Effects of Processing on Pesticide Residues in Milk

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EFFECTS OF PROCESSING ON PESTICIDE RESIDUES IN MILK 1, 2, 3

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SINCE the discovery, over 25 yr. ago, that certain chlorinated hydrocarbons had potential for use as insecticides or pesticides, man has proceeded to disseminate these chemicals throughout his environment. Marth (1965) indicated they can be found in biological material almost everywhere some form of life exists. The length of time they will remain in the environment is unknown.

As a result of their presence and persistence in soil, water, and biological material, these pesticides enter the food chain in many ways. Under present and future management and food production practices we can expect to find small quantities of pesticide residues in our food supply. The significance of minute amounts of these chemicals in the food supply, over a long period, on human health is a much discussed and unanswered question. Will there be a genetic effect over a number of generations? This is just one part of the new interest by man in controlling his environment.

Man's food can serve as a continual source of chemical residues which may accumulate in lipide-material of the human body (Durham, 1963). It is important that the food supply, at the point of consumption, is monitored and a running record is kept to determine any changes in amounts of residues present in the normal human diet.

The Food and Drug Administration has carried on a testing program since 1963 for foods purchased in the marketplace (Duggan and Dawson, 1967). Samples are obtained from 30 cities in the U.S. A total of 30 samples per year per city are analyzed. The data indicated that a nutritionally well-balanced U.S. diet also contained the following residues:

- chlorinated organic chemicals—0.02 ppm
- organic phosphate chemicals—0.003 ppm
- chlorophenoxy chemicals—0.003 ppm
- carbamate chemicals—0.05 ppm

Duggan and Dawson (1967) noted a slight increase from 0.08 mg./day to 0.12 mg./day in chlorinated pesticides from 1963 to 1964, but the levels have remained static since 1964. Dairy products, eggs and fish were listed as foods needing close monitoring for changes.

Many tolerances on raw agricultural products are now set and others appear to be forthcoming. The dairy industry finally succeeded in obtaining a DDT tolerance (Federal Register, 1967). With the residues present on raw products and the interest in residues at the consumer level, it became important to know the effects of processing on residues present in foods. This is important from two aspects: (1) effects of normal processing on residues with (2) possible use of processing as a means of intentionally removing residues from foods.

Possibilities for removal of residues during processing of foods include concentration in one fraction and discarding of that fraction, destruction or removal by processing procedures or reduction in toxicity during processing. A summary by Crosby (1965) revealed that limited information was available on processing to remove residues from food. Virtually no research had been reported using animal food products. As reported by Henderson (1965), residues in milk were present and caused some concern in industry circles. Since 1964, research has increased. The advent of easier and more sensitive methods of analysis for many chemical residues in biological materials may be responsible.

Recent reports (Kim and Harmon, 1967; Li and Bradley, 1967; Montoure and Muldoon, 1967; Kroger, 1967; Bills and Sloan, 1967) included research on effects of cheese manufacturing and ultraviolet irradiation on residues in milk, and effects of residue on lactic cultures and use of distillation for removal of residues from milk-fat. Ultraviolet light degraded chlorinated hydrocarbons but rendered the milk unacceptable in flavor at the same time (Li and Bradley, 1967). Over 95% of selected insecticides were removed from milk-fat by distillation (Kroger, 1967; Bills and Sloan, 1967), which could be useful if the need arises.

Research at Purdue on the effects of processing dairy products on chlorinated insecti-
icide residues was initiated during 1961. The first requirement was the development of an analytical technique. A clean-up procedure of samples prior to electron capture gas chromatography was developed (Langlois et al., 1964; Stemp et al., 1964). This consisted of a one-step florisil column extraction and clean-up procedure. Sample sizes of products used for analysis varied with the fat content of the samples.

Sensitivity of the procedure varied with the insecticide being analyzed (Langlois et al., 1964). The sensitivity of the procedure was increased by using a larger sample and by other modifications (Stemp and Liska, 1965). The sensitivity as described proved suitable for our research needs but is less than some procedures in use now.

