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Occurrence and Dietary Risk Assessment of Pesticides in Wheat Fields of Ghaziabad City, India

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The aim of this study is to assess the pesticides residues in wheat and soil samples from Ghaziabad city of India. Herein, wheat and soil samples were collected from fields in Ghaziabad city, India from 2017 to 2019 and analyzed on GC-MS/MS & LC-MS/MS using QuEChERS method of extraction. One or multiple pesticide residues were detected in the wheat and soil samples. Cypermethrin, cyahalofep butyl and chlorpyrifos were frequently detected in the soil samples. Concentrations of carbendazim and chlorpyrifos in the paired soil and wheat samples exhibited significant positive correlations. The monitoring results showed that the concentrations of some pesticides in the wheat flour samples exceeded the FSSAI MRL standard, which implies possible intake risks *via* consumption. Hence, dietary risk assessments were conducted. The resulting hazard quotient (HQ) values fell within 3.89-7.25 indicates that dietary risk of studied crop is low and their current residue concentrations in wheat would be safe for human consumption.

Keywords: Pesticides residues, Dietary risk assessment, Hazard quotient, Hazard index, QuEChERS.

INTRODUCTION

Wheat (*Triticumaestivum* L. emThell.) is one of the important crop of India. It is a main source of food as it is a major diet component and income for millions of small holder farmers. In the world, wheat is grown in almost every region. India stands in the second position in terms of largest producer of rice, wheat and other cereals. Wheat cultivation is dominated by northern region of India. Uttar Pradesh, Punjab, Haryana, Madhya Pradesh, Rajasthan, Bihar and Gujarat states of India are the major wheat growing states in India. As per Agricultural &Processed Food Products Export Development Authority report (APEDA), the country has exported 2, 17,354.22 metric tons of wheat worth of Rs. 439.16 crores/61.84 USD Millions to the world during the year of 2019-20. Weeds adversely affect the crop growth and yield by competing with crops for light, water and nutrients [1,2]. Uncontrolled growth of weeds on an average caused about 48% reduction in grain yield of wheat when compared with weed free condition [2]. To control these weeds, pesticides are used and its usage is increasing day by day. Organochlorine pesticides (OCPs) such as DDT, HCB, chlordane, dieldrin, endrin, HCH or heptachlor were used in the majority of the developed countries for the protection of agricultural crops against insects. These legacy OCPs are classified as persistent organic pollutants (POPs) [3]. These POPs chemical stability is very high that their residues are still detected in the environment. DDT although banned but still in use in some regions of the world to control mosquitos and thus prevent malaria. The Ministry of Agriculture and Farmers Welfare performed "Pesticide Residue Monitoring" at the national level under the Department of Agriculture, Cooperation & Farmers Welfare during the year 2017-18. The monitoring data indicated that 1.0% wheat samples were found above MRLs [4]. In soil, residual pesticides are taken up by plants and maycontaminate the food and affecting human and animal health [5,6].

Humans are exposed to pesticides on the job, during product handling and application, or *via* the consumption of pesticide treated food. Adverse consequences have been found in laboratory animals dosed with pesticides for an extended period of time. Human exposure to these chemicals in the food and the possible health consequences are of concern to government [7,8]. Chronic pesticide exposure is thought to have a detrimental

impact on birth weight, motor and neurological development, as well as an increased cancer risk [9].

Therefore, the aim of the present study was to estimate the pesticides residues in wheat as it is one of the important crop in India with highest production after rice and to assess the dietary risk of human consumption.

EXPERIMENTAL

Reference standards were procured from Sigma Aldrich, India, Dr. Erhenstorfer, Chem Service, Agilent Technologies with purity > 98.0 % while acetonitrile (ULC/MS grade) and methanol (ULC/MS grade) were procured from Biosolve. The other chemicals *viz*. ethyl acetate (RANKEM, HPLC grade), *n*-hexane (Merck India, HPLC grade), magnesium sulphate anhydrous (Qualigens), formic acid for LC-MS LiChropur and sodium acetate, ammonium formate, primary secondary amine (PSA) (all analytical reagents grade) were procured. The C-18 column from Agilent Technologies, Type-1 Water from Milli Q water purification System (Merck Millipore) was used.

Standard solutions preparation: Pesticide stock solution of 1000 mg/ L was prepared using methanol or ethyl acetate, acetonitrile with respect to the solubility of particular pesticide CRM. Concentration was calculated considering purity of standard and labeled with obtained concentration at -20 ºC. LCMS/MS & GCMS/MS pesticides divided in to two groups and intermediate working stock solution prepared by transferring appropriate volume of each standard stock solution into 10 mL volumetric flask containing appropriate solvent and make up the volume up to the mark with the same. For GC-MS/MS and LC-MS/MS, ethyl acetate and methanol was used for standard preparation, respectively and stored at -20 ºC. A mixture of linearity dilutions was prepared with concentrations of 5, 10, 20, 50, 100, 200 µg/L from intermediate working stock solution. Mixed matrix extracts were prepared with concentrations of 5, 10, 20, 50, 100, 200 µg/L by adding appropriate volume of standard from intermediate working stock solution to blank matrix extracts (wheat).

