

# Quantification of Organochlorine Pesticide Residues in the Buffalo Milk Samples of Delhi City, India

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## ABSTRACT

The ill effects of green revolution include residues of extensively used chemical pesticides in various environmental components. The present study was designed to analyze the levels of organochlorine pesticide residues along with chemical composition in buffalo milk samples collected from different localities of Delhi. Milk monitoring can yield information about the kinds and quantities of pesticides in the environment as well as in our daily diet. In this study, the residue of three different organochlorine pesticides, namely Hexachlorocyclohexane (HCH), Dichlorodiphenyltrichloroethane (DDT) and Endosulfan have been reported. Residues of Lindane exceeded the Maximum Residual Limit values in 50% of the samples is a cause of serious concern. The p,p'-DDT was detected in 70% of the samples with p,p'-DDE (dichlorodiphenyldichloroethylene) in 80% of the milk samples of different parts of Delhi state. DDD (Dichlorodiphenyldichloroethane) another metabolite of p,p'-DDT was detected in 65% of the milk samples. The analysis indicates that DDT is the major contaminants in different parts of Delhi state.  $\alpha$  and  $\beta$  endosulfan were detected in 35% and 40% of the samples analyzed. The statistical correlation shows no significant correlation between chemical compositions of the samples. The presence of multiple chemicals in virtually all samples of buffalo milk raises new questions about the possible toxicological impacts of chemical mixtures on an infant's developing nervous and immune systems and reproductive organs.

**Keywords:** Organochlorine Pesticides; Residues; Buffalo Milk; Delhi

## 1. Introduction

The milk and its products, which are nutritionally enriched, with superior biological potential and the one without health risks, are usually demanded [1-3] which include neurodevelopmental delay [4], reproductive effects [5], preterm & small-for-gestational-age babies [6] and immunotoxicity [7]. The presence of any chemical in milk is a cause for concern and great strides are taken throughout the dairy industry to assure the purity of the milk. The presence of multiple chemicals in virtually all samples of milk raises new questions about the possible toxicological impacts of chemical mixtures on an infant's developing nervous and immune systems and reproductive organs. During key stages of development, these parts of the body are known to be very sensitive to the exposures of chemicals, including pesticides. Milk is nearly a perfect natural food widely used in all segments

of the population in all stages of life [8,9]. Milk is considered as a nearly complete food as it contains a good source of protein, fat and major minerals [10] which serves as a source of energy. For the marketing in many developed countries such as the US and Switzerland, milk is highly used by cosmetics industry in manufacturing several skin whitening soaps, body lotions, shampoos, hair conditioners creams and after shave lotions [11].

Being one of the highest levels of the trophic chain and due to its lipophilic nature [12,13], milk has been usually studied as an indicator of the bioconcentration process of environmentally persistent organic micropollutants, such as organochlorinated (OC) pesticides [14]. Organochlorine pesticides were extensively used to increase the production of agricultural crops by preventing losses due to pest [15]. Worldwide production and use of Organochlorine compounds (OCs) since 1950s have resulted in their widespread occurrence in the environment. They have also been used to control various factors,

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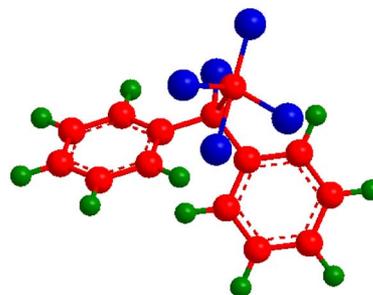
which spread diseases like malaria or plague [16,17]. Serious health problems such as heart diseases, cancers, damage the nervous system, reproductive and endocrinal damages, Alzheimer's and Parkinsonism disease may be the consequences of pesticides in food. As pesticides persist in the environment for a long time and as a consequence, they enter the human body through the food chain [8,18,19]. Poisoning cases in human beings are characterized by headache, dizziness, gastrointestinal disturbances, numbness, apprehension and hyperirritability and weakness of the extremities. Adverse health effects are not expected from consuming water with pesticides below the maximum residue limits. Maximum residue limits for parent OC pesticides have been set by several organizations such as FAOCodex Alimentarius [20] and European Union [21].

The cow, milker, extraneous dirt, environment or unclean water may be the reason of milk contamination [22]. The possible number of ways in which pesticides can reach milk are as follows: 1) high level of pesticide residues in foodstuffs from post-harvest treatment or by drift during commercial aerial application, inhaled air or contaminated water, 2) foodstuffs manufactured from plant material that has been treated during the growing season with insecticides *i.e.* contamination through feed, grass/hay [23], 3) use of insecticides directly on the animals against disease vectors, 4) use of insecticides in stables for the treatment against flies, 5) in milk processing factories for hygienic treatments against insects. The contamination of milk from source 1) and 2) with pesticide depends on the stability of the compound, its mode of application, the duration of intake or exposure and its metabolic fate in the animal. Due to their lipophilic properties [13], pesticides are primarily stored in fat-rich tissues and subsequently translocated and excreted through milk fat [24,25].