Lindane, DDT, dieldrin, heptachlor, endrin, telodrin, methoxychlor, chlor dane and endosulfan were either fed to lactating dairy cows or added directly to milk (Langlois et al., 1964). In some cases the cow metabolized the parent compound to yield metabolites which appeared in the milk. This was especially true for heptachlor, DDT, and endosulfan. When residue levels in the milk reached the desired level, the milk was processed into various dairy products using pilot plant or laboratory scale equipment (Langlois et al., 1964).

Following separation, residues were found almost entirely in the fat fraction and the skim milk fraction was essentially free of residues. Contaminated milk therefore, could be separated to salvage the skim milk portion which could be used fresh or dried without danger of residues being present above acceptable levels. In a short study, butteroil produced from milk containing DDT showed that 28 to 53% of the DDT could be removed during processing (Liska, 1965). Modifications of the process might improve the efficiency of DDT removal.

Butter, cheese and ice cream were processed from milk containing selected residues. In brief, there was no destruction or removal of residues from the products. The residue content expressed on a fat basis remained fairly constant throughout processing and storage (Langlois et al., 1964; Langlois et al., 1965). This is not surprising since heat applied to these products during processing is not severe.

In further experiments, contaminated milk was processed into spray and drum-dried whole milk and sterilized or evaporated milk. With the heat treatments used for processing of these products some significant changes were noted in residue content during processing. A summary of the results is presented in tables 1 and 2. There was a reduction in concentration of both heptachlor epoxide and dieldrin during condensing. This reduction represented about one-half of the insecticide present in the raw milk. Heptachlor and endrin were not affected by condensing. There was some reduction in concentration of heptachlor, heptachlor epoxide, dieldrin, and endrin during spray and drum drying. Heptachlor showed the largest reduction during the drying operation.

The only significant reduction of DDT and lindane occurred during the manufacture of dry whole milk. Concentrations of both DDT and lindane were reduced during the spray drying and roller drying. Similar results were obtained in duplicate experiments.

Sterilization caused some degradation of DDT to form DDD and DDE. Except for this shift in structure no other detectable changes in the structure of either DDT or lindane were detected during the manufacture or storage of dairy products.

In general, except for reduction of insecticide concentration during condensing, drying or sterilizing the results indicate that the insecticides studied are quite stable under the conditions used in this study. The amount of insecticide in butter and cheese is less than

<table>
<thead>
<tr>
<th>Product</th>
<th>DDT</th>
<th>Lindane</th>
<th>Dieldrin</th>
<th>Heptachlor</th>
<th>Heptachlor epoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw milk</td>
<td>26.0</td>
<td>25.0</td>
<td>19.3</td>
<td>3.7</td>
<td>21.2</td>
</tr>
<tr>
<td>Condensed milk</td>
<td>23.1</td>
<td>26.4</td>
<td>11.4</td>
<td>3.9</td>
<td>11.0</td>
</tr>
<tr>
<td>Sterilized milk</td>
<td>25.1</td>
<td>25.6</td>
<td>11.2</td>
<td>3.8</td>
<td>12.6</td>
</tr>
<tr>
<td>Spray-dried milk</td>
<td>9.9</td>
<td>4.4</td>
<td>8.5</td>
<td>0.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Drum-dried milk</td>
<td>4.3</td>
<td>9.3</td>
<td>9.1</td>
<td>0.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>

* Average of three trials.

b Averaged to nearest 0.1 ppm.
PESTICIDE RESIDUES IN MILK

TABLE 2. DESTRUCTION OF TELODRIN, METHOXYCHLOR, CHLORDANE, ENDOSULFAN AND ENDOSULFAT SULFATE DURING THE PROCESSING OF MILK INTO STERILIZED AND DRIED MILK

<table>
<thead>
<tr>
<th>Product</th>
<th>Telodrin</th>
<th>Methoxychlor</th>
<th>Chlordane</th>
<th>Endosulfan</th>
<th>Endosulfan sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw milk</td>
<td>18.3 b</td>
<td>23.1</td>
<td>19.7</td>
<td>15.9</td>
<td>15.2</td>
</tr>
<tr>
<td>Condensed milk</td>
<td>17.8</td>
<td>21.1</td>
<td>17.5</td>
<td>11.4</td>
<td>12.6</td>
</tr>
<tr>
<td>Sterilized milk</td>
<td>10.2</td>
<td>18.6</td>
<td>10.8</td>
<td>9.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Spray-dried milk</td>
<td>16.3</td>
<td>22.7</td>
<td>14.7</td>
<td>10.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Drum-dried milk</td>
<td>16.5</td>
<td>23.3</td>
<td>9.9</td>
<td>8.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

a Average of two trials.
b Averaged to nearest 0.1 ppm.

during the manufacture of evaporated milk. The loss varied from 40 to 50%.

