



Research article

Human health risk assessment of pesticide residues in vegetable and fruit samples in Gujarat State, India

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ARTICLE INFO

Keywords:

Pesticide residues
Fruits and vegetables
Dietary intake
Human consumption
Health risk

ABSTRACT

The present study was initiated with the purpose to evaluate possible health risks associated with pesticide residues through consumption of vegetables and fruits by general population of Gujarat, India. A total of 1075 samples comprising of twelve different varieties of commonly consumed food commodities were collected from twenty-five divergent locations in Gujarat. The collected samples were extracted using QuEChERS method and analyzed for the presence of organophosphorus (OPs), organochlorine (OCs) and synthetic pyrethroids (SPs) pesticides using UHPLC-HR/MS, GC- μ ECD and GC-MS/SIM. The results indicated that 2.3% of vegetable and fruit samples showed the presence of pesticide residues exceeding maximum residue limits (MRLs). The results suggested that, detected residue levels in samples were within safe limits and their consumption will not pose any significant health risk to human. The outcomes present significant information regarding the status of vegetable and fruit contamination and pointed out the prerequisite for further studies with reference to monitoring of pesticides and other toxic contaminants in different samples for assessing cumulative health risk.

1. Introduction

In recent years, there has been a substantial growth in usage of pesticides to fulfil the growing demand for food commodities through agricultural practices (Hashmi et al., 2020). Pesticide residue levels in food commodities are a major concern owing to their chemical properties striking a direct implication on human health across the globe. The exposure to pesticide residues in food and its presence in the environment is known to have effects in genetic polymorphism and promote initiation of diseases (Zhu et al., 2018). It is progressively being recognized that scores of chronic pathologies are closely associated with pesticide residues. Studies have also pointed towards the fact that, adverse effects of cumulative exposure to multiple-pesticide residues are much graver than any single exposure (Moser et al., 2005). Pesticide poisoning can lead to numerous disorders such as dyslipidemia, diabetes, liver, kidney and cardiovascular diseases (Aramjoo et al., 2021). Indiscriminate use of pesticides will precede to occurrences of residues of pesticides in vegetables and fruits. It has been proven that, residues exceeding certain limits in food products possess a possible risk to the general population, majorly due to their potential mutagenicity properties (Wu et al., 2017; Cheng et al., 2017; Zhu et al., 2017). These toxic

pesticides being banned for use on crops, remain to be detected with high frequencies in the environment (Hashmi et al., 2020; Kafaei et al., 2020) and biomedica due to their long degradation half-life, migration and bioaccumulation potencies (Hashmi et al., 2020; Venugopal et al., 2020).

Over a period of time, policy makers have stressed for implementation of regulatory requirements of pesticide residues in food commodities (Xu et al., 2012). Potential dietary exposure of pesticide residues is primarily calculated using MRLs established by the Codex Alimentarius Commission, European Union and other countries around the world (Zentai et al., 2016). The data of residue analysis, resulting from food monitoring programs can play a vital role to ensure enforcement of regulations as well as compliance to good agriculture practices (Blankson et al., 2016). Studies indicate that on an average 30% of fruits and vegetables amongst total food consumption are contaminated with pesticides (WHO, 2003; Quijano et al., 2016). Whilst studies have been performed throughout the world for pesticide residue analysis, but till date to best of our knowledge no studies has been performed with regards to health risk assessment of pesticide residues in general population of Gujarat. Therefore, this study was planned to quantify and confirm pesticide residues in fruits and vegetables using UHPLC-HR/MS, GC-MS/SIM and GC- μ ECD in turn to evaluate health risk assessment of

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the population of Gujarat, India. Health risk assessment would be evaluated by calculating Estimated Daily Intake (EDI), Hazard Quotient (HQ) as well as Hazard Index (HI). The results obtained could provide the status of potential health risk associated with pesticide residues in general population. These outcomes can also be used by regulatory bodies in an attempt to understand percolation of pesticide residues amongst fruit and vegetables consumed and in turn design corrective measures to reduce usage of pesticides to safeguard public health.

2. Materials and methods

2.1. Chemicals and reagents

Pesticide reference standards with certified purity of >99% were obtained from AccuStandard (New Haven, CT, USA). Optima LC-MS grade methanol and acetonitrile, water (ACS, Certified) was procured from Fisher Scientific (Law Fair, NJ, USA). Acetic acid (CH_3COOH), anhydrous magnesium sulphate (anhyd MgSO_4) and anhydrous sodium acetate (anhyd $\text{C}_2\text{H}_3\text{NaO}_2$) were procured from Sigma Aldrich (USA). The lock-mass internal standard leucine-enkephalin was purchased from Waters India Pvt Ltd. Primary secondary amine sorbent (PSA, 40 μm , Bondesil) was obtained from Agilent Technologies (USA).