Reagents preparation: Methanol solution (50%) was prepared by transferring 50 mL methanol to 100 mL of volumetric flask, added water and made up to the mark and de-gassed in an ultrasonic bath. Mobile phase A was prepared by transferring 0.3153 ± 0.03 g of ammonium formate to 1000 mL of Type-I water, added 100 µL of formic acid and de-gassed in an ultrasonic bath. Mobile phase B was prepared by transferring 0.3153 ± 0.03 g of ammonium formate to 1000 mL of methanol, added 100 µL of formic acid and de-gassed in an ultrasonic bath. Matrix blank was prepared as per sample extraction procedure using blank matrix. Reagent blank was prepared as per sample preparation procedure without using matrix.

Study area: Ghaziabad is located between Ganges and Yamuna which are the two main rivers in India. Its geographical coordinates are 28º40′0″ north, 77º26′0″ east and situated 204 m above sea level. The average annual temperature is 24.5 ºC (| 76.1 ºF) in Ghaziabad. The annual rainfall is 764 mm (30.1 inch). Decadal growth rate of the district is 41.3%. It is higher than the state average of 20.20% [10]. Total area in sq. Km of Uttar Pradesh is 240,928.00 and of District Ghaziabad is 777.9 sq km on the basis of 2011 census.

Sampling methods: Soil and grain samples were collected during the harvest seasons of wheat in the month of April 2017, 2018 and 2019 from three locations (Loni, Dasna & Raispur villages) of Ghaziabad. From each farm, three locations has been selected covering the two corners and centre of the field and the three sets of plant samples including the soil from each location has been taken. For soil sample collection, standard procedure was followed [11]. Soil samples were collected at a depth of 0-25 cm with stainless steel augur from 3 points with a distance of 20 m from each other in both the directions and mixed into one sample to form one composite sample, and stored separately in polyethylene. At the same time, wheat spikes were collected with scissors and stored in nylon mesh bag. Like this three samples collected from each location of the farm. Before collecting the next soil sample, the soil auger was thoroughly cleaned to prevent cross contamination between soil samples. Samples were sent to laboratory and were kept in a refrigerator for a week until sample preparation started for the analysis. Before starting the sample preparation, roots, shoots, leaves and seeds separated and labelled in a clean plastic bag and further analysis carried out.

Sample extraction procedures: Homogenized wheat sample (5.0 ±0.1 g) was weighed into a 50 mL polypropylene centrifuge tube. Added 10 mL of water to the sample and mixed well for 30 s. Then added 10 mL of acetonitrile and shaked by hand for 1 min. Added 4 g of $MgSO_4$, 1 g of NaCl, 1 g trisodium citrate dihydrate and 0.5 g of potassium hydrogen citrate sesquihydrate [12]. Shaked vigourasly for 1 min, centrifuged the sample for 10 min at 4000 rpm at 4.0 ± 2 ºC and the transferred 8.0 ml of extract into a 15 mL centrifuge tube and stored in the deep freezer at -20.0 ± 4 ºC for 1 h. Centrifuge at 4000 rpm for 5 min in the same cold condition. Transferred 6.0 mL of cold extract into a 15 mL centrifuge tube conaining 150 mg primary secondary amine (PSA) and 900 mg $MgSO_4$ for clean-up and vortexed for 30 s and centrifuged for 5 min at 4000 rpm.

LC-MS/MS analysis: After centrifugation, transfer 2.0 mL of supernatant liquid in to Ria vial and evaporate it to dryness under nitrogen evaporator at 35 ± 2 ºC and then reconstituted with 1 mL of methanol:water (50:50 v/v).Transferred into auto sampler vial and injected into the LC-MS/MS.

GC-MS/MS analysis: After centrifugation, transfer 2.0 mL of supernatant liquid in to Ria Vial and evaporated it to dryness under nitrogen evaporator at 35 ± 2 ºC and reconstituted with 1mL of ethyl Acetate. Transferred into auto sampler vial and Injected into the GC-MS/MS.

Sample extraction procedure for soil

Sample extraction: Weighed 10 g soil sample with ≥ 70% H_2O content into a 50 mL centrifuge tube. Alternatively, weighed 3 g air-dried soil sample into a 50 mL tube and added 7 mL water, vortex and allow to hydrate for 30 min. Added 10 mL of acetonitrile to each sample and shaked samples for 5 min to extract pesticides. Finally, added 4000 mg magnesium sulphate, 1000 mg NaCl, 500 mg sodium citrate dibasic sesquihydrate, 1000 mg sodium citrate tribasic dehydrate in to each

centrifuge tube. Immediately shaked the samples for at least 2 min and centrifuged for 5 min at 3000 rpm.

Sample cleanup: Transferred 1 mL aliquot of supernatant to 2 mL tube containing 150 mg $MgSO_4$, 50 mg PSA, 50 mg C18 Vortex samples, mixed for 1 min and then centrifuged for 2 min at 5000 rpm. Filtered the supernatant through a 0.2 µm syringe filter directly into a sample vial and analyze by injecting 10 µL of sample.