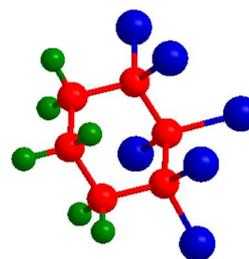
Studies have been carried out on pesticidal contamination of food stuff from different parts of the world [26-32]. Limited information is available from India on the nature of pesticide residues in milk. Milk samples from various parts of India contained DDT (Dichlorodiphenyltrichloroethane) and HCH (Hexachlorocyclohexane) residues [7,33-37]. The Organochlorine Pesticide (OCP) residues in buffalo and goat milk from Lucknow have been reported [38]. Kathpal *et al.*, (1992) and Kumar and Nath (1996) have reported residues of DDT in milk collected from Haryana and Himachal Pradesh, respectively [39, 40]. Human milk has also been reported to be contaminated by various pesticides in a range of  $0.1 \text{ mg}\cdot\text{l}^{-1}$  -  $25.7 \text{ mg}\cdot\text{l}^{-1}$  concentrations [41].

The presence of residues of persistent organochlorine pesticides in various components of the environment is a matter of great concern all over the world. The purpose of the present study was to determine the concentration

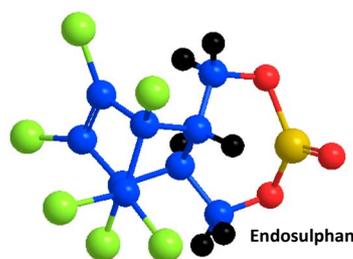
of DDT (Dichlorodiphenyltrichloroethane), HCH (Hexachlorocyclohexane) and endosulphan residues in buffalo milk samples collected from different locations of Delhi, India. The structures of the DDT and HCH are mentioned below.



Dichlorodiphenyltrichloroethane ( $\text{C}_{14}\text{H}_9\text{Cl}_5$ )



Hexachlorocyclohexane ( $\text{C}_6\text{H}_6\text{Cl}_6$ )



