns, and the evaporation of the relatively large volumes of solvents.

Thus, the usefulness of paper chromatography as a screening procedure depends on the probability of not missing samples containing substantial residues. Of the 23 phase A samples found by the districts to contain substan-

tial residues by paper chromatography, 17 were also analyzed by the appropriate quantitative method. Four of the 17 samples showed no residues. Obviously, these samples can only indicate the extent of false positive results by chromatography whereas we are also concerned with false negatives. A number of districts analyzed some negative phase A and B samples by both paper chromatography and by quantitative methods. Of the 49 samples, there were no false negative results, that is, cases in which the quantitative method revealed substantial residues and paper chromatography did not.

Results

Of a total of 936 phase A samples, 23, or 2.5 percent, contained substantial amounts of residue (an estimated 0.1 ppm or more). DDT, DDE, and DDD were most commonly found. Toxaphene, chlordane, and BHC were encountered less frequently. The results for each district for the 4-month period are given in table 1. No trend was noted toward a higher incidence of samples with substantial residues during any particular month.

During October and November, each district submitted 10 duplicate samples to the Food and Drug Administration's Division of Food for check analysis. These were analyzed by paper chromatography and by fly bioassay. Table 2 summarizes the results by the two methods. By paper chromatography, the Division of Food found substantial residues in 5 of 168 samples (3.0 percent). This figure compares well with that found by the districts. DDT and DDE, DDD, dieldrin, chlordane, BHC, and lindane were found in that order. Indications of aldrin and of heptachlor or its epoxide or both were noted in a few cases. The florisil column eluates of 67 percent of the samples produced no symptoms in flies. Fifteen percent of these eluates caused mortality of more than 10 percent (more than 10 of 100 flies). The MgO column eluates caused no symptoms in 46 percent of the cases and mortality of more than 10 percent in 39 percent of the cases. The higher mortality for the MgO eluates may be due to minute traces of dieldrin, aldrin, or heptachlor epoxide; flies are especially sensitive to these pesticides.

Ten districts found one or more phase A

Table 1. Results on phase A samples examined by Food and Drug Administration Districts

FDA District	Chromatography				Identified by chromatography [1]				
	Number of samples	Number negative or with trace amounts	Number with substantial amounts	Percent with substantial amounts by districts	DDT	BHC	Toxaphene	Chlordane	DDD (TDE)
Atlanta	60	60	0	0					
Baltimore	60	58	2	3.3	1		1		
Boston	60	59	1	1.6		1			
Buffalo	60	59	1	1.6			1		
Chicago	60	60	0	0					
Cincinnati	60	57	3	5.0	2		1		
Denver	60	59	1	1.6	1				
Kansas City	60	55	5	8.3	3			2	
Los Angeles	60	60	0	0					
Minneapolis	30	30	0	0					
New Orleans	60	59	1	1.6	1				
New York	60	59	1	1.6	1				
Philadelphia	60	57	3	5.0	1				2
St. Louis	64	64	0	0					
San Francisco	62	57	5	4.2	[2] 5				
Seattle	60	60	0	0					
Total	936	913	23	2.5	15	1	3	2	2

[1] Samples with substantial amounts only.

[2] Some conversion to DDD.

Table 2. Results by Food and Drug Administration's Division of Food on 1958 check of milk samples

FDA District	Number of samples	Chromatography					Fly bioassay					
		Florisil column			MgO column[1]		Florisil column			MgO column		
		Number negative	Number showing traces	Number with significant amounts	Number negative	Number showing traces	No symptoms	Mortality <10 percent	Mortality >10 percent	No symptoms	Mortality <10 percent	Mortality >10 percent
Atlanta	10	------	10	--------	------	------	8	1	1	3	1	6
Baltimore	12	------	12	--------	------	12	9	1	2	1	1	10
Boston	10	4	6	--------	------	------	5	5	0	7	3	0
Buffalo	10	4	6	--------	4	6	4	3	3	4	5	1
Chicago	10	4	6	--------	------	------	10	0	0	8	0	2
Cincinnati	10	4	6	--------	5	5	10	0	0	10	0	0
Denver	10	5	5	--------	2	8	5	5	0	1	0	9
Kansas City	10	2	8	--------	------	------	10	0	0	15	0	5
Los Angeles	10	------	10	--------	------	------	6	1	3	6	4	0
Minneapolis	9	------	9	--------	------	9	9	0	0	9	0	0
New Orleans	10	6	4	--------	5	5	9	1	0	8	1	1
New York	10	1	8	1	3	7	4	1	5	2	2	6
Philadelphia	10	------	10	--------	------	10	7	1	2	0	0	10
St. Louis	17	6	11	--------	7	10	4	9	4	6	7	4
San Francisco	10	------	7	3	------	------	4	1	5	2	1	7
Seattle	10	------	9	1	------	------	9	0	1	5	0	5
Total	168	36	127	5	26	72	113	29	26	77	25	66
Percent		21. 4	75. 6	3. 0	[2]	[2]	67. 3	17. 3	15. 5	45. 8	14. 9	39. 3

