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Residues of Chlorinated Pesticides in Processed Foods Imported into Hawaii from Western Pacific Rim Countries

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For the past several decades, considerable attention has been focused on pesticide residues in or on foods and foodstuffs produced in the United States. This concern was initially formalized in 1954 with the passage of the Miller Amendment to the Food, Drug, and Cosmetic Act (Thoney and Bisogni 1992). Initially, interest was centered on application procedures and their safety (Kilgore and Akesson 1980), as well as on the pesticide residues remaining in food (FDA 1992) and their implications related to human health (Doll and Peto 1981; Takei et al. 1983). More recently, significant interest has been directed to pesticide residues in foods imported into the U.S. from developing countries, as well as from a number of the nations which border on the Pacific Rim (GAO 1992; Wehr 1992). In the United States, the risks associated with the legal, appropriate uses of natural and synthetic pesticides fall well below those of microbiological contamination in food and of nutritional excesses and deficiencies (Hall 1992; Gold et al. 1992). It might be difficult, however, to create a comparable ranking of hazards for foods imported into the United States, especially for processed food. It might also be difficult to predict where on that ranking pesticide residues should be placed. Although a number of Pacific Rim countries, such as Japan, Taiwan, and Korea, have been developing tolerance levels for pesticide residues in unprocessed food commodities, in general the number of tolerances and the number of associated commodities are far less than those established in the United States (Wehr 1992). In addition, the use of a number of pesticides has been severely restricted or totally eliminated in the United States; but, use of some of these pesticides is still allowable in other counties (Moses 1992).

We chose to focus our attention on processed foods, rather than fresh commodities for two reasons; first,

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there are substantial legal requirements associated with moving fresh products in and out of Hawaii; second, there is an enormous variety of processed foods from foreign countries which are widely available throughout Hawaii. We selected processed foods which are common to diets in Hawaii, which are routinely imported from various western Pacific Rim counties, and which could be found in Oriental or Asian food sections of many supermarkets in the continental U.S. Thus, the primary objective of this study was to determine whether or not these food products from Pacific Rim counties contained residues of selected pesticides lindane, heptachlor, chlorpyrifos, gamma chlordane, dieldrin, and pp'-DDT).

MATERIALS AND METHODS

Food Products: About 40 different food products were purchased from large supermarkets in the Honolulu metropolitan area; nineteen of these products were analyzed for pesticide residues (Table 1).

Table 1. Imported processed food products categorized by extraction procedure.

Non-Fatty samples	Fatty Samples
Dry/dried food Arare cracker[1] Dried seaweed (nori) Dried radish Oriental cracker[2] Pepper leaves Somen noodles[3] Tempura batter mix Udon noodles[4]	Oriental-style noodle soup Oriental party beans[5] Prepared seaweed (furikake)[6] Roasted green peas[5] Sesame seeds
Canned food Baby corn Bamboo shoots Black bean sauce Prepared vegetables[7] Water chestnuts	Mandarin oranges

[1] Rice and nori (seaweed) cracker
[2] Rice cracker
[3] Very fine wheat noodles
[4] Large wheat noodles
[5] Snack foods, dried and flavored; party beans = horse beans
[6] Condiment which contains sesame seeds, seaweed and spices
[7] Chinese cabbage, daikon radish, eggplant, Japanese cucumber

Some of the foods were highly processed, such as tempura batter, crackers and noodles. Other foods were purchased dried, such as sesame seeds, seaweed or "nori", and "furikake." Still others were canned, such as mandarin oranges and baby corn. Countries of origin of the products included Korea, Japan, Thailand, China (Mainland and Hong Kong), and Malaysia.

All foods were analyzed for residues of six pesticides: pp'-DDT, lindane, heptachlor, dieldrin, chlordane, and chlorpyrifos. Most or all of the registered uses of the first five compounds in the U.S. have been canceled; chlorpyrifos is still widely used in U.S. agriculture in a number of formulations (Meister 1992).