Endosulphan

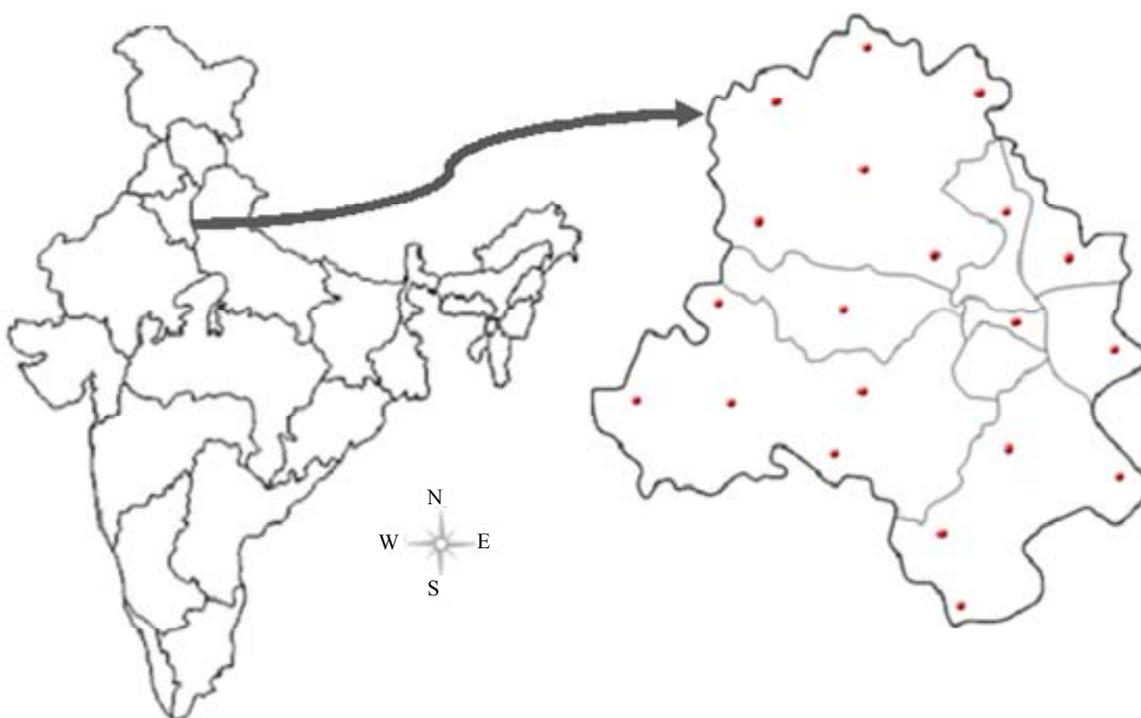
## 2. Materials and Methods

### 2.1. Milk Samples

Twenty fresh buffalo's milk samples were collected from several farms located in different districts of Delhi, viz., south (S), south west (SW), west (W), north (N), north east (NE), north west (NW), east (E) and central delhi (CD), in clean and sterilized glass bottles (**Figure 1**). The sampling was carried out during the period of January 2012 to September 2012. The milk samples were kept on ice immediately after collection, transferred to the environmental science laboratory at Jamia Millia Islamia and preserved at  $-20^\circ\text{C}$  until analyzed.

### 2.2. Chemicals and Pesticide Standards

All the chemicals used in the study were of analytical



**Figure 1.** Map of the study area showing the different sampling locations.

reagent (AR) grade. Dichloromethane, hexane, and acetone used were all pesticide grades, while silica gel, sodium chloride, and anhydrous sodium sulfate were all analytical grades. These chemicals were purchased from Sigma Aldrich. Organochlorine Pesticide (OCP) standards of Dichlorodiphenyltrichloroethane (DDT), Hexachlorocyclohexane (HCH) and Endosulfan were purchased from Accustandards.

## 2.3. Methods of Analysis

### 2.3.1. Chemical Analysis

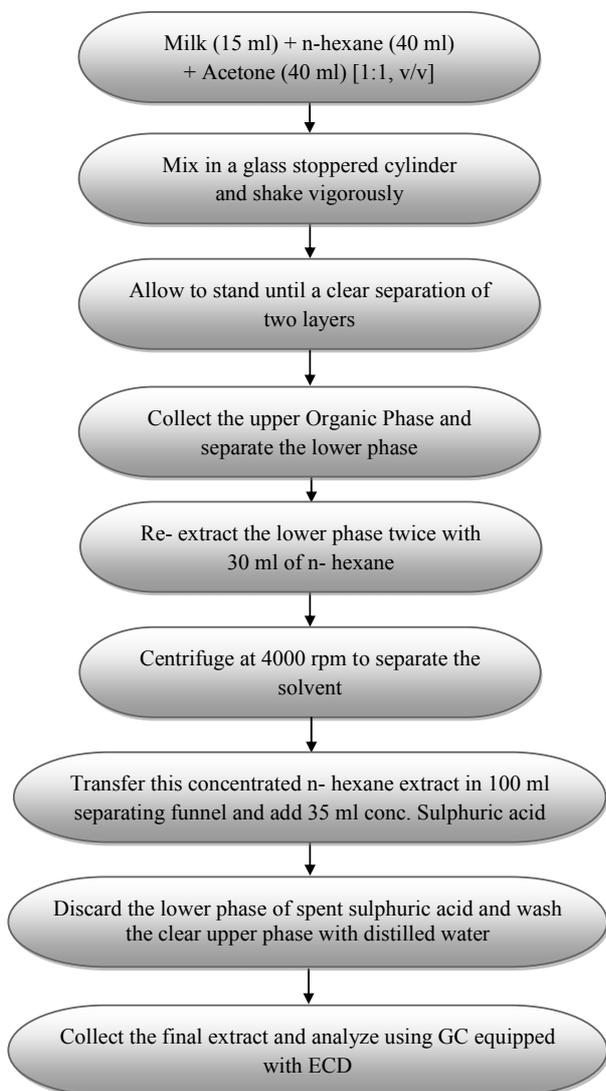
The physicochemical parameters, viz., pH, total solid (T.S %), fat (%) and ash (%), for all the collected milk samples from different locations of delhi, were analyzed according to the AOAC (1995) [42]. The pH of the milk samples were analyzed with potentiometric method, total solids and ash were analyzed by gravimetric method and fat content by Gerber method with the help of butyrometer.

### 2.3.2. Extraction

As the occurrence of pesticide residues in milk has been extensively studied, vast choice of methodologies is available for the determination of pesticide residues. Milk falls into the category of fatty foods, the analysis of OC as well as OP pesticide residues follows the conventional approach of the multi-matrix, multiresidue methods in which the total residues are extracted together with

the total" fatty material [43-47].