LC-MS/MS analysis: A total of 28 types of pesticides were analyzed using Agilent Technologies LC-MS/MS, triple quadrupole mass spectrometer (Model 6610). Chromatographic seperation was performed using Agilent Zorbax Eclipse, XDB C-18 Column 150 mm × 4.6 mm × 5.0 m. Chromatographic conditions, pump ramping and MRM Transitions are mentioned in Tables 1-3, respectively.

TABLE-1
CHROMATOGRAPHIC CONDITIONS FOR LC-MS/MS

Mobile phase	A: 5 mM ammonium formate in water + 0.01% formic acid B: 5 mM ammonium formate in methanol + 0.01% formic acid
Flow rate	0.5 mL/min
Injection volume	10 µL
Column temperature	40 °C
Column	Agilent Zorbax Eclipse XDB-C-18 150 mm × 4.6 × 5.0 µm
Auto sampler temperature	5 °C
Run time	24.0 min
Mode	Gradient
Acquisition mode	MRM
Ion source	Electrospray ionization (positive and negative ion mode)
Resolution	Unit

TABLE-2
PUMP GRADIENT PROGRAM FOR PESTICIDE RESIDUES

Time (min)	%B	Time (min)	%B
0.01	20	18	95
5	70	22	20
15	95	24	20

GC-MS/MS analysis: A total of 70 types of pesticides were analyzed using Agilent Technologies GC-MS/MS in split less mode with Auto sampler (7000B, Triple quadruple with mass hunter soft-ware) having capillary column (HP-5MS; 30 m × 0.25 mm × 0.25 µm). Column flow rate was 1.0 mL/min, the initial column temperature was 60 ºC, while the injector temperature was 300 ºC. Column oven ramping: Initial Temp.: 60 ºC with 1.0 min hold time. Temperature raised at the rate of 40 ºC/min to 170 ºC with no hold time and the at the rate of 10 ºC to 310 ºC with 3 min. Chromatographic conditions, oven ramping and MRM Transitions are shown in Tables 4-6, respectively.

Quality control: A spiked sample used to monitor the performance of analytical method and to assess the integrity and validity of the results of the unknown samples. Blank sample having no interference was taken and spiked at LOQ level to check the process efficiency and recovery percentage. Analysis performed was performed using bracketing standard at the start and end of every sequence. In a batch, blank control sample (with no interference) and spike sample was injected after every ten samples. Method was validated by performing experiments. Sensitivity/Linearity was evaluated using at least five concentration levels. Concentrations were 5, 10, 20, 50, 100 µg/kg. Matrix effect was evaluated by injecting solvent standards and matrix standards at levels (post spiking in blank matrix) and compared for the responses. The matrix matched calibration is commonly used to compensate for matrix effects. LOQ is the limit of quantitation and evaluated by injecting six replicates at lowest spiked concentration. Mean recovery at LOQ level was within 70-120% with an associated repeatability % RSD of 20, for all analytes within the scope of a method and LOQ signal to noise ratio (S/N) was greater than 10. Matrix matched calibration curves were used during the quantitative analysis of samples and concentration found below LOQ assigned as BLQ.

Dietary intake risk calculation: Estimated daily intake of a pesticide residue is based on the most realistic estimation of residue levels in food, food consumption data for a specific population [13]. The prediction of EDI usually carried out at the national level with known residue level for a particular commodity. Dietary intake risk assessment was conducted based on daily dietary patterns data in the food lists for different populations by the governments around the world [14]. Estimated daily intake (EDI) was calculated using estimated residue value of pesticide in the wheat matrix per day considering average body weight and daily consumption quantity of wheat for general population [15]. Reference Indian weight for all different age groups were fixed for a normal BMI by Indian Council of Medical Research, National Institute of Nutrition [16]. Wheat consumption per capita is 143 g/day as per NSS [17]. It is then compared with recommended acceptable daily intake value which is obtained from toxicological assessments. Hazard Quotient (HQ) expressed as HQ and HQ < 100 indicates that calculated HQ does not pose a risk. HQ >100 % indicates an unacceptable risk [14,15]. Hazard index (HI) is a measurement of potential risks of adverse health effects from a mixture of pesticides residues evaluated in a specific study. The HQ's were summed up to get the HI of pesticides residues.

$$\text{Estimated dietary intake (EDI)} = \frac{R_i \times F_i}{bw} \quad (1)$$

where R_i is the estimated residue value of the target compound in the wheat matrix (mg/kg) ; F_i is the daily consumption of wheat for the general population (kg); bw is the body weight.

$$\text{Risk quotient (HQ)} = \frac{EDI}{ADI} \quad (2)$$

where ADI is the acceptable dietary intake (mg/kg bw) and bw is body weight in kg.

