Mirex in Milk from Southeastern United States

by

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Throughout the Southeastern United States the imported fire ant(Solenopsis invicta Buren) is a major pest on ranches and dairy farms. Large mounds built by this ant interfere with haying and pasture maintenance, and the ants occasionally attack the cattle themselves. During the time this paper was written, the most effective and recommended means of controlling this pest is a bait containing the insecticide mirex (ANON. 1968) which is applied at the rate of 1.7 g actual toxicant/ acre once a year. In obtaining a registration and tolerance level for this material, Allied Chemical Company in the fall of 1961 monitored for mirex in whole milk and milk fat in a small herd of cattle grazing on a pasture treated with a single application of bait. They reported 0.002 to 0.007 ppm in whole milk and 0.03 to 0.13 ppm in milk fat (ANON. 1964, LOFGREN et al. 1964). The accuracy of these figures has been in doubt, however, since the same residue levels were found in pretreatment samples and in milk of untreated check animals. Eventually a tolerance level of 0.01 ppm for whole milk and 0.1 ppm for milk fat was established (ANON. 1969) and no further work or residues studies on mirex in milk was undertaken.

In the last 3 years, our laboratory at Gulfport has initiated a series of experimental studies on the movement and persistence of mirex in the environment and the occurrence of mirex in foods. The extensive use of mirex, the ability of cows to concentrate other chlorinated pesticides in their milk (ANON. 1959,HARDEE et al. 1964, SMITH and ARANT 1967) and the lack of recent attempts to monitor for it in milk were felt to indicate that this should be an extremely important area of study using the newer methods of pesticides monitoring.

COLLECTION OF SAMPLES

Field inspectors of Plant Protection & Quarantine Division, U. S. Department of Agriculture, were assigned the task of collecting the necessary samples. Living in the area, the inspectors were familiar with the various dairy farms and processing plants, and either knew or could easily determine the local treatment history. Inspectors were instructed to choose areas which had received two or more mirex treatments. A 1-quart milk sample was taken from the storage tank of a dairy or processing plant after verifying that all the milk had come from cows that had grazed

Bulletin of Environmental Contamination & Toxicology,
Vol. 11, No. 3

on treated areas. Ten or more such samples were to be taken from different locations in each of the States of Florida, Georgia, Louisiana, Mississippi, and South Carolina. After collection, 3 tablespoons of 38% M.F. formalin was added to each of the samples and shipped without refrigeration to the U. S. Department of Agriculture, Plant Protection & Quarantine Division laboratory at Gulfport, Mississippi, for analysis.

PROCESSING MILK SAMPLES

In processing, each milk sample received in the laboratory was thoroughly shaken 1 minute and a 100 ml sample removed, mixed with 10 ml aqueous potassium oxalate solution and 100 ml ethanol in a separatory funnel and shaken for 1 minute. Next, 200 ml of diethyl ether were added and the mixture shaken for 2 more minutes. Finally, 100 ml of pentane were added, the mixture shaken for 1 minute and then allowed to stand for 10 minutes. The aqueous layer was drawn off and discarded and after 10 more minutes of standing, any more residual water was separated and discarded. The extract was concentrated in a steam bath to approximately 20 ml or less, returned to a small separatory funnel and enough hexane added so that when the aqueous layer was again drawn off, 50 ml of solution remained. Next, the solution was washed twice with 10 ml of concentrated sulfuric acid and then washed two more times with 25 ml of distilled water. The sample was finally concentrated down to approximately 5 ml on a hot plate, run through a florisil column and concentrated under an air flow and steam bath to 2.5 ml in centrifuge tube.

ANALYSIS OF SAMPLES

Samples were analyzed on a Hewlett-Packard Model 402 using an Electron Capture detector. A 4-foot glass column packed with 3% DC-200 on 100-120 mesh Gas Chrom Q was employed using methane-argon as carrier gas. Temperature settings were: injection port, 240°C; oven, 200°C; and detector 205°C. A rapid carrier flow of 100 ml/min along with the high oven temperature allowed a fast retention time of 20 minutes to mirex.

One nanogram of standard solution gave approximately 25 peak height-units on this chart. Based on this, it was determined that a 10 ml injection (out of the 2.5 ml solution equalling 100 ml of original milk sample) should give an excellent degree of detection at 0.3 ppb. Other pesticides were not specifically analyzed for, although DDT and its by-products were found in most milk samples. The sulfuric acid wash also broke all organophosphate compounds and many of the other chlorinated hydrocarbon compounds.

RESULTS AND DISCUSSION

A total of 66 samples was received from 5 states. Six of these were from untreated areas and were processed for use as checks. The remaining samples were from areas which had been treated 2 to 5 times. Mirex applications are primarily made during spring or late fall to be most effective in controlling the imported fire ant. Eight of the samples were from areas where a spring treatment already had been applied a month or more before the sample was collected.

Twenty-six of the samples were from areas which had been treated the previous fall. The remainder of the samples was from areas which had received their last treatment a year or more prior to collection. Of the 60 samples analyzed, none had detectable mirex residues at the level of detection, 0.3 ppb. Many of the samples, however, did contain small but questionable peaks at the retention time for mirex. Attempts to confirm these peaks by TLC, fortifying and using additional columns were inconclusive. The lack of positive residues at the 0.3 ppb level was actually rather surprising. It has already been shown that beef cattle grazing on treated pastures can accumulate very small residues of mirex (on an average less than 10 ppb) and the grass from such pastures has been found to contain small traces of mirex (less than 0.1 ppb). It is therefore presumed that milk cattle must be receiving some small amounts of mirex, but apparently not enough to show up in the milk at the residue levels we were searching for. Mirex will probably be found as additional improvements are made in the analytical techniques to improve its range of detection to less than 0.3 ppb, or if the sample were taken closer to the time of treatment.

In general, it has been established by these experiments that milk coming from cattle grazed on treated areas may contain extremely minute quantities of mirex; but the amounts are so small that they are at least 100 times lower than the presently established tolerance levels for milk.

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