Twenty or forty gram samples of each food were extracted. Depending on the cleanup procedure used to extract the residues, each sample was categorized as either fatty or non-fatty (Table 1).

Non-fatty samples: A 40-g sample was blended with 400 mL hexane and then vacuum filtered through glass fiber backed by a paper filter. The extract was dried through anhydrous sodium sulfate and then evaporated to 1 mL on a rotary evaporator. The sample was then cleaned up on a 1.4 mm O.D. x 10 cm highly activated Florisil column; eluates of 25 mL hexane, 25 mL 5% diethyl ether in hexane, and 50 mL 10% diethyl ether in hexane were collected. The hexane eluate contained heptachlor and a portion of pp'-DDT; the 5% diethyl ether eluate contained lindane, chlorpyrifos, gamma chlordane, and the remainder of pp'-DDT; and the 10% diethyl ether eluate contained dieldrin. Eluates were evaporated to appropriate volumes and injected into a gas-liquid chromatograph (GLC) for analysis.

Fatty samples: A 40-g sample was blended with two 200 mL portions of 35% water in acetonitrile, and each time vacuum filtered through glass fiber backed by filter paper. The combined filtrate was shaken with 100 mL hexane in a 1 L separatory funnel. 10-mL of a saturated sodium chloride solution and 400 mL water were added. The mixture was shaken and the phases allowed to separate. The hexane phases were combined in the 250-mL separatory funnel and washed gently with two 100-mL portions of water. The hexane extract was filtered through anhydrous sodium sulfate into a 250 mL round-bottom flask and evaporated to 1 mL on a rotary evaporator. The sample was cleaned up on Florisil and analyzed as for non-fatty samples.

Two GLCs, each having either identical Hall electrolytic conductivity detectors or electron capture detectors, were operated simultaneously. Conditions for the first GLC: 1) 1.0 μm methyl silicone, 0.75 mm I.D. x 30 M megabore capillary column 2) Column flow: 11 mL/min helium 3)Temperature program: 100°C initial temperature, 4-min hold time, 10°C/min rate, 275°C final temperature, 0-min final hold time 4) Injector temperature: 275°C. Conditions for the second GLC used for confirmation: 1) 1.5% OV17/1.95% OV210 mixed phase, 2mm I.D. x 3M packed column 2) Column flow: 30mL/min helium 3) Temperature program: 150°C initial temperature, 2-min hold time, 5°C/min rate, 195°C final temperature, 7-min final hold time 4) Injector temperature: 250°C.

RESULTS AND DISCUSSION

Of the nineteen food products whose samples were analyzed, nine foods contained evidence of chlorinated hydrocarbon residues, the levels of which ranged from at or near the sensitivity of the analytical technique (0.25-0.50 ppb) to about 10-12 ppb. As shown in Table 2, heptachlor and dieldrin residues were measured and confirmed in only one product each: "somen"/very fine wheat noodles and oriental party beans, respectively. Chlorpyrifos and gamma chlordane residues were detected each in two different food products: chlorpyrifos in oriental-style noodle soup and roasted peas; gamma chlordane in oriental party beans and prepared seaweed. Lindane was detected in three foods: black bean sauce, prepared seaweed, and sesame seed. pp'-DDT was the most consistent contaminant; residues were detected in four products (black bean sauce, pepper leaves, sesame seeds, and udon noodles).

The results from this investigation clearly indicate that low levels of various chlorinated pesticide residues are present in some processed foods that are imported from western Pacific Rim countries into Hawaii. These foods are also available in ethnic food sections of supermarkets in the continental United States. Residues were found at or near the limit of detection for the method. Thus, further study is warranted in which a large enough sample would be processed which would provide enough material for confirmation by FT-IR or mass spectrometry. Alternatively, a GLC method is which compounds are converted to metabolites for confirmation could be used.