For milk, the bulk of fat together with lipophilic pesticide residues can be obtained by extraction using light petroleum-diethyl ether (1:1, v/v), potassium oxalate and ethanol [43] (Helrich, 1990), n-hexane-acetone (1:1, v/v) [11], or acetone extraction followed by a partition into dichloromethane [46]. Liquid-Liquid Extraction with n-hexane-acetone (1:1, v/v) was used. Milk sample (15 ml) was transferred to a clean glass-stoppered cylinder and 80 ml of acetone: n-hexane (1:1, v/v) was added to it and shaken vigorously. The homogenate was allowed to stand until a clear separation of two layers had occurred. After the removal of the upper organic phase, the lower phase was re-extracted twice with 30 ml n-hexane. The precipitate was centrifuged at 4000 rpm and the remaining solvent was also combined. The concentrated n-hexane extract was taken in a 100 ml separating funnel and 35 ml concentrated sulphuric acid (sp. Gravity 1.84) was added to it drop wise. The mixture was allowed to stand until a clear separation of two layers. The upper clear phase was collected and lower phase of spent sulphuric acid was discarded. The collected upper phase was then washed with the distilled water. The collected extract was evaporated to dryness using a rotary evaporator and concentrated to about 5 ml with n-hexane. The final extracts were transferred to autosampler vials for GC analysis. The flow diagram of extraction process of buffalo milk samples for multiresidue analysis of pesticides is shown in **Figure 2**.



**Figure 2.** Flow diagram of extraction of liquid Buffalo milk samples for multiresidue analysis of pesticides.

Recoveries were determined by spiking of milk with pesticides solution of known concentration. The average recoveries of fortified samples were exceeding 95%.

## 2.4. Statistical Analysis

All the data on the pesticide concentrations in milk samples were subjected to analysis of variance using SPSS 9.0 software. A correlation between the physicochemical parameters of milk samples and the experimentally determined pesticides residues, were calculated on Microsoft Excel version 2007.

## 2.5. Pesticide Residues Analysis

The separation and detection of analyzing pesticides were performed by high resolution Gas Chromatography. Gas chromatography (GC) analysis was performed using

an Agilent 7890A Gas Chromatograph equipped with  $^{63}\text{Ni}$  electron capture detector (ECD). The GC system was equipped with DB-5 (30 m length  $\times$  0.25 mm diameter  $\times$  0.25  $\mu\text{m}$  film thickness) capillary column. Hydrogen (99.9% purity) was used as the carrier gas, while nitrogen was used as an auxiliary gas for the ECD. The separation was operated under the following conditions: Oven temperature program: 100°C for 2 min, 15°C/min to 160°C, 5°C/min to 270°C; Nitrogen flow rate 2 ml/min; Injector mode splitless and temperature: 225°C; injection volume: 1  $\mu\text{l}$ ; Detector temperature 300°C. Quantitative and qualitative analysis were done by comparison with external standard. To determine the quality of the method, the recovery study was performed.

