Bull. Environ. Contam. Toxicol. (1996) 56:381-388

Bulletin of Environmental Contamination and Toxicology

Insecticide Residues in Baby Food, Animal Feed, and Vegetables by Gas Liquid Chromatography

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Received: 11 June 1995/Accepted: 30 August 1995

India is among a few developing countries where organochlorines are still used for controlling pests due to economic constraints. DDT and HCH are still used for controlling pests of public, health especially malaria vector. The residues of these pesticides are known to find their way into milk and milk products (Mukherjee and Gopal 1992a). In our earlier publication (Mukherjee and Gopal 1992a), baby milk food was not included, it was considered of interest to monitor baby milk food, and animal feed samples for the presence of persistent compounds (Matsumura 1975). For evaluating the level of contamination and for identification of persistent and harmful chemicals, monitoring studies are essential. Besides monitoring of baby milk food and animal feed for organochlorines, vegetables samples were procured for quantifying the residues of various pesticides currently being used in Delhi and surrounding areas. The study can indicate which pesticides need to be banned or require longer waiting period.

The following pesticides were surveyed in different consumable food products (a) isomers of DDT, (b) isomers of HCH, (c) organophosphorus pesticides and (d) synthetic pyrethroids.

MATERIALS AND METHODS

Baby milk food and milk powders of different brands were purchased from the market. The milk food was prepared as per instructions given on the container. The milk samples were extracted and cleaned-up following the procedure of Mukherjee and Gopal (1992a).

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Different types of animal feed (for cow, buffalo, cattle and poultry) were collected from different parts of Delhi . 12 samples were analysed for HCH residues and 12 for DDT residues in triplicate. 25g animal feed sample was homogenised in a Waring blender with acetone (3x50 ml) . The extract was concentrated under reduced pressure. It, was trasferred to a separatory funnel and saline water (2%, 150 ml) was added to it . The extract has partitioned into hexane (3x30 ml) . The hexane extract was subjected to clean up by the addition of concentrated sulphuric acid (25 ml) . The cleaned hexane port i on was washed with water , dried over sodium sulfate and subjected to analysis.

Various vegetable samples (15) were procured from farms in Delhi during 1992-93 . The time of sampling was morning . Representative treated and control samples of cauliflower , cabbage , spinach , eggplant , raddish (roots and leaves) , okra, pea and chickpea pods were collected when they were ready for sale at the farm gate . The details (history)of application were ascertained and the samples were analysed for various organophosphorus insecticides and synthetic pyrethroids used on the vegetables.

The vegetable samples (50 g) were extracted with acetone (3x50 ml) . The acetone extract was concentrated under reduced pressure . Saline water (2%, 150 ml) was added to it and the organophosphorus pesticide partitioned into chloroform (3x50 ml). The chloroform extract was concentrated under vacuum to 5 ml and subjected to column clean up by passing through a prewashed column of celite, magnesia, charcoal (2:1:2, by weight). The column was eluted with a mixture of hexane -acetone (9:1 by volume, 100 ml). The eluate was concentrated and subjected to gas chromatography.

For metasystox the chloroform portion was concentrated and subjected to oxidation with potassium permanganate (Mukherjee and Gopal 1993). It was estimated as metasystox sulfone.

The concentrated acetone extract was transferred to a separator-y funnel and saline water (2%, 150 ml) was added to it. The solution was subjected to liquid-liquid partitioning using hexane (3x30 ml). The synthetic pyrethroids were subjected to column clean-up by following the procedure given by Mukherjee and Gopal (1992b).

The cleaned samples of baby milk food, animal feed and vegetables were analysed by gas liquid chromatography (glc) on a Varian GLC3400 . Organophosphorus pesticides malathion , methyl parathion, monocrotophos and metasystox-R were estimated using thermionic specific detector (TSD) . The details of temperature, column used and retention time are given in Table 1. The flow of the carrier gas was 30 ml/min, that of air and hydrogen were 100 and 4.5 ml/min, respectively. The synthetic pyrethroids fluvalinate , fenvalerate , cyhalothrin and organochlorines , e . g . HCH and DDT were determined

by using Ni^{63} electron capture detector . The identity of all the pesticides was confirmed by carrying out the analysis on an alternate column of varying polarity.