A slight decrease in methoxychlor content on a fat basis was also obtained for the evaporated milk. High-temperature treatment appears to destroy a portion of the telodrin and methoxychlor residues in milk.

Results obtained by separating raw milk containing telodrin and methoxychlor into cream, skimmilk, and butteroil were not encouraging, although a higher telodrin content on a fat basis was noted in cream as compared with raw milk, the methoxychlor content on the fat basis was relatively unchanged from that detected in raw milk (Stemp and Liska, 1966). The skimmilk contained no insecticide residues except for a trace of telodrin in one sample. These results indicated that the insecticide residues were not removed during the separation procedure but were concentrated in the high milk fat-containing product. Further conversion of the cream into butteroil indicated that the insecticide residues were further concentrated into the milk fat portion. The insecticide residue levels detected in the butteroil on a fat basis were approximately equal to those noted in raw milk. Thus, no removal of telodrin and methoxychlor residues was obtained during the preparation of butteroil.

The distribution of endosulfan sulfate, the oxidized metabolite of endosulfan, and chlordane was studied in various manufactured dairy products prepared from milk of cows administered these insecticides. The amount of endosulfan sulfate in condensed milk represented a 17.1% decrease (fat basis) as compared with levels in the fat from raw milk. Chlordane decreased 11.2% during this manufacturing process. Further decreases in the endosulfan and chlordane residues of milk were noted as the condensed milk was processed into dried or evaporated milk. The endosulfan sulfate found in spray-dried evaporated and roller-dried milk represented approx-
imately 42.0, 42.0 and 70.0% decrease, respectively, of that present in the milk prior to processing. The percentage decrease of chlordane for these products was approximately 25.0, 45.0 and 50.0%, respectively.

The data accumulated indicate that there was a similar reduction of endosulfan and chlordane residues found in various manufactured dairy products prepared from milk to which the insecticides were added. A relatively small percentage of destruction of the insecticides occurred during the condensing process. During the processing of milk into spray-dried, evaporated, and roller-dried milk, the percentage decrease of endosulfan was approximately 37.5, 38.7 and 50.0, respectively, of the amount found in raw milk while the percent decrease of chlordane was 11.0, 24.0, 25.0, 45.0 and 50.0% respectively. In general, the data show a greater decrease of endosulfan and endosulfan sulfate than chlordane during the manufacture of milk powder and evaporated milk from raw milk containing the insecticides.

Other research on processing effects included poultry meat. In brief, edible tissue could be processed by rendering out the fat, which also removed the insecticide residues; the processed meat was essentially free of insecticide (Liska et al., 1967). This same procedure should apply to other meats.

Summary

Chemicals of various types will enter the food chain and eventually be consumed by man. The amount at present appears to be at a safe low level. Continued monitoring is essential to determine if changes occur.

The studies on effects of processing on selected chlorinated insecticide residues in milk indicated that heat treatments used for milk drying and sterilization destroyed some of the residues present. The amount of residue destroyed varied with processing treatment and nature of the insecticide residue.

Spray drying destroyed in excess of 80% of the lindane residues in raw milk while sterilization caused essentially no change in lindane residues. Heptachlor was destroyed more easily than heptachlor epoxide. Of the insecticides studied, methoxychlor was the most stable to heat treatments used in milk processing.

Most chlorinated insecticides are relatively resistant to processing techniques used for milk and dairy products. Once residues get into milk they are stable and difficult to remove; therefore, the best policy is to prevent their entrance into milk by proper and careful management of the dairy cow.

Literature Cited