2.2. Standard preparation

The analytical standards were prepared as follows; 100 mg L^{-1} individual standard solution were prepared from 1000 mg L^{-1} in a 10 mL volumetric flask. Standard mixture of 5 mg L^{-1} concentration were prepared from 100 mg L^{-1} individual standard solutions. The standard solutions were labelled, sealed and stored at a temperature of -20°C . The standard mixtures were used for determination of method detection limits (LOD_m) and method quantitation limits (LOQ_m), accuracy,

precision, linearity and recovery in different matrices. The target pesticides in our study were chosen based on their usage for agricultural activity in Gujarat state.

2.3. Sampling

A total of 1075 fruit ($n = 433$) and vegetable ($n = 642$) samples were collected from twenty-five different districts of Gujarat viz., Ahmedabad, Gandhinagar, Rajkot, Mehsana, Dahod, Radhanpur, Anand, Kheda, Narmada, Surat, Bhavnagar, Valsad, Patan, Surendranagar, Navsari, Amreli, Sabarkantha, Panchmahal, Bharuch, Vadodara, Dang, Bhuj, Jamnagar, Porbandar and Junagadh (Figure 1). The pesticide residue analysis was performed on these vegetable and fruit samples which included potato ($n = 93$), tomato ($n = 92$), onion ($n = 86$), okra ($n = 94$), brinjal ($n = 91$), cabbage ($n = 94$), cauliflower ($n = 92$), apple ($n = 100$), orange ($n = 81$), banana, ($n = 83$), mango ($n = 72$) and grapes ($n = 97$), respectively.

2.4. Sample preparation

The sample extraction was carried out utilizing Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method (Lehotay, 2007). Two kilograms of sample was mixed and blended using a high-volume homogenizer to obtain a representative sample. 15 g of these homogenized sample was accurately weighed into a 50 mL polytetrafluoroethylene (PTFE) centrifuge tube followed by addition of 15 mL of 1% CH_3COOH in acetonitrile. The resultant mixture was vigorously shaken for 2 min. Post this, 1.5 g of anhyd $\text{C}_2\text{H}_3\text{NaO}_2$ and 6 g of anhyd MgSO_4 were added, and the mixture was again shaken for a minute and then centrifuged for 3 min at 3500 rpm (5°C). An aliquot (6 mL) of the supernatant was transferred into a 15 mL PTFE tube, which contained 300 mg of PSA as well as 900 mg of anhyd MgSO_4 . The tube was again vigorously shaken for 30 s and