RESULTS AND DISCUSSION

Method performance: Analytical method was validated to check the performance of analytical method and its validity as per SANTE/12682/2019. Sensitivity/linearity, specificity, limit of quantification, matrix effect, recovery/trueness, accuracy, within lab repeatability and robustness tests were performed

TABLE-3
DETAILS OF MRM TRANSITION FOR PESTICIDES ANALYZED ON LC-MS/MS

Compound name	Product ion-1	CE-1	Product ion-2	CE-2	Instrument
2,4-D	219.00 > 161.10	11	219.00 > 124.90 0.00	27	LC-MSMS
Azoxystrobin	404.00 > 372.15	-15	404.00 > 344.15	-26	LC-MSMS
Bitertanol	338.10 > 99.15	-15	338.10 > 269.25	-9	LC-MSMS
Carbaryl	202.00 > 145.10	-11	202.00 > 127.10 0.00	-27	LC-MSMS
Carbendazim	191.90 > 160.15	-18	191.90 > 132.15 0.00	-32	LC-MSMS
Carbofuran	222.00 > 123.15	-23	222.00 > 165.10 0.00	-15	LC-MSMS
Chlorimuron-ethyl	415.10 > 186.00	-18	415.10 > 185.30	-27	LC-MSMS
Clodinafop-propargyl ester	350.10 > 266.10	-16	349.90 > 91.15	-29	LC-MSMS
Difenoconazole	406.00 > 251.10	-26	405.90 > 111.10	-54	LC-MSMS
Epoxyconazole	330.00 > 121.00	-22	330.00 > 101.00	-48	LC-MSMS
Ethion	385.00 > 199.00	-11	385.00 > 143.00 0.00	-24	LC-MSMS
Fenoxaprop-ethyl	362.00 > 288.10	-19	362.00 > 91.15	-36	LC-MSMS
Fipronil	435.00 > 330.10	15	435.00 > 250.05	26	LC-MSMS
Iodosulfuron-methyl	508.10 > 167.10	-20	508.10 > 58.10	-55	LC-MSMS
Isoprothiolane	290.90 > 231.10	-11	290.90 > 145.00	-32	LC-MSMS
Isoproturon	207.00 > 72.15	-22	207.00 > 46.20 0.00 0	-17	LC-MSMS
Kresoxim-methyl	314.10 > 267.20	-8	314.10 > 115.95	-15	LC-MSMS
Malathion	347.90 > 127.15	-17	347.90 > 99.10 0.00 0	-27	LC-MSMS
Mesosulfuron methyl	504.10 > 182.10	-24	504.10 > 139.00	-52	LC-MS/MS
Methabenzthiazuron	222.00 > 165.20	-14	222.00 > 150.10	-35	LC-MSMS
Methyl chlorophenoxy acetic acid (MCPA)	199.00 > 141.15	14	201.00 > 143.15	-13	LC-MS/MS
Metribuzin	215.00 > 187.20	-18	215.00 > 49.20	-28	LC-MSMS
Metsulfuron-methyl	381.90 > 167.10	-17	381.90 > 77.20	-53	LC-MSMS
Monocrotophos	240.90 > 224.10	-7	240.90 > 127.10 0.00	-21	LC-MSMS
Oxydemeton-methyl	246.90 > 169.05	-14	246.90 > 109.05 0.00	-27	LC-MSMS
Phenthoate	321.10 > 247.15	-11	321.10 > 79.05 0.00 0	-46	LC-MSMS
Picoxystrobin	368.00 > 145.10	-22	368.00 > 205.10	-10	LC-MSMS
Pinoxaden	401.20 > 317.25	-23	401.20 > 57.05	-31	LC-MSMS
Propiconazole (stereo isomer)	341.90 > 159.00	-30	341.90 > 69.20	-20	LC-MSMS
Pyraclostrobin	388.10 > 163.10	-25	388.10 > 164.15	-18	LC-MSMS
Sulfosulfuron	471.10 > 211.10	-13	471.10 > 261.10	-18	LC-MSMS
Sulfoxaflor	278.0 > 174.0	-12	278.0 > 154.0	-29	LC-MSMS
Tebuconazole	308.00 > 70.15	-24	308.00 > 150.95	-26	LC-MSMS
Thiamethoxam	291.90 > 211.10	-13	291.90 > 181.10	-23	LC-MSMS
Thiometon	246.90 > 61.05	-32	246.90 > 89.30 0.00 0	-9	LC-MSMS
Thiophanate-methyl	343.00 > 151.15	-21	343.00 > 311.10	-10	LC-MSMS
Triadimefon	293.90 > 69.10	-22	293.90 > 197.15	-15	LC-MSMS
Triasulfuron	402.00 > 167.05	-18	402.00 > 141.00	-22	LC-MSMS
Trichlorfon	256.90 > 109.10	-18	256.90 > 221.00 0.00	-9	LC-MSMS
Tridemorph	298.10 > 130.20	-26	298.10 > 98.10	-30	LC-MSMS
Trifloxystrobin	409.00 > 186.10	-18	409.00 > 145.10	-43	LC-MSMS

TABLE-4
CHROMATOGRAPHIC CONDITIONS FOR GC-MS/MS

Column	HP-5MS; 30 m × 0.25 mm × 0.25 µm
Column oven	60 °C
Injector temperature	300 °C
Injection mode	Splitless
Carrier gas	Helium
Flow rate	1.0 mL/min
Injection volume	1.0µL
Run time	22.75 min
Mode	MRM
Source temperature	220 °C
Interface temperature	310 °C
Solvent delay	3.00 min