## 3. Results and Discussion

### 3.1. Chemical Composition

**Table 1** describes the determined chemical composition of buffalo's milk samples. The pH range of the milk

**Table 1.** Chemical composition in the milk samples collected from different regions of Delhi, India.

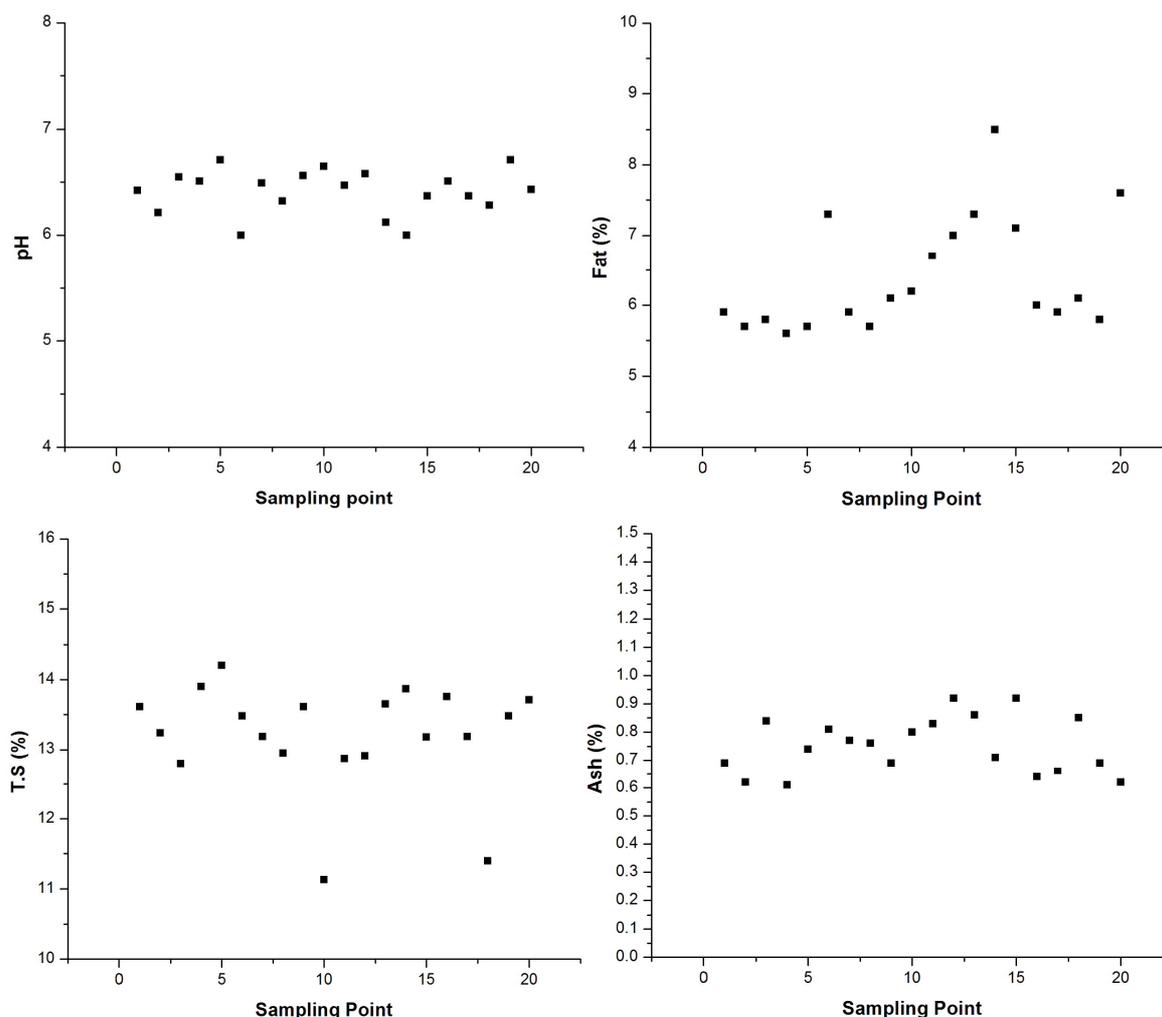
S.No.	Sample ID	District	pH	Fat %	T.S %	Ash %
1	S-1	South	6.42	5.9	13.61	0.69
2	S-2	South	6.21	5.7	13.24	0.62
3	S-3	South	6.55	5.8	12.8	0.84
4	SW-1	South West	6.51	5.6	13.9	0.61
5	SW-2	South West	6.71	5.7	14.2	0.74
6	SW-3	South West	6	7.3	13.48	0.81
7	W-1	West	6.49	5.9	13.19	0.77
8	W-2	West	6.32	5.7	12.95	0.76
9	W-3	West	6.56	6.1	13.61	0.69
10	E-1	East	6.65	6.2	11.13	0.8
11	E-2	East	6.47	6.7	12.87	0.83
12	N-1	North	6.58	7	12.91	0.92
13	N-2	North	6.12	7.3	13.65	0.86
14	NE-1	North East	6	8.5	13.87	0.71
15	NE-2	North East	6.37	7.1	13.18	0.92
16	CD-1	Central Delhi	6.51	6	13.76	0.64
17	CD-2	Central Delhi	6.37	5.9	13.19	0.66
18	NW-1	North West	6.28	6.1	11.40	0.85
19	NW-2	North West	6.71	5.8	13.48	0.69
20	NW-3	North West	6.43	7.6	13.71	0.62
	Average		6.413	6.395	13.206	0.7515
	Maximum		6.71	8.5	14.2	0.92
	Minimum		6	5.6	11.13	0.61
	Mean		6.413	6.395	13.2065	0.7515

samples varied from 6 to 6.7 with the mean value of 6.413. The fat value was observed between 5.6% and 8.5% with mean value of 6.395%. This difference in percent fat content may be due to the difference in feeding, management practices, season and breed of the animals [48]. The mean value of fat content is 6.395% which is lower than the standard content of 7.45% [49]. Total solids are one of the parameters used for the quality of milk [50]. The concentration range of total solids is from 14.2% to 11.13% with the mean value of 13.20% as shown in **Figure 3**. These results showed that the amount of total solids recorded is low in the range as recorded in the literature [49]. The overall mean ash content of milk is reported as 0.75%. The amount of ash content in milk should be closer to 0.78% [49] and similar readings are also reported [50]. The statistical analysis presented in the **Table 2**, showed that the pH, fat, total solids, ash content,  $\Sigma$ -DDT,  $\Sigma$ -HCH and  $\Sigma$ -Endosulfan of all the samples were significantly different from each other. The pH and Endosulfan shows negative co-relation with all

other parameter. Only endosulfan shows some good relation with Fat% and rest all show slight co-relations, but to a negligible extend.