Why might residues of these pesticides, whose use in the U.S. is either restricted or eliminated, be appearing in the imported foods? Data on worldwide production and use of pesticides is not reliably available (Ekstrom 1990). It appears, nonetheless, that estimates of current patterns and amounts of

Table 2: Ppb[1] chlorinated pesticide residues in foods as measured on capillary columns.

	Lindane	Heptachlor	Chlorpyrifos	Gamma Chlordane	Dieldrin	pp'DDT
Black bean sauce	1.08	N.D.	N.D.	N.D.	N.D.	1.45
Oriental-style noodle soup	N.D.[2]	N.D.	4.70	N.D.	N.D.	N.D.
Oriental party beans	N.D.	N.D.	N.D.	2.70	3.45	N.D.
Pepper leaves	N.D.	N.D.	N.D.	N.D.	N.D.	4.23
Prepared seaweed (furikake)	3.12	N.D.	2.08[3]	0.48	N.D.	N.D.
Roasted peas	N.D.	N.D.	10.95	N.D.	N.D.	N.D.
Sesame seeds	2.34	N.D.	N.D.	N.D.	N.D.	1.08
Somen noodles	N.D.	0.62	N.D.	N.D.	N.D.	<1.00[3]
Udon noodles	N.D.	N.D.	N.D.	N.D.	N.D.	1.65

[1] Parts per billion
[2] Not detected, below detection limit
[3] Not confirmed

pesticides use in the United States, Canada, and Western Europe are similar; herbicides constitute the majority of all agricultural pesticide use in these countries. Pesticide use patterns in other parts of the world, including the Asia-Pacific region, may, however, be more representative of the United States in the 1950's, when chlorinated insecticides were heavily used. China, South Korea and Indonesia are large consumers of pesticides in the Asia-Pacific region; a number of these pesticides are the chlorinated hydrocarbons whose agricultural uses are either restricted or eliminated in the United States (Moses 1992).

With the cooperation of the U.S. Customs Service, the Food and Drug Administration (FDA) systematically monitors imported food commodities from over 100 countries for pesticide residues; the largest number of samples were from Mexico (Wessel 1991). In 1991, less than 1% of the samples tested had above tolerance residues, and 2% had residues for which there was no tolerance for that particular pesticide/commodity combination. However, fewer than a thousand imported products, in total, were tested from the nearly 20 countries in the western Pacific Rim region; and, the vast majority of these foods were fresh or minimally processed products (FDA 1992).

Some would argue that the residues which we have detected do not result from current purposeful uses, but rather are due to the stability of the chemicals in the environment and their persistence from past times of heavy, widespread use (Wessel 1991). However, Moses (1992) has suggested that about one-third of the pesticides not useable in the United States are still being manufactured and exported to other countries. Unfortunately, in many cases, the use of these pesticides is still legal in the country of import. Finally, the fact that we have found residues in highly processed foods argues against the persistence theory. Low background levels of a pesticide present in a raw commodity from past usage should be reduced substantially or eliminated completely with extensive processing (Elkins 1989, Wessel 1991); yet we are able to detect evidence of one or more chlorinated pesticides in about half of the processed foods that we analyzed.

Do these residues in processed foods present a danger to health? If so, to whom? It is difficult, if not impossible, to argue that these minute traces of pesticides pose any substantial risk for acute toxicity. However, concern about chronic toxicity may not be so easily brushed aside, especially for more susceptible sectors of the population such as children (NRC/NAS 1993), the elderly (Lu 1991), or persons with compromised immune system function (Thomas and House 1989). For example, children have a longer time to live and a longer time to be exposed than adults. Furthermore, their food consumption patterns may differ from adults and their periods of rapid growth and development may make them differentially more susceptible to absorption of trace amounts of substances in their diet. Thus, these trace contaminants may represent legitimate concerns, but further research must be conducted in order to determine their relative risk in specific population groups.

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