Table 1. GLC conditions of pesticides

S. No.	Pesticide	Column (liquid phase*)	Temperature(°C) Column	Injection port	Detector	Retention Time (min)
1.	Malathion	OV-101	200	250	280	2.50
2.	Methyl Parathion	OV-101	200	220	280	2.34
3.	Monocrotophos	OV-101	195	225	275	11.00
4.	Oxydemeton-methyl sulfone	OV-101	210	230	280	6.73
5.	Fenvalerate	OV-210+ OV-17	265	275	300	7.80 8.40
6.	Fluvalinate	OV-210+ OV-17	255	265	300	11.50
7.	Cyhalothrin	OV-101	230	265	350	8.00
8.	Endosulfan	OV-225	240	300	350	alpha 1.20 beta 2.40 sulfate 4.28
9.	Lindane	HP-17 megabore	150	200	250	2.50
10.	HCH	OV-210+ OV-17	program $	220	250	HCH 4.68 HCH 5.99 HCH 7.32 HCH 8.15
11.	DDT	"	"	"		"p,p'DDE 14.28 p,p'DDT 16.55 p,p'DDD 16.60

* 3%, $ programmed from 175°C for 8 min and raised @ 5°C/min to 220°C

Results and Discussion

The milk samples were analysed for organochlorines. A typical aspect of this pollution was observance of low level of residues, often near the detection limit . It is evident from Table 2 that DDT is detected in most samples of baby milk food. Although, the use of DDT has been banned in agriculture it is still used in cowsheds and around it to keep it free of flies and ants. This explains why DDT is still detected in baby milk food. MRL of DDT in milk is 0.05ug/g (whole milk basis, FAO/WHO 1986). This value is exceeded in five out of six samples showing an alarming situation.

The use of HCH in agriculture has been restricted, though it is still used in paddy fields and on pulse crops. HCH isomers were detected in substantial amounts in baby milk food (Table 3). Our earlier communication on dairy milk also observed that the dairy milk contained HCH. In milk powder the gamma content (lindane) was below the permissible limit (MRL<0.004ug/g) in four out of six samples . This is due to higher water solubility of lindane in comparison to its stereoisomers . The samples of baby milk had average residue levels ranging from non-detectable to 0.225 ug/g for DDT and from 0.002 to 0.102ug/g for HCH.

Table 2. DDT residues in baby milk food

Sample	p,p' DDE	p,p'DDD	p,p'DDT	Total Residues (ug/g)
1.Brand I	0.066	0.097	0.062	0.225
2.Brand II	ND	0.048	0.022	0.070
3.Brand III	ND	0.029	0.022	0.051
4.Brand IV	0.057	0.057	0.030	0.146
5.Brand V	ND	ND	ND	ND
6.Brand VI	0.001	0.015	0.035	0.051

ND-not detectable

In animal feed and its components average DDT residues ranged from non detectable to 0.251ug/g (Table 4). The highest residue was recorded in rice husk (0.251ug/g) followed by cotton seed cake (0.072 ug/g) , whereas mustard seed cake contained 0.069ug/g of the total DDT. Mustard seed cake and cotton seed cake are often present in animal feed and this may be one of the sources of contamination in bovine milk.

Table 3. HCH residues in baby milk food

Sample	Alpha	Beta	Gamma	Total Residues (ug/g)
1.Brand I	0.007	ND	0.092	0.099
2.Brand II	0.004	0.006	0.008	0.018
3.Brand III	0.005	0.001	0.001	0.007
4.Brand IV	0.025	ND	0.077	0.102
5.Brand V	0.002	ND	ND	0.002
6.Brand VI	0.007	ND	ND	0.007

ND- Non detectable

Table 4. DDT residues in animal feed and its components

Commodity	Average Residues (ug/g) P,P' DDE	P,P' DDD	P,P' DDT	Total Residues (ug/g)
1. Wheat straw	0.018	ND	0.045	0.063
2. Paddy straw	ND	ND	ND	ND
3. Rice husk	0.128	ND	0.123	0.251
4. Gram straw	ND	ND	ND	ND
5. Mustard cake	0.010	ND	0.059	0.069
6. Cotton seed cake	0.051	ND	0.021	0.072
7. Wheat grain	0.034	ND	0.001	0.035
8. Gram grain	ND	ND	ND	ND
9. Maize grain	ND	ND	ND	ND
10.Animal feed(straw+cake+water)	ND	ND	0.011	0.011
11.Green fodder	0.02	0.002	0.004	0.026
12.Berseem	ND	ND	ND	ND

HCH residues (average of three replicates, alpha, beta and gamma isomers) ranged from 0.007 ug/g in mustard seed cake to 1.860 ug/g in gram straw (Table 5). As compared to DDT residues in mustard and cotton seed cake, the HCH residues were much less these commodities. Gram grain and gram straw contained HCH residues in significant amount. This may be due to the use of HCH, which is recommended for controlling pests

of pulse crops.