### 3.2. Pesticide Residue

The frequency distribution of organochlorine pesticide residues detected in the analyzed buffalo milk samples are shown in **Table 3-5**. Hexachlorocyclohexane (HCH) is used against sucking and biting pests and as smoke for control of pests in grain stores. It is used as dust to control various soil pests such as flea beetles and mushroom flies. It is also present in the list of banned pesticides in India (with effect from April 1, 1997). Hexachlorocyclohexane, previously called BHC (benzene hexachloride), is a mixture of eight isomers out of which five are found in the crude product ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ). Only the  $\gamma$ -isomer or lindane has powerful insecticidal properties. The presence of  $\gamma$ -HCH (Lindane) detected in 100% of the analyzed milk samples in the range of 0.0001 to



**Figure 3.** Chemical composition of Buffalo's milk samples collected from different districts of Delhi.

**Table 2. Statistical correlation between chemical composition of milk samples.**

	pH	Fat %	T.S%	Ash%	$\Sigma$ -HCH	$\Sigma$ -DDT	$\Sigma$ -Endo
pH	1	-0.577	-0.172	-0.075	-0.37014	-0.51187	-0.05254
Fat %		1	0.2528	0.2828	0.886488	0.442419	-0.16151
T.S%			1	-0.618	0.075122	0.040057	-0.22823
Ash%				1	0.359993	0.241355	-0.10587
$\Sigma$ -HCH					1	0.156254	-0.05517
$\Sigma$ -DDT						1	-0.098
$\Sigma$ -Endo							1

**Table 3. Quantitative determination of  $\Sigma$ -HCH in the milk samples collected from different regions of Delhi, India.**

S.No.	Sample ID	District	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	$\Sigma$ -HCH
1	S-1	South	0.002	0	0.001	0	0.003
2	S-2	South	0	0.014	0.018	0	0.032
3	S-3	South	0.008	0	0.002	0	0.01
4	SW-1	South West	0.007	0	0.003	0	0.01
5	SW-2	South West	0.141	0	0.001	0	0.142
6	SW-3	South West	0.212	0	0.12	0	0.332
7	W-1	West	0.001	0	0.013	0	0.014
8	W-2	West	0.08	0.013	0.01	0	0.103
9	W-3	West	0.018	0	0.009	0	0.027
10	E-1	East	0	0.355	0.014	0	0.369
11	E-2	East	0.017	0.982	0.002	0	1.001
12	N-1	North	0.002	0.511	0.11	0	0.623
13	N-2	North	0.03	0	0.856	0	0.886
14	NE-1	North East	0.182	0	0.94	0	1.122
15	NE-2	North East	0	0.86	0.06	0	0.92
16	CD-1	Central Delhi	0.023	0.005	0.036	0	0.064
17	CD-2	Central Delhi	0.022	0	0.0001	0	0.0221
18	NW-1	North West	0.205	0	0.001	0	0.206
19	NW-2	North West	0	0.012	0.004	0	0.016
20	NW-3	North West	0.01	0	1.081	0	1.091
	Average		0.048	0.1376	0.1640	0	0.34965
	Maximum		0.212	0.982	1.081	0	1.122
	Minimum		0	0	0.0001	0	0.003
	Mean		0.048	0.1376	0.164055	0	0.349655

$\alpha$ -HCH: alpha-Hexachlorocyclohexane;  $\beta$ -HCH: beta-Hexachlorocyclohexane;  $\gamma$ -HCH: gamma-Hexachlorocyclohexane;  $\delta$ -HCH: delta-Hexachlorocyclohexane;  $\Sigma$ -HCH: Sum of Hexachlorocyclohexane.

**Table 4. Quantitative determination of  $\Sigma$ -DDT in the milk samples collected from different regions of Delhi, India.**

S.No.	Sample ID	District	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	$\Sigma$ -DDT
1	S-1	South	0.097	0.009	0	0	0.106
2	S-2	South	0.083	0.005	0	0.003	0.091
3	S-3	South	0.002	0.086	0	0	0.088
4	SW-1	South West	0.073	0.003	0	0.094	0.17
5	SW-2	South West	0.005	0.012	0.018	0.051	0.086
6	SW-3	South West	0.97	0.046	0	0	1.016
7	W-1	West	0	0	0.017	0.085	0.102
8	W-2	West	0.064	0.001	0.0004	0.13	0.1954
9	W-3	West	0	0	0	0	0
10	E-1	East	0.024	0	0	0.078	0.102
11	E-2	East	0.068	0.002	0.023	0.01	0.103
12	N-1	North	0.31	0.038	0	0.063	0.411
13	N-2	North	0.006	0.001	0.006	0.006	0.019
14	NE-1	North East	0.242	0.094	0	0.095	0.431
15	NE-2	North East	0.027	0.003	0	0.093	0.123
16	CD-1	Central Delhi	0.002	0.001	0	0	0.003
17	CD-2	Central Delhi	0.001	0.001	0.001	0.055	0.058
18	NW-1	North West	0	0	0	0	0
19	NW-2	North West	0.018	0.011	0	0.002	0.031
20	NW-3	North West	0	0	0	0	0
	Average		0.0996	0.01565	0.00327	0.03825	0.15677
	Maximum		0.97	0.094	0.023	0.13	1.016
	Minimum		0	0	0	0	0
	Mean		0.0996	0.01565	0.00327	0.03825	0.15677

