Persistent Organic Pollutants (POPs) in Human and Bovine Milk from Northern Part of India

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Introduction

Milk is an excellent source of nutrition for every age group because it contains the balanced blends of fat, carbohydrates, protein etc and it possesses a powerful immune factor that imparts resistance towards chronic diseases like asthama and allergies. Globally, milk is considered complete food item due to its nutritional value. In India, a large population is vegetarian and drink milk as major dietary intake in daily food items [1,2,3].

Persistent organic pollutants (POPs) comprise the group of pollutants that are semi-volatile, bioaccumulative, persistent and toxic. Organochlorines (OCs) such as polychlorinated biphenyls (PCBs) and chlorinated pesticides represent an important group of POPs that cause worldwide concern as toxic environment contaminants[4,5,6]. Chlorinated pesticides (CPs) have been used extensively especially in tropical countries in malaria control programme as well as for agricultural pests. CPs have been prohibited in most of the countries but 70% of the banned pesticides are still used in India due to misuse and lack of awareness and because of their low cost[7]. In India, DDT and HCH are banned for agricultural uses since 1985 and 1997, respectively but 7500 metric tones of DDT and 36,000 metric tones of HCH is still used for public health [8]. Being highly lipophilic, CPs are primarily stored in fat-rich tissues in the mammals and excreted through milk fat. Hence, milk is considered as one of the important foodstuffs for measuring CPs residues. Widespread contamination of CPs in bovine milk and human milk samples have been reported [9,10].

Environmental occurrence of POPs is a global problem rather than regional or national. Therefore, a study was undertaken to monitor the trace levels of some chlorinated pesticide residues in human and buffalo milk of Agra region, India to assess the risk to infant and other consumers.

Materials and Methods

Agra and its neighborhood located in the state of Uttar Pradesh (27^0 10'N78^0 02 E') was chosen for the study. It is located in the north central part of India. Bovine and mother milk samples were collected monthly at random from several dairy farms and hospitals. Human milk was collected from age group of 20-40 years who live in rural parts in the region. The milk samples were immediately analysed after collection without storing in the laboratory. Extraction of milk (human and buffalo) for CPs was done with the mixture of acetone, acetonitrile and n-hexane and cleanup of the co-extractives was done using glass column with Florisil[11]. Analysis of CPs in milk samples was achieved using a Thermofinnigan trace model GC equipped with ^{63}Ni ECD. The carrier gas was (IOLAR I) Nitrogen. The injector port was splitless with an injection volume of 1μl. A BP_5 5% phenyl 95% dimethyl polysiloxane (30 m x 0.25 mm x 0.25 μm, film thickness). The operating conditions were: injection port temperature, 250^0C; column temperature, 150^0C hold initial 5 min then increased @ 10^0C/min to 280^0 C hold 10 min; detector temperature, 350^0C. To predict and check the quality of the method, a recovery study was performed on spiked milk samples. Limit of detection (LOD) and limit of quantitation (LOQ) were 1.0 μg L^{-1} and 2.5 μg L^{-1} for all the CPs. Spiked milk samples at 0.5 mg L^{-1} level of each pesticide were analysed in triplicate. Mean recovery percentage with standard deviation (± SD) for pesticide namely, α-HCH, β-HCH, γ-HCH, δ- HCH, p,p′-DDT, o,p′-DDT, aldrin, heptachlor and heptachlor epoxide were 89.9± 2.0, 87.8 ±1.8, 90.7± 1.1, 87.9± 2.4, 96.2± 1.9, 86.9± 2.4, 93.2± 3.2, 89.0 ±1.3 and 91.2 % ± 2.3.

Results and Discussion

Milk samples were analyzed in triplicate for recovery efficiency and mean percentage recovery values were recorded to check the quality of method. The mean percentage recovery was 86.9±2.4 to 96.2 %±1.9 with standard deviation less than 9 indicating good recovery for the method. Bovine and human milk samples recorded presence of CPs namely p,p′-DDT, o,p′-DDT, α-HCH, β-HCH, γ-HCH, heptachlor and heptachlor-epoxide, while δ- HCH and aldrin were not present in any sample. The data on the amount of the pesticides detected in human and bovine milk are presented in Table 1. Total concentration of DDT residues in human and bovine milk was 15.2 and 18.3 μg L^{-1} on whole milk basis. Isomer of DDT *viz*. p,p′-DDT was predominant contaminant and was frequently detected in the milk samples rather than o,p′-DDT. Isomers of HCH *viz.*α-HCH, β-HCH and γ-HCH having mean concentrations 9.45, 14.5 and 9.98 μg L^{-1}, respectively were present in bovine milk while 7.87, 17.8 and 12.1 μg L^{-1} in human milk.