TABLE-5
OVEN RAMPING

Rate (°C/min)	Final temp. (°C)	Hold time (min)	Run time (min)
–	60	1	1
40	170	0	3.75
10	310	3	20.75

to verify the methodology. According to SANTE/12682/2019, the average recovery threshold at each stage is 70-120%. At each level, the RSD should be less than 20%. Linearity was achieved for all the analyte with correlation coefficient (r) ≥ 0.99 and the deviation of back calculated concentration from true concentration was also ≤ 20 %.Recovery at LOQ was within the acceptable range of 70-120%, with an associated RSD of less than or equal to 20%. The recovery rate in this investigation was greater than 80%, indicating a good and well-validated analytical method. The relative intensities or ratios of selective ions reported as a ratio relative to the most intense ion were determined using a minimum of two product ions. In MS/MS, ion ratios from sample extracts should not differ by more than 30% (relative) from the average of calibration stan-

TABLE-6
DETAILS OF MRM TRANSITIONS FOR PESTICIDES ANALYZED ON GC-MS/MS

Compound name	Product ion-1	CE-1	Product ion-2	CE-2	Instrument
Trifluralin	306.10 > 264.10	8	306.10 > 206.10	14	GC-MSMS
Triallate	268.00 > 184.00	25	268.00 > 226.00	15	GC-MSMS
Pendimethalin	252.10 > 162.10	10	252.10 > 191.10	8	GC-MSMS
Carfentrazone-ethyl	340.10 > 312.10	14	340.10 > 151.10	28	GC-MSMS
Diclofop-methyl	340.00 > 253.00	14	340.00 > 281.00	10	GC-MSMS
Cypermethrin	181.10 > 152.10	22	181.10 > 127.10	22	GC-MSMS
Deltamethrin	252.90 > 93.00	20	252.90 > 171.90	26	GC-MSMS
Chlorpyrifos	313.90 > 257.90	14	313.90 > 285.90	8	GC-MSMS
Dichlorvos	185.00 > 93.00	14	185.00 > 109.00	14	GC-MSMS
Phorate	260.00 > 75.00	8	260.00 > 231.00	4	GC-MSMS
Cyhalofop-butyl	357.10 > 256.10	10	357.10 > 229.10	14	GC-MSMS

dards from the same sequence. Retention time identification criteria was also checked. The analyte in the extract should have the same retention period as the calibration standard with a tolerance of ±0.1min.In the validation study, both ion ratio and retention time criteria met for every batch sequence.

Occurrence of pesticides in wheat samples and soil: The concentration of pesticides in wheat samples and soil are summarized in Table-7 for the three consecutive year survey 2017, 2018 and 2019 (Fig. 1). In 2017, five pesticides (carbendazim, chlorpyrifos, cypermethrin, thiomethoxam and propiconazole) were detected in wheat with a detection frequency of 50% for carbendazim, chlorpyrifos, cypermethrin, propiconazole, 25% for thiomethoxam. In soil, carbendazim, chlorpyrifos, cypermethrin and cyahalofep butyl were detected with a detection frequency of 25% except carbendazim having 50% detection frequency. Chlorpyrifos was higher in concentration in wheat as well as in soil with a median value of 0.033 mg/kg and less than LOQ for wheat and soil respectively, which is less than its maximum residual limit of 0.5 mg/kg. Chlorpyrifos detected residue range in wheat was 0.0-0.113 mg/kg with mean value of 0.037 mg/kg. carbendazim was second highest in residue concentration with a median value of 0.012 mg/kg and 0.041 mg/kg for wheat and soil, respectively, which is less than its maximum residual limit of 0.05 mg/kg. Detection range of carbendazim was 0.0-0.051 mg/kg with a mean value of 0.018 mg/kg for wheat and 0.0-0.118 mg/kg with a mean value of 0.050 mg/kg in soil. One sample had a concentration exceeds MRL (both FSSAI and CODEX) in wheat and soil sample.

In 2018, three pesticides (carbendazim, chlorpyrifos and malathion) were detected in wheat and soil sample. All three pesticides were found to be present both in wheat and soil with detection frequency of 25% for malathion, 50% for carbendazim and 75% for chlorpyrifos. Carbendazim was found higher among three with a median value of 0.02 and 0.01 mg/kg in wheat and soil, respectively. Detection range of carbendazim was 0.0-0.081 mg/kg with a mean value of 0.030 mg/kg for wheat and 0.0-0.101 mg/kg with a mean value of 0.031 mg/kg in soil.Carbendazim with detected value of 0.081 mg/kg is exceeding the MRL value of 0.05 mg/kg in one of the sample as perlimit set by FSSAI and Codex Alimantarious. In soil, chlorpyrifos and malathion was detected in the range of 0.0-0.078 mg/kg and 0.0-0.032 mg/kg.