p,p'-DDE: para, para- Dichlorodiphenyldichloroethylene; p,p'-DDD: para, para- Dichlorodiphenyldichloroethane; o,p'-DDT: ortho, para- dichlorodiphenyltrichloroethane; p,p'-DDT: ortho, para- dichlorodiphenyltrichloroethane;  $\Sigma$ -DDT: sum of dichlorodiphenyltrichloroethane.

1.081  $\mu\text{g}\cdot\text{g}^{-1}$ . It is higher than reported by Ashnagar *et al.*, 2009, John *et al.*, 2001, Aman and Bluthgen, 1997. The presence of lindane in all the samples might be because of the fact that  $\gamma$ -HCH is more resistant to biological and chemical degradation under aerobic conditions [51] and it is also most commonly used. The presence of lindane above its Maximum Residual Limit in about 50% of the samples is a cause of serious concern. It is essentially a nutritional food for infants and the aged. As it is carcinogenic in nature, it may affect the functioning of vital organs of the body [52]. It is also detected in 85% and 76.5% of the samples of fresh and pasteurized cow's milk, respectively [21]. The  $\beta$ -isomer of HCH is environmentally the most persistent among HCH isomers. It is eliminated slowly from the human body than lindane. It is because of this reason that this pesticide is detected in 40% samples only [53]. It has a longer half life in fatty components [54]. Most of the milk samples contained  $\alpha$ -HCH residues but their concentration was less. Lower concentration of  $\alpha$ -HCH isomer in the samples can be

explained by the fact that this isomer is highly volatile and less persistent [55]. There are few places in Delhi where the concentration of HCH is very high as shown in **Figure 4**.

Dichlorodiphenyltrichloroethane (DDT) is a potent nonsystemic insecticide. Although the use of DDT has been banned in agriculture since 1993 but it is still in use for the National Malaria Eradication Program (NMEP) of Govt. of India. It could therefore be the reason of the presence of DDT and its analogues in the environment. p,p'-DDT was detected in 70% of the samples at mean levels of 0.01565  $\mu\text{g}\cdot\text{g}^{-1}$  similar readings are also reported [56]. A major metabolite of DDT namely 2,2-bis(p-chlorophenyl)-1,1-dichloroethylene (p,p'-DDE) was detected at mean levels of 0.0996  $\mu\text{g}\cdot\text{g}^{-1}$  in the range of n.d–0.97  $\mu\text{g}\cdot\text{g}^{-1}$  in 80% of the milk samples of different parts of Delhi state which is higher in comparison with Waliszewski *et al.*, 1996 [57]. DDE is more persistent than DDT. 2,2-bis(p-chlorophenyl)-1,1-dichloroethane (DDD) another metabolite of p,p'-DDT was detected at

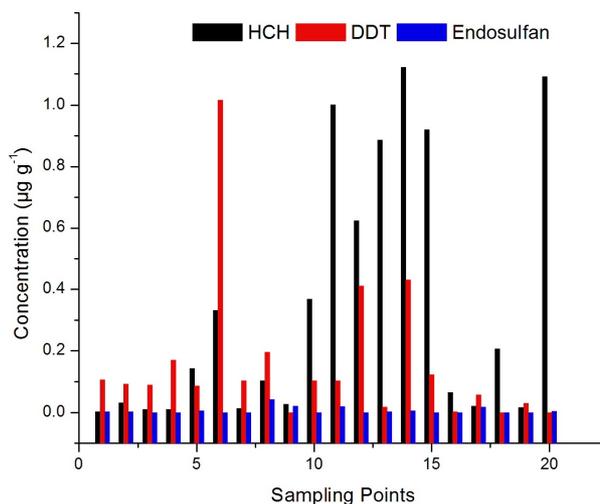
**Table 5. Quantitative determination of  $\Sigma$ -Endosulfan in the milk samples collected from different regions of Delhi, India.**