Table 1. Residues levels in chlorinated pesticides in bovine and human milk samples

Chlorinated Pesticide	Residues of pesticides in μg L^{-1}	
	Bovine milk n = 27	**Human milk n= 21**
α-HCH	R: 2.0 - 15.0 (9.45 ± 0.06)	R: ND – 13.0 (7.87 ± 1.2)
β-HCH	R: 3.4 – 21.2 (14.5 ± 0.09)	R: 5 – 26.1 (17.8 ± 1.7)
γ-HCH	R: 4.2-16.4 (9.98 ±1.23)	R: 5.4-19.0 (12.1 ± 0.5)
δ-HCH	ND	ND
HCH (Total)	(33.93 ± 0.66)	(37.77 ± 0.62)
p,p′-DDT	R: ND- 15.2 (8.5 ± 2.91)	R: 3.4 – 16.6 (9.9 ± 3.2)
o,p′-DDT	R: ND – 10.2 (6.7 ± 1.91)	R: ND- 14.3 (8.4 ± 1.2)
DDT (Total)	(15.2 ± 0.70)	(18.3 ± 1).4
Aldrin	ND	ND
Heptachlor	R: ND-11 (6.4 ± 0.80)	R: ND- 9.0 (6.4 ± 1.09)
Heptachlor epoxide	R: ND-10.3 (5.3 ±0.78)	R: ND- 14.5 (5.6 ± 0.9)
Heptachlor (Total)	(11.7 ± 0.014)	(12.0 ±0.13)

n, Number of samples; R; range; Figures in parentheses donate mean value and standard deviation (± SD); ND, non detectable

β-HCH isomer was one of the most common isomer present in human and bovine milk because it is most persistent HCH isomer and eliminates slowly from the body than γ-HCH[11]. Total mean value of HCH in bovine and human milk was 33.39 ± 0.66 and 37.77 ± 0.62 μg L^{-1} that shows human milk was slightly more contaminated than bovine milk. Total DDT residues in human milk were comparatively higher than in bovine milk. Maximum residue limits prescribed by WHO for aldrin, HCH and heptachlor in milk are 0.15, 0.1 and 0.15 mg kg^{-1}, respectively. Levels of DDT and its isomers were below the prescribed MRL of 0.05 mg L^{-1}. None of the bovine and human milk samples had violative residues of CPs.

In the present study, the mean total DDT level in the human milk was 18.3 μg L^{-1}. Hence a 3 kg infant consuming 500 ml of milk daily will ingest 0.003 mg /kg/body wt/ day which is lower than the recommended 0.005 mg kg^{-1} ADI for DDT by WHO[15]. The results obtained from other monitoring studies from other parts of India were compared and are presented in Table 2. Results indicated that concentrations of the CPs are on decline in human as well as in bovine milk.

Table 2. Concentration (μg L^{-1}) of organochlorine pesticide residues in bovine and human milk in various parts of India

Cities	Σ-HCH	Σ-DDT	Aldrin	Heptachlor	References

Human milk					
Delhi	175.0	26050.0	--	--	Nair et al.[12] 1996
Mumbai	289.0	510.0	--	--	Sharma et al.[13] 2001
Agra	37.77	18.8	ND	12.0	Present study
Bovine milk					
Delhi	71.0	150.0	--	--	Mukhejee et al.[10] 1993
Mumbai	30.0	41.0	--	--	Pandit et al.[14] 2002
Lucknow	177.0	23.0	--	--	Nigam et al.[9] 2001
Agra	33.93	15.2	ND	11.7	Present study

$\sum$-HCH = α-HCH+β-HCH+γ-HCH+δ-HCH, $\sum$-DDT = p,p′-DDT + o,p′-DDT

The presence of chlorinated pesticides is the cause of concern if their residues are violative. So it is necessary to monitor these contaminant residues in food and environmental samples regularly. This study showed the presence of the CPs in trace level in bovine and human milk due to their use and misuse in sanitation and agricultural purpose. These POPs cannot be eliminated from environment by simply avoiding their use, as many years are required for them to disappear from the environment due to their inherent persistency.

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