[1] None showed significant amounts.
[2] Percentages not computed because of insufficiency of data.

samples to contain substantial residues. Nine of these districts proceeded to collect phase B followup samples. In table 3 are given the number of phase B samples collected by each of these districts and the results. Some of the negative results on the phase B samples may be attributed to a transient contamination with pesticide residues or to a delay in followup.

The eight producers whose milk was found to contain substantial residues in phase B were visited by Food and Drug Administration inspectors, usually accompanied by a State or local milk inspector, under phase C of the survey. The producers were questioned about their spraying practices around and in the barn, type and source of feed, and other likely sources of contamination. Samples of milk in all cases, and feed materials where indicated, were collected and analyzed for pesticide residues.

The Baltimore District investigated two producers in January 1959. Milk samples from these farms were negative for pesticide residues. The cows on both farms were fed a similar diet consisting of mixed dairy feed, clover or alfalfa hay or both, and grass or alfalfa silage. On one farm only one item, clover hay, was found to contain traces of DDT. On the other farm, alfalfa hay and alfalfa silage contained traces of toxaphene.

The Kansas City District investigated two producers under phase C. These producers were delivering milk to two different dairies. Followup at one farm revealed no detectable pesticide residues in any of the samples of hay, grain, and silage being fed. The sample of milk collected at the farm contained 0.03 ppm DDT. The source of the DDT in this producer's milk might have remained a mystery except for the investigation of the second producer. At the latter farm, samples of milk, hay, mixed grain, and silage were collected. The mixed grain, of intrastate origin, contained 0.32 ppm DDT and the milk, 0.3 ppm DDT. On questioning this farmer, the inspector learn-

ed that a commercial exterminator had sprayed this farmer's barn. The inspector visited the exterminator and found that he had sprayed a number of barns in the area with a 0.5 percent DDT solution. He acknowledged knowing that use of DDT around dairy barns was prohibited but finally admitted that he had used DDT because it was cheaper than some of the pesticides approved for use in dairy barns. Among the producers whose barns were sprayed by this exterminator, the inspector found the name of the first producer he had visited.

The New Orleans District investigated one producer under phase C. None of the feed materials—whole corn, wheat shorts, and cottonseed meal—contained pesticide residues although the milk contained 0.06 ppm DDT. A tentative explanation was contamination of pasture with DDT from an unknown source.

The San Francisco District found two producers' milk on one bulk tank route to contain substantial residues of DDT and DDD. Joint inspections were undertaken in December 1958 by the Food and Drug Administration, California Bureau of Dairy Inspection Services, and the fieldman of the dairy bottling plant which received this milk. At one producer's, no substantial residues were found in the milk. The second producer's milk contained 6.3 ppm DDT (8.0 ppm calculated as DDD). Subsequent samples of milk and corn silage from this producer, analyzed by the State Bureau of Dairy Inspection, revealed 4.8 ppm DDT in the milk and 12 ppm DDT in the silage. The State Bureau of Dairy Services suspended this producer from shipping milk. After this producer's milk was eliminated, a retest of the bulk tank route revealed only trace amounts of DDT. Contaminated corn silage grown on the producer's farm was the source of the pesticide residue in the milk.

The milk of the producer on the second route investigated by San Francisco District in February 1959 contained 2.0 ppm DDT. A sample of alfalfa hay being fed to the herd did not contain detectable residues of DDT. The inspection did not reveal the source of pesticide residue in this producer's milk supply.

Table 3. Results on phase B samples

FDA District	Number of bulk tank routes sampled	Number of samples	Number with less than 0.1 ppm	Number with substantial residues
Baltimore	2	21	19	2
Boston	1	9	9	0
Buffalo	1	10	10	0
Denver	1	11	11	0
Kansas City	2	17	16	1
New Orleans	1	2	1	1
New York	1	12	12	0
Philadelphia	1	13	13	0
San Francisco	2	21	18	3
Total	12	116	109	[1] 7

[1] Percent of samples with substantial residues: 6.0.