S. No.	Sample ID	District	A	B	C	D
1	S-1	South	0	0.003	0	0.003
2	S-2	South	0.002	0.0013	0	0.0033
3	S-3	South	0	0	0	0
4	SW-1	South West	0	0	0	0
5	SW-2	South West	0.005	0	0.0017	0.0067
6	SW-3	South West	0	0	0	0
7	W-1	West	0	0	0	0
8	W-2	West	0.021	0.022	0	0.043
9	W-3	West	0	0.022	0	0.022
10	E-1	East	0	0	0	0
11	E-2	East	0.006	0.014	0	0.02
12	N-1	North	0	0	0	0
13	N-2	North	0	0.001	0.0019	0.0029
14	NE-1	North East	0.002	0.004	0	0.006
15	NE-2	North East	0	0	0	0
16	CD-1	Central Delhi	0	0	0	0
17	CD-2	Central Delhi	0.001	0.015	0.002	0.018
18	NW-1	North West	0	0	0	0
19	NW-2	North West	0	0	0	0
20	NW-3	North West	0.004	0	0	0.004
Average			0.00205	0.004115	0.00028	0.006445
Maximum			0.021	0.022	0.002	0.043
Minimum			0	0	0	0
Mean			0.00205	0.004115	0.00028	0.006445

A:  $\alpha$ -Endosulfan, B:  $\beta$ -Endosulfan, C: Endosulfan Sulfate, D:  $\Sigma$ -Endosulfan.

mean levels 0.0383 in 65% of the milk samples, the concentration is lower than reported by Ashnagar *et al.*, 2009 [56] and Kampire *et al.*, 2011 [10]. The mean concentrations of o,p'-DDT was observed as 0.013  $\mu\text{g}\cdot\text{g}^{-1}$  in the buffalo's milk samples of the studied area which is less as reported by Ashnagar *et al.*, 2009 [56]. Kannan *et al.* (1992) evaluated milk from India and found levels of DDT as 0.110 mg/kg which was above those found in the present study [58].

Total DDT (sum of pp'-DDE + pp'-DDD + op'-DDT + pp'-DDT) was detected in 85% of samples collected. Since DDT is known to undergo metabolic conversion

**Figure 4. Residues of total Organochlorine in Milk Samples of Delhi.**

and dehydrochlorination presence of metabolites of DDT *i.e.* DDD and DDE encountered in this study might be due to such metabolic processes. This analysis indicates that DDT is the major contaminants in different parts of Delhi state.

Endosulfan, an organochlorine insecticide of the cyclo-diene subgroup acts as a poison to a wide variety of insects and mites on contact and as a stomach acaricide. Technical grade endosulfan contains 94%  $\alpha$  and  $\beta$  endosulfan. The Alpha ( $\alpha$ ) and beta ( $\beta$ ) isomers are present in the ratio of 7:3 respectively. Alpha ( $\alpha$ ) isomer has been shown to be 3 times more toxic than the beta ( $\beta$ ) isomer. In other study, bovine milk was analysed in India to determine OC pesticides [59]. Mean levels was 0.0065, 0.0229 and 0.0198  $\text{mg}\cdot\text{kg}^{-1}$  with  $\alpha$ -Endosulfan,  $\beta$ -Endosulfan and Endosulfan Sulfate respectively. Those values are higher than that detected in the present study. As shown in **Table 5**,  $\alpha$  and  $\beta$  Endosulfan were detected in 35% and 40% of the samples analyzed with 0.0020 and 0.0041  $\mu\text{g}\cdot\text{g}^{-1}$  respectively. Endosulfan Sulfate a reaction product found in technical grade Endosulfan as a result of oxidation is considered to be equally toxic and more persistent than the parent compound. However it was not detected in any of the samples. Thus  $\Sigma$ -Endosulfan ranged from ND to 0.043  $\mu\text{g}\cdot\text{g}^{-1}$ .

#### 4. Conclusion

It could be concluded that OC pesticide residues were detected in buffalo's milk as they were persistent in nature due to their slow decomposition rate, long half-life and high stability in the environment. In most cases, the values of detected OC pesticides were exceeded the tolerance levels of FAO/WHO. HCHs are the main contributors to the total OCs burden in milk, suggesting recent usage of HCHs in Delhi. DDT was detected in al-

most all buffalos milk samples collected from different regions of Delhi City which were found contaminated with the presence of one or more of the investigated pesticides. Although  $\alpha$  Endosulfan was detected in less analyzed milk samples than  $\beta$  Endosulfan, it was 3 times more toxic. Endosulfan sulfate is not detected. Nevertheless, the organochlorine residues monitoring studies in milk as well as in cattle feed and storage condition should be investigated further in order to improve food safety since these compounds represent a potential risk to human health.

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