Bull. Environ. Contam. Toxicol. (1987) 39:587–592

Environmental Contamination and Toxicology

Occurrence of DDE in Dairy Feeds in the Arizona Milk Shed

F. M. Whiting, O. G. Lough, and W. H. Brown

Department of Animal Sciences, University of Arizona, Tucson, Arizona 85721

Dichloro-diphenyl-dichloroethylene (DDE), a chlorinated metabolite of the insecticide Dichloro-diphenyl-trichloroethane (DDT), and also an ingredient of the acaracide (miticide) Dichloro-alpha-trichloro-methylbenzhydrol (dicofol, Kelthane)[1] continues to occur in feeds of importance to the dairy industry in the State of Arizona (Whiting 1984). Dicofol has apparently replaced DDT as the primary source of environmental DDE and contains as much as 0.6% DDT (Camoni et al 1983), 10% alpha-chloro-DDT (Anonymous 1985) and 1.5% DDE [Personal communication Ware GW (1980) Assoc. Dir. Agr. Expt. Sta., U. of Arizona, Tucson]. Brown et al (1986) established that the major dicofol impurity, alpha-chloro-DDT, undergoes facile photochemical dechlorination, thereby providing a probable source for environmental DDE. As DDE is lipid soluble, it is readily secreted with milk fat by the cow. Research has shown that the most common route of entry of chlorinated hydrocarbons into the cow is through the ingestion of contaminated feedstuffs (Witt et al. 1966B). Feeding a diet above 0.100 ppm in total chlorinated hydrocarbon residues (on an as fed basis) can result in residues above the legal limit (0.050 ppm) in finished milk products (Witt et al. 1966A). When $\geq$ 0.041 ppm total chlorinated residues occur in raw milk, the United Dairymen of Arizona (the major milk marketing agency in Arizona) assesses a monitary penalty to the dairyman. [Personal communication Billotte MS (1987) United Dairyman of Arizona, P.O. Box 26877, Tempe, Arizona.]

DDE was reported in Arizona grown forages as early as 1961 and has been found primarily in crops grown adjacent to or rotated with cotton (Maiorino et al. 1980, Whiting 1984A). Amounts of DDE increased in soil, plant material and milk until use of the parent compound, DDT, was limited to non-agricultural uses by a state imposed moratorium in 1968. This was followed in 1972 by a national ban on the use of DDT. From that time detection of DDE diminished until chromatographic traces became masked by the presence of chlorinated camphene (Toxaphene[2]), the next chlorinated insecticide to become popular for use in Arizona agriculture.

Send reprint requests to F.M. Whiting at the above address.
[1]Rohm & Haas Co., Philadelphia, PA
[2]Hercules, Inc., Wilmington, DE

The State of Arizona imposed a moratorium on the use of Toxaphene for agriculture in 1979. Since that time, DDE has been the principle organochlorine residue found in locally grown dairy feedstuffs. When Toxaphene use was curtailed, it was analytically impossible to determine whether DDE found in livestock feed originated from the historic use of DDT, or from current use of the acaracide dicofol on such crops as citrus, cotton and ornamentals. The objectives of this study were to determine if feedstuffs could be responsible for the DDE contamination of Arizona milk and which commodities were the major offenders.

MATERIALS AND METHODS

Beginning in 1979 and continuing through 1985 the major feed commodities from six dairies located in the Salt River Valley (the primary milk shed in Arizona) were monitored. About 40% of the dry roughage and 100% of the wet roughage used by the dairies is produced in this same geographic region. Also about 70% of both the high energy ration components and by-product feedstuffs fed to dairy animals are grown in Arizona. The six subject dairies milked from 300 to 4,000 cows and were judged by the State Dairy Extension Specialist to be typical in size, mode of operation and production for the area [Personal communication, Armstrong DV (1986), Arizona Dairy Extension Specialist, Dept of Animal Sciences, U of Arizona, Tucson]. During this seven year time span, two operations sold out and were replaced by similar units in close proximity to the original dairies. All sample sites were located within a 50 km radius. Six of the seven years, samples were taken in late February or early March. In 1984 a similar series was also taken in October. Results were so nearly alike, the two sets of data were combined and are presented in averaged form for 1984. The following year (1985) samples were taken in the fall only. Because of lack of verifiable records concerning various feeds origins, no attempt was made to determine the mechanism by which DDE found its way onto or into feed materials. Contamination was assumed to be by sublimation, as described by Ware (1968) for DDT and by Whiting et al. (1984B) for DDE.