Discussion

Although it is difficult to compare the findings in this survey with those in the 1955 survey because more sensitive procedures have since been devised, it is quite clear that there has been a definite improvement in the milk residue picture. As in the 1955 survey, DDT was the most notorious offender in the current survey. Where the sensitive bioassay procedure was employed in essentially the same manner in both surveys (florisil column, table 2) 33 percent of the 1958 samples gave a positive test (which includes trace amounts) for chlorinated organic pesticide residues, as compared with 62 percent in the 1955 survey. Moreover, in the 1955 survey the samples consisted of market milk pasteurized and ready for the consumer; in other words, they represented the mixed output of many individual producers.

In the 1958 survey the primary purpose was to pinpoint the source of contamination. The samples were drawn from bulk tank trucks in which was mixed the raw milk output of only a few producers, generally less than a dozen. Thus, in the 1958 survey one might have expected a higher incidence of very excessive residues, but we did not find this.

Summary

In a 1958 survey conducted by the Food and Drug Administration, 936 samples of raw milk

from 48 dairies in 16 metropolitan areas in all sections of the United States were analyzed by the 16 Food and Drug Administration's Districts for residues of chlorinated organic pesticides by a paper chromatographic method. The survey was conducted over a 4-month period starting in August. Twenty-three samples (2.5 percent) showed residues of 0.1 ppm or more. Of the 936 samples, 168 were further examined by the Food and Drug Administration's Division of Food. By paper chromatography, five of these, or 3.0 percent, showed significant residues.

These 168 samples were also analyzed in the Division of Food by a fly bioassay procedure. Depending upon the cleanup technique employed, toxic reactions were noted in 33 percent of the samples (florisil column) and in 54 percent of the samples (MgO column). Significant mortalities (taken as more than 10 percent of 100 flies) were 15.5 and 39.3 percent, respectively. The difference in incidence between the chromatographic and bioassay methods is due to the fact that the bioassay reflects the sum of all residues toxic to the housefly. Also, flies are extremely sensitive to certain pesticides (lindane, heptachlor or its epoxide, dieldrin, and others) and a few hundredths of a ppm of these might not register on the paper chromatogram. Comparable figures for the previous and the present survey are: 67 percent positive reactions in 1955 and 33 percent in 1958.

Investigations to determine the source of pesticide residues were limited to eight producers whose milk was found to contain "substantial" residues. Of these, the source of contamination was definitely accounted for in only three cases. Feeding of DDT-contaminated corn silage (1.2 to 12 ppm DDT) was responsible for high residues, 4.8 and 6.33 ppm DDT, in one producer's milk. The contamination of the milk of the other two producers was traced to the careless spraying of barns with a concentrated DDT solution by a commercial exterminator.

The survey did not reveal any seasonal monthly differences in the occurrence of pesticide residues.

The survey showed that paper chromatography is a useful procedure in detecting substantial residues of organic chloride pesticides in fluid milk.

REFERENCES

(1) Jester, W. R., Wright, W. W., and Welch, H.: Antibiotics in fluid milk. Fourth nationwide survey. Antibiotics & Chemother. 9: 393–397, July 1959.

(2) Welch, H., Jester, W. R., and Burton, J. M.: Antibiotics in fluid market milk. Third nationwide survey. Antibiotics & Chemother. 6: 369–374, May 1956.

(3) Clifford, P. A.: Pesticide residues in fluid market milk. Pub. Health Rep. 72: 729–734, August 1957.

(4) Mitchell, L. C.: Ascending paper chromatography: A way to do it. J. A. Off. Agric. Chemists 40: 997–1029 (1957).

(5) Mills, P. A.: Detection and semiquantitative estimation of chlorinated organic pesticide residues in foods by paper chromatography. J. A. Off. Agric. Chemists 42: 734–740, November 1959.

Deaths From Septicemia

Septicemia and pyemia caused 1,633 deaths in 1958. Of these, 353 were staphylococcal, 64 streptococcal, and 30 pneumococcal. Other agents were specified for 90 of the deaths and 1,126 were unspecified. The increase in all deaths from septicemia and pyemia over the previous year was about 23 percent, and for staphylococcal septicemia it was about 63 percent. The number of deaths from sepsis among the newborn (infants under 1 month) was 1,055, an increase of about 27 percent over 1957. Deaths from septicemia during the period 1949 through 1957 were reported in *Public Health Reports*, April 1959, p. 354.