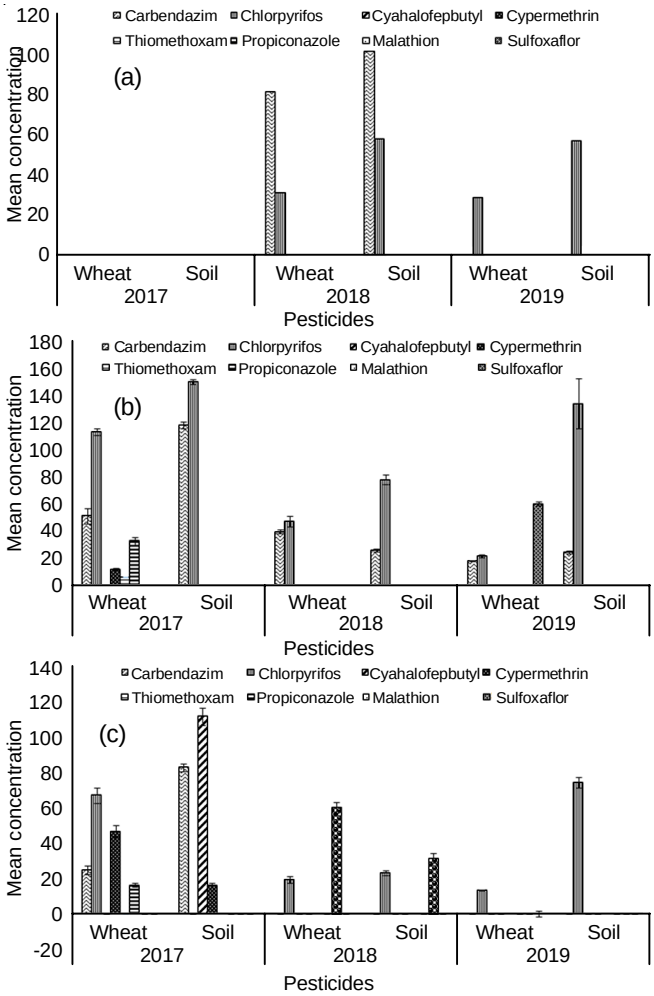

Fig. 1. Pesticides detected in Raispur (a), Loni (b) and Dasna village (c) of Ghaziabad city, India

In 2019, three pesticides detected named chlorpyriphos, carbendazim and sulfoxaflor with detected value of median 0.017 mg/kg in chlorpyrifos and < LOQ in carbendazim and sulfoxaflor in wheat. Detection frequency of chlorpyriphos, carbendazim and sulfoxaflor was found to be 75%, 25% and 25%, respectively. Detection range of chlorpyriphos, carbendazim and sulfoxaflor was 0.0-0.029, 0.0-0.017 and 0.0-0.060 mg/kg, respectively in wheat. Two pesticides were detected in

TABLE-7
RESIDUE CONCENTRATION OF PESTICIDES IN WHEAT AND SOIL SAMPLES IN 2017-2019

Pesticides	LOQ (mg/kg)	Year 2017		Year 2018		Year 2019		MRL (FSSAI)
		Wheat (mg/kg)	Soil (mg/kg)	Wheat (mg/kg)	Soil (mg/kg)	Wheat (mg/kg)	Soil (mg/kg)	
Azoxystrobin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.20
Bitertanol	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Carfentrazone ethyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Chlorimuron ethyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Clodinafop-propargyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.10
Deltamethrin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	2.00
Difenoconazole	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.02
Epoxyconazole	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Fenoxaprop-*p*-ethyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.02
Fipronil	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Iodosulfuron Methyl Sodium	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Isoproturon	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.1
Kresoxim Methyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Mesosulfuron Methyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Methabenzthiazuron	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.50
Methyl chlorophenoxy acetic acid (MCPA)	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.20
Metribuzin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.03
Pendimethalin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Picoxystrobin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Pinoxaden	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.700
Propiconazole	0.01	0.0-32.32	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Pyraclostrobin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Sulfosulfuron	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.02
Tebuconazole	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.15
Thiamethoxam	0.01	0.0-5.29	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Thiophanate-methyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.03
Triadimefon	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.5
Triallate	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Triasulfuron	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.01
Tridemorph	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.10
Trifloxystrobin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.20
Trifluralin	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Diclofop	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.10
Cypermethrin	0.01	0.0-46.71	0.0-15.91	< LOQ	< LOQ	< LOQ	< LOQ	2.00
Cyahalofepbutyl	0.01	< LOQ	0.0-111.66	< LOQ	< LOQ	< LOQ	< LOQ	
Chlorpyrifos	0.01	0.0-113.36	0.0-150.60	0.0-46.77	0.0-77.85	0.0-28.51	0.0-134.17	0.50
Malathion	0.01	< LOQ	< LOQ	0-60.24	0.0-31.65	< LOQ	< LOQ	10.00
Carbendazim	0.01	0.0-50.85	0.0-118.30	0-81.18	0-101.36	0.0-17.45	0.0-23.96	0.50
Sulfoxaflor	0.01	< LOQ	< LOQ	< LOQ	< LOQ	0.0-59.99	< LOQ	
2,4-Dichlorophenoxy acetic acid	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	2.00
Carbaryl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	2.00
Carbofuran	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.10
Dichlorvos	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	7.00
Ethion	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.03
Monocrotophos	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.03
Phenthoate	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Phorate	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Thiometon	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.03
Trichlorfon	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.05
Oxydemeton-methyl	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.02

LOQ = Limit of quantification; MRL = Maximum residual limit; FSSAI MRL stands from India food safety and standards regulation

soil named carbendazim and chlorpyrifos with a range of 0.0-0.024 & 0.0-0.057 mg/kg.