Table5 . HCH residues in animal feed and its components

Commodity	HCH Residues(ug/g)			Total Residues (ug/g)
	Alpha	Beta	Gamma	
1. Wheat straw	0.008	0.075	0.029	0.112
2. Paddy straw	0.011	0.013	0.011	0.035
3. Rice husk	0.299	0.271	0.334	0.904
4. Gram straw	0.270	1.025	0.565	1.860
5. Mustard cake	0.007	ND	ND	0.007
6. Cotton seed	0.013	0.078	ND	0.091
7. Wheat gram	0.003	0.016	ND	0.110
8. Gram grain	0.198	0.050	ND	0.248
9. Maize grain	0.002	ND	0.008	0.010
10.Animal feed(straw+cake+water)	0.035	ND	0.032	0.067
11.Green fodder	0.004	0.007	0.05	0.016
12.Berseem	0.011	0.004	0.002	0.01

Appropriate methods for recovery of malathion, metasystox-R, methyl parathion, monocrotophos, fenvalerate, fluvalinate, lindane and cyhalothrin residues from the edible portion of various substrates on which they were applied , were carried out. before attempting the estimation of residues in the farm gate samples of Vegetables . The level of fortification were I and 5 mg/kg. Recovery values ranged from 78 to 98%, hence no correction has been incorporated in the actual residues recorded,

The results are exhibited in Tables 6. The level of residues of various pesticides were low (not detectable to 0.09 ug/g) in most of the commodities . However , monocrotophos residues were found to be around 0.6ug/g on eggplant malathion 0.30 ug/g on cauliflower and fenvalerate around 0.6 ug/g in eggplant fruit.

The maximum residue level (MRL) of monocrotophos and

fenvalerate on egplant is not available . Taking the values of other organophosphorus and synthetic pyrethroid (cypermethrin) on eggplant for comparison, it is observed that MRL of phorate and malathion is 0.1 and 0.5 ug/g, respectively, and MRL of cypermethrin on eggplant is 0.2 ug/g (FAO/WHO 1986) . The observed residues for monocrotophos and fenvalerate exceed the MRL of a similar group of pesticides.

Table 6. Pesticide residues in farm gate samples

S.No.	Pesticide	Commodity/Vegetable	Average* Residues (ug/g)
1.	Malathion	Cauliflower	0.30
2.	Metasystox	Cauliflower	0.01
3.	Fenvalerate	Cauliflower	0.08
4.	Metasystox	Cabbbage	0.06
5.	Spinach	Methyl Parathion	ND
6.	Eggplant	Monocrotophos	0.60
7.	Eggplant	Fenvalerate	0.16
8.	Raddish root	Methyl Parathion	0.005
9.	Raddish leaf	Methyl Parathion	ND
10.	Okra	Endosulfan	0.22
11.	Okra	Malathion	0.50
12.	Okra	Malathion	ND
13.	Pea	Cyhalothrin	0.07
14.	Chickpea	Lindane	0.05
15.	Chickpea	Fluvalinate	0.03

*Average of three replicates

The pesticides surveyed in milk, animal feed and vegetables indicate that though pesticides are detected in these food commodities, they are not present in such significant amounts , that they may pose health hazard except in case of milk. If the need based application of pesticides is made in recommended **dosage** and appropriate pesticide is used specific for the crop insect pest and disease and proper disposal, transportation and storage is adhered to the problem of environmental pollution will not be a threat.

Acknowledgments Thanks are due to Dr. Ram Singh of Vegetable Sciences discipline of IARI for arranging farm gate samples of vegetables and Head. Division of Agricultural Chemicals for facilities provided . Contribution No. 576 of the Division of Agricultural Chemicals.

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