Bull. Environ. Contam. Toxicol. (1994) 53:524–527
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Environmental Contamination and Toxicology

HCB Levels in Spanish Sterilized Milk

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Received: 12 August 1993/Accepted: 27 March 1994

HCB contamination arises from its use to protect wheat from the blight (*T. foetidae* and *T. caries*), against which diseases it is very effective. However, although its use has been banned since the seventies, it is still found in food products due to its persistence in the enviroment (it has a half life of approximately eight years in soil) and because it is found as a contaminant in other fungicides: quintozene (pentachloronitrobenzene) and the herbicide dacthal (1,4-benzenedicarboxylic acid, 2, 3, 4, 5, 6-tetrachlorodimethyl ester). Due to its high degree of toxicity, HCB is responsible for cutaneous porphyria in man (Vetorazzi, 1975). Although the FAO/WHO (1974, 1978) has been recommending a careful study of this compound in foodstuffs for several years, it is still found in studies of dairy products and human milk. (Krauthacker et al. 1986 and Krauthacker, 1991). Because of its importance, we have studied the levels of HCB in Spanish sterilized milk and the influence which the sterilizing process has on these levels.

MATERIALS AND METHODS

A total of 208 samples of Spanish sterilized milk were analyzed after extraction of the fat content by acetone and petroleum ether in accordance with Belgie Norm (1979). The fungicide was extracted using the method of Bush et al. (1983), in a florisil column eluted with hexane. Several pesticides were thus obtained, including HCB. Florisil was activated by heating at 200°C for 12 hours and deactivated with 2% double distilled water.

The HCB was determined with a Hewllet Packard 5890 gas chromatograph with electron capture detector, using a 2 m x 2 ml i.d. glass column packed with 5% QF-1 on Chromosorb (80-100 mesh). The operating temperatures were: injector 225°C, oven 190°C and detector 225°C. The carrier gas was argon-methane at a flow-rate of 34 ml/min. Quantification was carried out using the external standard method.

The material used for fat and HCB extraction was cleaned up using the method of Garrido et al. (1992).

Solvents were distilled according to the Food and Drug Administration (1975) using, in addition, a glass column with Rasching rings with sodium hydroxide and calcium hydroxide and active carbon. Purity tests were carried out in all cases. No peak should be higher than 1 cm.

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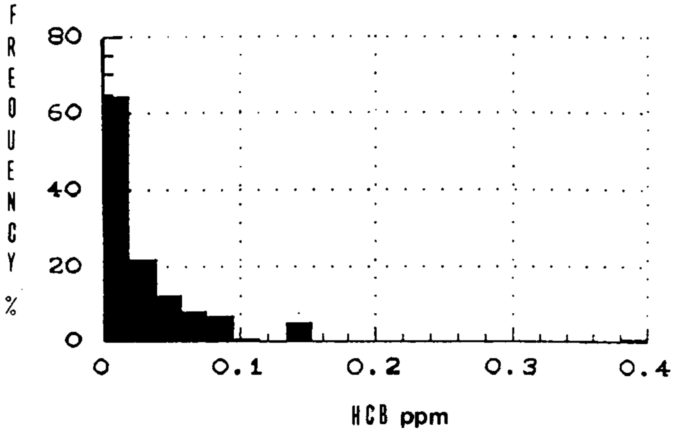

Figure 1. Frequency of HCB in Spanish sterilized milk. Data correspond to 208 samples.

To study the effect of the sterilization temperature on HCB, a certified milk was used from a farm periodically submitted to control by the Spanish Ministery of Health. The fat content (Rösse-Gottlieb) was determined in quadruplicate.

100 ml of milk was added to nine screw-top flasks with a capacity of 250 ml, five of which were contaminated with 3 ppm HCB. Two flasks contained uncontaminated milk as blank. Sterilization was carried out in an automatic autoclave at 115°C for 15 minutes. The last two flasks were contaminated with the same quantity of HCB (3ppm) but were not submitted to heat treatment. Fat and pesticides were extracted according to the techniques previously described.

RESULTS AND DISCUSSION

The mean level of HCB contamination in the milk samples studied was 0.019 ppm, below that detected by several authors (Pozo et al. 1977; Martínez and Juárez 1979; Lauro et al. 1984; Pompa et al. 1984 and Frank et al. 1985). Contamination ranged from 0.0007 to 0.382 ppm (fig.1). 57.7% of the sterilized milks contained HCB, lower than the 76% of Pompa et al. (1984) and Lauro et al. (1984), but similar to the 60% found by Frank et al. (1985).

A comparison of our results with those of Pozo et al. (1977) and Martínez and Juárez (1979), who also studied Spanish sterilized milk, shows that the concentration of HCB in milk has been reduced by about 93%, similar to the reductions noted in Canada after restrictions were imposed on the use of HCB (Frank et al. 1985).

However, in spite of this reduction, 24% of the samples analysed still exceed EC Regulation (1986), which limit HCB concentration in milk and dairy products with a fat content equal to or abcve 2% to 0.025 ppm. The average daily intake of HCB from milk was calculated as 0.000209 mg per person. This figure is based as the average daily consumption of milk in Spain (343 ml/person/day), according to the National Institute of Statistics (1985), and the mean concentration of HCB in the milk samples studied (0.019 ppm) and is one hundred times less than the ADI recommeded maximum of 0.0006 mg/kg of body weight. Spanish sterilized milk, then, does not represent an immediate health risk to the consumer as regards HCB content although the possible long term mutagenic and carcinogenic effects should not be ignored and the fat that is found in so many samples should cause concren. Its use as fungicide and its presence in other fungicides, such as pentachloronitrobenzene (PCNB), should perhaps be further restricted.

Although the concentration of the synthetic fungicide in milk decreases with sterilization (115°C, 15 min) the compound is not totally eliminated. The mean drop in HCB concentration after treatment was 73.68%, the individual percentages in each of the five batches of contaminated milk being 73.38; 74.72; 74.32; 73.20 and 72.81 %, respectively. This result differs from that obtained by Renterghem (1976), who showed that HCB increases after the same treatment. This can be explained if we take into account the observations of Mendez et al. (1979) concerning the affinity of organochlorines for fat, namely that they are found in the lipid phase of the milk and are associated to polar compounds. This makes their quantitative extraction difficult although technological processes, which act by breaking up the fat globules, disassociating casein micelles, etc, facilitate their extraction. This could be the cause of the apparent increase in HCB content in milk observed by Renterghem (1976), since the milk used in his experiments had previously been homogenized.

In our experiment the milk used was not homogenized before being sterilized and so HCB might have been more difficult to extract. Differences also seem to arise according to whether the pesticides were added to the milk or entered it physiologically (Renterghem, 1976). However, Hugunin and Bradley (1971) and Ang and Dugan (1973), when studying the results obtained by extracting dieldrin from physiologically and artificially contaminated milk, found no significant differences due to the method of contamination.

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