All samples in each defined period were taken within a 24 hour time span. Pre-mixed concentrate was taken from the hatch at the bottom of bulk storage silos (3-5 subsamples). High energy ingredients and alfalfa cubes were sampled around the perimeter of the bulk storage piles or across the front of the commodity storage compartments (5-30 subsamples). Silages were sampled at random heights along the exposed face of the pit (5-10 subsamples) and greenchop was collected directly from feed wagons (2-6 subsamples). Baled ration components were taken by using a coring device (15-75 subsamples). Depending on the product, from 1-3 kg of material were taken at each sample site. Samples were transported in plastic bags and frozen upon arrival at the laboratory. Prior to extraction and analysis, composited material was extensively mixed before subsampling. Silages and greenchop were oven dried to a constant weight at 37^{o}C. Extraction of

Table 1. Yearly average DDE content (ppm) of Arizona dairy feeds.

Feed	1979	1980	1981	1982	1983	1984	1985
				Wet Roughages			
Alfalfa Silage	*.280$_1$	NS	.230$_1$	.220$_1$	.120$_1$	.057$_4$	.144$_2$
Alfalfa Green Chop	NS	NS	.230$_1$	.207$_3$	.123$_3$	.068$_3$	.145$_2$
Sorghum Silage	040$_1$	.160$_2$	.140$_2$	.100$_1$	NS	NS	.053$_1$
Corn Silage	.077$_3$	.167$_5$	.367$_3$	.040$_4$	.083$_3$	.085$_{10}$	.089$_5$
				Dry Roughages			
Alfalfa Hay	.015$_5$	.054$_{10}$	.075$_8$	.046$_{11}$	.045$_8$	.048$_{31}$	.069$_{16}$
Oat Hay	.030$_1$	.090$_2$	NS	NS	.065$_2$	.019$_4$	.020$_1$
Alfalfa Cubes	.050$_2$	.120$_1$	.020$_1$	.160$_2$	.080$_1$	.076$_2$	.046$_1$
				By-Product Feeds			
Almond Hulls	NS	.060$_1$	.030$_1$	.015$_2$	.005$_2$	.007$_7$	.007$_5$
Citrus Pulp	NS	.001$_1$	NS	0$_1$	0$_1$	NS	.020$_1$
Cottonseed Hulls	.002$_2$	.004$_4$	.002$_1$	0$_2$	0$_1$	.001$_5$	.001$_2$
Beet Pulp	.105$_2$	NS	.153$_3$	.037$_3$	.067$_3$	.005$_8$	.013$_3$
				High Energy Feeds			
Concentrate Mix	.050$_2$	0$_3$	.017$_4$	.007$_3$	0$_2$	.001$_7$	0$_2$
Barley	.001$_3$	0$_1$	.005$_2$	0$_3$	.001$_2$	0$_{13}$	.001$_6$
Corn Gluten	.047$_3$	0$_1$	.003$_1$	.020$_1$	NS	0$_1$	NS
Cottonseed Meal	NS	.040$_1$	.002$_1$	0$_3$	0$_2$	.001$_2$	0$_3$
Ammoniated Whole Cotton Seed	.002$_1$	.009$_4$	.015$_2$	NS	NS	.004$_4$	.001$_3$
Whole Cotton Seed	.010$_1$	NS	.006$_2$	0$_3$	0$_5$	.001$_{10}$	0$_3$

NS = No Sample
*Subscripts 1-31 = No. of samples/mean

plant material was carried out by the methyl alcohol-chloroform method of Whiting et al. (1968). Florisil[1] column cleanup was by the method of Witt et al. (1966A). Quantitative analysis of pesticide residues in plant material was done using the method of Whiting et al. (1968).

RESULTS AND DISCUSSION

Comparison of feedstuffs, shown in Table 1, demonstrate that from 1979 through 1985 roughages were the primary contributor to the chlorinated hydrocarbon dietary load in the Arizona milk shed. Wet feeds were by far the worst offenders and DDE was the only organochlorine residue detected which was of significance.

Although the seven year trend was generally toward less DDE in all

[1]Floridin, Dallas, TX.

Table 2. Arizona sales of dicofol (1000's kg)

Year							
1978	1979	1980	1981	1982	1983	1984	1985
8.2	5.0	24.9	48.5	25.6	10.9	9.2	10.4

feedstuffs, different roughages peaked at various apparently unrelated times during this survey. In examining these data it is critical to keep in mind that except for 1984, the sampling date was a calendar year later than when most of the material was grown. This difference is important, as green chop is fed during the same time-frame in which it is grown while the other roughages and high energy feeds are often held for long periods before feeding.