Detection rate of chlorpyrifos in the present study is the highest among all detected pesticides which is 66.67% (Fig. 2). Carbendazim is the second highest in terms of detection frequency. Carbendazim, chlorpyrifos and cypermethrin were detected in the current study which is in correlation with the study of Tao *et al.* [15]. Also carbendazim was found in most of the samples exceeding MRL which is supported by the earlier study conducted by Tao *et al.* [15]. Presence of carbendazim,

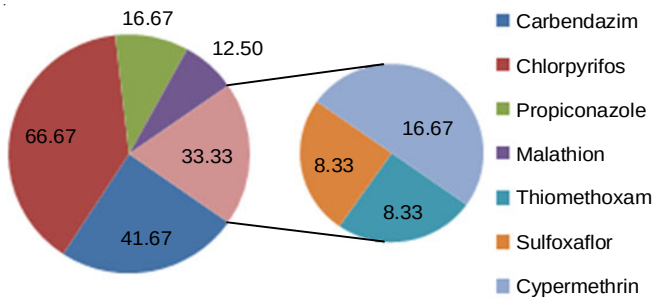

Fig. 2. Pesticides detection rate

chlorpyrifos, malathion in wheat is also supported by the study "Monitoring of Pesticide Residues in Products of Plant Origin in the European Union, Norway, Iceland and Liechtenstein 2001 Report". Malathion detected was below MRL, therefore presented no health risk to the consumers. Although the acute toxicity of malathion is modest (WHO Class III), it has neurotoxic potential and is a possible carcinogen and endocrine disruptor in the long-term. The malathion residues detection is in agreement with Soliman's report [18] and Pirsaheb *et al*. [19] which was lower than another reported value by Peterson *et al*. [20].

Residues correlation between the paired wheat and soil samples: A correlation analysis of residue concentrations between the wheat flour and corresponding soil samples was conducted, and the statistical results for the eligible pesticides were calculated. A $p < 0.05$ was obtained for carbendazim with correlation coefficients (r) of 0.608 and $p < 0.01$ was obtained for chlorpyrifos with correlation coefficients (r) of 0.632 indicating that the concentrations of these pesticides in the soil samples were significantly positively correlated with those in the wheat flour samples.Almost no correlations were observed between the paired wheat flour and soil samples for the other pesticides.

Chlorpyrifos, carbendazim and malathion were the main pesticides detected in soil. The fact that chlorpyrifos is somewhat persistent in soil helps explain its high detection frequency. Chlorpyrifos has a half-life of 60 to 120 days in soil, although it can range from 2 weeks to over a year depending on the soil type, temperature and other factors [21].

Dietary risk assessment: The monitoring study indicates that some pesticide concentrations above the MRL, implying that there is a danger of ingestion through consumption. As a consequence, a dietary risk assessment was performed to determine the degree of edible risk for wheat containing excess pesticides. For carbendazim, the concentration of all the samples ranged from 0.0-0.081 mg/kg and the EDI values calculated as per eqn. 1 was in the range of 0.00017 mg/kg bw to 0.00032 mg/kg bw in males and 0.00020 mg/kg bw to 0.00031 mg/kg bw in females. The estimated daily intake (EDI) for other pesticides were calculated and tabulated in Table-8. The hazard quotient (HQ) was also calculated and found to be higher for chlorpyrifos but less than 100%.The results of HQ and HI are summarized in Tables 8 and 9.

Contaminants' presence and buildup in the human body can cause health problems. Pesticide toxicity, as well as the quantity and duration of individual exposure to pesticide residues, influence the negative health effects of pesticides. As a result, determining the risk of pesticides on human health is a challenging task [9,22]. The risk evaluation of a consumer's

TABLE-8
DIETARY RISK ASSESSMENTS FOR PESTICIDES IN WHEAT SAMPLES FOR MALES

Pesticides	Number of samples	Residue conc. (mg/kg)	ADI (mg/kg bw)	Source	EDI (mg/kg bw)				HQ (%)				HI			
					Adult	10-12 year	13-15 year	16-18 year	Adult	10-12 year	13-15 year	16-18 year	Adult	10-12 year	13-15 year	16-18 year
Cypermethrin	2	0.047	0.02	JMPR 2004	0.00010	0.00019	0.00013	0.00010	0.50073	0.93259	0.64450	0.50540	3.894	7.252	5.012	3.930
Thiomethoxam	1	0.0053	0.08	JMPR 2010	0.00001	0.00002	0.00001	0.00001	0.01412	0.02629	0.01817	0.01425	–	–	–	–
Propiconazole	2	0.032	0.07	JMPR 2004	0.00007	0.00013	0.00009	0.00007	0.09741	0.18142	0.12537	0.09831	–	–	–	–
Chlorpyrifos	8	0.113	0.01	JMPR 1999	0.00024	0.00045	0.00031	0.00024	2.40777	4.48438	3.09911	2.43020	–	–	–	–
Malathion	1	0.06	0.3	JMPR 2016	0.00013	0.00024	0.00016	0.00013	0.04262	0.07937	0.05485	0.04301	–	–	–	–
Carbendazim	5	0.081	0.03	JMPR 2019	0.00017	0.00032	0.00022	0.00017	0.57531	1.07149	0.74050	0.58067	–	–	–	–
Sulfoxaflor	1	0.06	0.05	JMPR 2018	0.00013	0.00024	0.00016	0.00013	0.25569	0.47622	0.32911	0.25807	–	–	–	–

TABLE-9
DIETARY RISK ASSESSMENTS FOR PESTICIDES IN WHEAT SAMPLES FOR FEMALES

Pesticides	Number of samples	Residue conc. (mg/kg)	ADI (mg/kg bw)	Source	EDI (mg/kg bw)				HQ (%)				HI			
					Adult	10-12 year	13-15 year	16-18 year	Adult	10-12 year	13-15 year	16-18 year	Adult	10-12 year	13-15 year	16-18 year
Cypermethrin	2	0.047	0.02	JMPR 2004	0.00012	0.00018	0.00013	0.00012	0.592	0.894	0.656	0.584	4.602	6.953	5.103	4.544
Thiomethoxam	1	0.0053	0.08	JMPR 2010	0.00001	0.00002	0.00001	0.00001	0.017	0.025	0.018	0.016	–	–	–	–
Propiconazole	2	0.032	0.07	JMPR 2004	0.00008	0.00012	0.00009	0.00008	0.115	0.174	0.128	0.114	–	–	–	–
Chlorpyrifos	8	0.113	0.01	JMPR 1999	0.00028	0.00043	0.00032	0.00028	2.846	4.300	3.155	2.810	–	–	–	–
Malathion	1	0.06	0.3	JMPR 2016	0.00015	0.00023	0.00017	0.00015	0.050	0.076	0.056	0.050	–	–	–	–
Carbendazim	5	0.081	0.03	JMPR 2019	0.00020	0.00031	0.00023	0.00020	0.680	1.027	0.754	0.671	–	–	–	–
Sulfoxaflor	1	0.06	0.05	JMPR 2018	0.00015	0.00023	0.00017	0.00015	0.302	0.457	0.335	0.298	–	–	–	–

dietary intake to pesticide residues was critical since food is the major route for human exposure to environmental pollutants. Estimates of food consumption paired with pesticide residue levels have allowed the dietary intake of target chemicals to be calculated [23]. The concentration of detected pesticide residue in a sample, reliable food consumption statistics and the defined ADIs are used to assess the risk of pesticide-related chronic dietary exposure [24]. To avoid over estimating the EDI, the residual amount above LOQ was used in the EDI calculation [24]. Average body weight taken for male population as 65 kg, 34.9 kg, 50.5 kg, 64.5 kg for adult,10-12 years, 13-15 years, 16-18 years, respectively and for female population as 55 kg, 36.4 kg, 49.6 kg, 55.7 kg for adult ,10-12 years, 13-15 years, 16-18 years, respectively [16].

ADI reference taken from Joint FAO/WHO meeting on pesticide residues [25-30]. Data results obtained showed the highest EDI value for chlorpyrifos followed by carbendazim in all the age groups of males and females. The highest HQ was for chlorpyrifos in all the evaluation of this study but less than 100% represents no health risk through the consumption of wheat. The HQ values of all detected pesticides were below 7.25% and their dietary risk is lower than previous research on the risk assessment done by Beduk [31,32]. As reported in earlier study, the HQ of malathion as 12.5% [31] but in the current study it is much lower. Thiamethoxam dietary risk for humans across was found to be every low in wheat, which was in line with other studies showing that this pesticide showed little dietary pathway related effects on humans compared to other pesticides [33-35].

The HQ's were also summed up to get the Health Index (HI) of pesticides residues. The HI was maximum for the age 10-12 years may be due to difference in nutritional requirements and dietary intake among children, adults, male, female. The HI evaluated decreased in the following order 10-12 years > 13-15 years > 16-18 years > adults in male population. In the female population, order is as 10-12 years > 13-15 years > adult >16-18 years. The maximum HI observed was 7.25% in males and 6.95% in females which is very low. When HI is greater than 100%, chronic dietary risk should be of concern.

Conclusion

In this study, the major pesticides residues of two pesticides chlorpyrifos and carbendazim were detected in the wheat and soil samples from Ghaziabad city of India. A simple or precise method was developed and validated for the quantitative analysis of pesticides in wheat. It was observed that all the pesticides found were below MRL except carbendazim, which was detected above MRL in few samples. The health risk assessment also indicated that Indian consumers, children, adults, male, female are not at significant non-carcinogenic health risk. However, frequent consumption of wheat and presence of pesticides underlies the need for further mitigation and should be monitored routinely. Further research should be conducted to ascertain the contaminated source and concentrations in the local sampling area. Continuous monitoring and risk assessment for carbendazim on this wheat field is also greatly needed. With one exception, pesticides that exceed the maximum residual levels do not pose a non-carcinogenic risk. The findings are useful for risk monitoring and management in wheat fields, as well as aiding the scientific and appropriate application of pesticides. Continuous monitoring and control of pesticide residues in food commodities should still be carried out to sustain the level of compliance.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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