The effect of record high sales of the acaracide dicofol (Table 2) (Council for Environmental Studies 1986) in 1981 seems to be directly reflected in the DDE analyses of all 1981 wet roughages (Table 1). It was assumed very few of the commodities studied were ever the major target crop for dicofol application (cotton being an exception). However, because dicofol is applied as either a dust or spray it is subject to atmospheric conditions which can cause it to drift onto other crops and soils. Early work by Gerhardt and Witt (1964) had shown major contamination beyond 3km with DDT. The conclusion being that most of the DDE detected in this study resulted from drift of dicofol applied to other crops. Although corn silage was the highest commodity tested both that year and during the entire study (0.367 ppm), green chop alfalfa and alfalfa silage were found to also contain relatively high amounts (0.230 ppm) in 1981. It seems consistent that when sampled in the spring of 1982, this same crop that had been cubed and stored for later use contained 0.160 ppm DDE, the highest level of contamination found in alfalfa cubes (Table 1) during this study. The DDE level for alfalfa silage was 0.280 ppm in 1979, however, the portion of this alfalfa crop which was processed into cubes to be fed in 1980 contained only 0.050 ppm DDE. No explanation for this dichotomy is evident. With the exception of cubed alfalfa (which peaked at 0.120 ppm in 1980 and 0.160 ppm in 1982), all dry roughages examined during this study were found to contain less than 0.100 ppm DDE. Oat hay was highest in 1980 (0.090 ppm) and in 1983 (0.065 ppm). This did not correspond to dicofol sales.

Although sorghum silage was often the wet commodity with the least DDE, it still contained enough residue to make a significant contribution to the dietary pesticide load. The elevated DDE levels in wet roughages in 1981 and corresponding high level in alfalfa cubes in 1982 can possibly be explained by the increased use of dicofol. This DDE containing acaracide was sold in 1981 at almost double the amounts in either 1980 or 1982.

Amounts of DDE in by-product feedstuffs does not seem to follow any logical pattern, and except for the two years that beet pulp contained over 0.100 ppm DDE, this category of feeds was residue free enough to be of no major concern. The relatively high amount of DDE found in beet pulp in 1981 probably has nothing directly to do with dicofol sales that year as this material was produced in 1980. At the beginning of this study certain commodities in the high energy portion of the milking ration (concentrate, corn gluten, cottonseed meal) contained enough DDE residue to cause concern, if fed alone with locally grown roughage. These feeds approached the 0.050 ppm DDE level, and if fed in disproportionate amounts in the diet along with contaminated feed, could have resulted in illegal residues in milk. From 1981 on, the level of DDE in this category of feeds, was low enough to be insignificant. More recent years have seen a general decline in DDE contamination levels of all feed commodities grown and utilized in the Arizona milk shed.

Most of the organochlorine residue problems in the Arizona milk shed originate in the roughage portion of the dairy ration, with the wet roughages being the prime offender. Residue levels in high energy feeds were of little or no consequence. DDE was the pesticide residue most often detected. During the time frame of 1979 through 1985, the source of this material probably originated in the acaracide dicofol.

Acknowledgments. Journal paper 4333 of the Arizona Agricultural Experiment Station.

REFERENCES

Anonymous (1985) DDT-contaminated pesticide can be used. Chem Eng News Aug 19, p 13

Brown MA, Ruzo LO, Casida JE (1986) Photochemical conversion of dicofal impurity alpha-chloro-DDT, to DDE. Bull Environ Contam Toxicol 37:791-796

Camoni I, Di Muccio A, Pontecorvo D, Citti P (1983) Study of p,p'- DDT impurities in commercial formulations based on dicofol (Kelthane). Nuovi Ann Ig Microbiol 33:241-247. Chem Abstr 101:34526v, 1984

Council for Environmental Studies (1986) Annual pesticide sales survey, Cooperative Extension Service, The University of Arizona, Tucson, Arizona

Gerhardt PD, Witt JM (1964) Pesticide residues and problems resulting from drift from aerial applications of dusts and sprays. Proc XIIth Intern Ext Congr, London 565

Maiorino RM, Whiting FM, Brown WH, Reid BL, Stull JW (1980) Quantitative determination of toxaphene in blood by Florisil extraction and gas chromatography. J Analyt Toxicol 4:192-198

Stull JW, Brown WH, Whiting FM, Witt JM (1968) An epidemiological study of pesticide contamination in milk on an operating dairy farm. Bull Envir Contamination Toxicol 3:135-140

Ware GW (1968) DDT-C^{14} translocation in alfalfa. J of Econ Entom 61:1451-1452
Witt JM, Angus RC, Stull JW, Brown WH, Whiting FM (1966A) Variations of pesticide residues in Arizona milk. J Dairy Sci 49:1406-1409
Witt JM, Whiting FM, Brown WH, Stull JW (1966B) Contamination of milk from different routes of animal exposure to DDT. J Dairy Sci 49:370-380
Whiting FM (1984A) Feed residues: 1984 update United Dairymen (The official journal of The United Dairymen of Arizona, Tempe, Arizona) 4:24
Whiting FM, Lingafeldt NE, Dobrenz AK (1984B) Translocation and sublimation of DDE in alfalfa. Arizona-Nevada Acad of Sci 19:101-105
Whiting FM, Stull JW, Brown WH, Milbrath M, Ware GW (1968) Comparison of extraction methods for analysis of DDT, DDE and DDD in alfalfa hay. J Dairy Sci 51:1039-1041

Received June 2, 1987; accepted June 16, 1987.