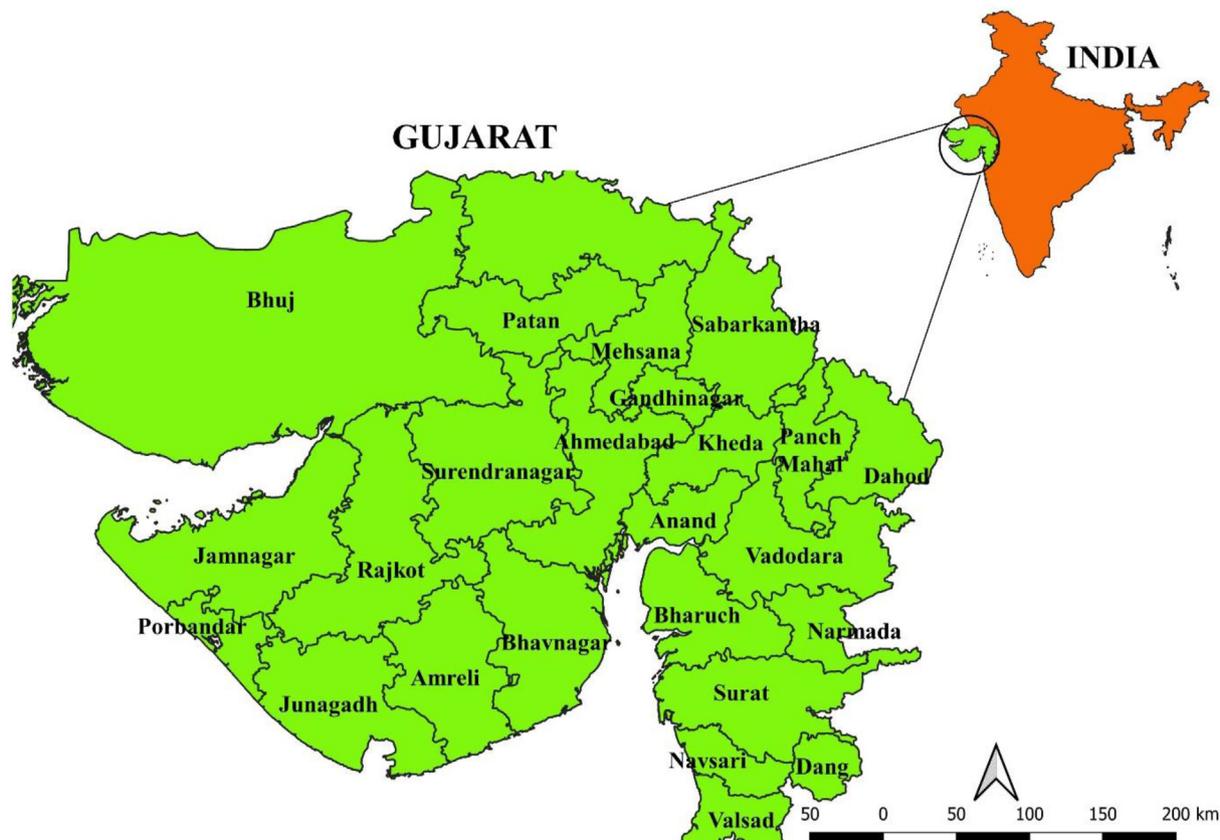


Figure 1. Map depicting sample collection locations from different districts in Gujarat, India.

centrifuged for 3 min at 2500 rpm (5 °C). 3 mL of aliquot was collected and then passed through PTFE syringe (0.22 µm) filter. The final extract 1 mL each were transferred into respective instrumental vials for analysis.

2.5. Instrumentation conditions

The quantification of organochlorine pesticides (OCs) and synthetic pyrethroids (SPs) were carried out utilizing Agilent Technologies 6890N Network GC system equipped with micro electron capture detector (µECD). The instruments operation conditions are enlisted in OCs and SPs in Tables S1 and S2. The operation of PerkinElmer Clarus 500 GC-MS system with SIM mode was proceeded for confirmation of OCs and SPs, respectively. The instrumental conditions and retention times (RT) along with qualifier ions of pesticides are described in Tables S3 and S4. The organophosphorus pesticides (OPs) were quantified and confirmed using UHPLC-HR-MS (Acquity, Synapt, Waters Inc., USA) and necessary instrumental conditions are cited in Table S5. The accurate mass was screened in the range of 50–500 *m/z* and an automated calibrant delivery was ensured to have accurate mass measurement of pesticide residue in samples. The UHPLC system was coupled with quadrupole time-of-flight mass spectrometer equipped with a 10 µL leucine-enkephalin (C₂₈H₃₇N₅O₇ at *m/z* 556.2771) being used as internal reference mass calibrant for accurate mass measurement utilizing lockspray devices. The MassLynx 4.1 outfitted with an application manager QuanLynx was used for data acquisition and quantification of pesticide residues.

2.6. Quality control and quality assurance

Quality control as well as quality assurance measures were included in the analytical scheme so as to ensure method efficiency. The LOD_m, LOQ_m, matrix-matched calibration, accuracy and precision of pesticides residues were evaluated by fortifying standard mixture of pesticides into homogenized untreated sample. Linearity was assumed when the regression coefficient was greater than 0.99 and the quantification was carried out through matrix-matched calibration. For matrix-matched calibration curves, blank sample extracts were enriched using working standard solutions in the final aliquot (SANTE, 2021). The required quantity of sample was also screened for pesticide residues resulting in absence of any residues. Therefore, it was considered a blank matrix and was used for method validation. Accuracy as well as precision was evaluated by means of recovery experiments in vegetable and fruit samples. Precision, usually expressed as repeatability of method, was determined in terms of relative standard deviation (%RSD) from recovery experiments at each fortification levels (n = 7) in each case. The %recovery and %RSD were evaluated at spiked concentrations of 10 µg kg⁻¹ for OCs, OPs and 25 µg kg⁻¹ for SPs, respectively to fulfil the criteria of recovery ranging within 70–120% and %RSD was less than 20%. LOD_m was established by multiplying the obtained standard deviation by 3.14 (student's t value for seven replicates, six degrees of freedom) and LOQ_m was estimated by multiplying 10 with the obtained standard deviation at the lowest spiking concentration as per analytical detection limit guidelines (Analytical detection limit guidance, 1996).

2.7. Health risk assessment

Health risk assessment was evaluated on the basis of integration of pesticide residues detected in analysed samples based on standardised food consumption rate for a 60 kg adult.

2.7.1. Estimated daily intake

The daily ingestion of pesticides depends on the type of food commodity and its pesticide concentration. Apart from that, human body weight may also affect the tolerance of pesticides. The EDI of pesticide residues in food samples for each combination was calculated (Eq. (1)) by the following formula:

$$EDI = C \times CR/BW \quad (1)$$

where EDI is estimated daily intake, C is mean concentration of the pesticide (mg kg⁻¹) found in a particular commodity; CR is the average daily consumption rate of each food (g d⁻¹) whereas BW is body weight (kg), which was set at 60 kg (WHO, 2010). The data related to average daily consumption rate was derived from NSS Report 2014, Government of India (NSSO, 2014).

2.7.2. Evaluation of health risk assessment in fruit and vegetable samples

For evaluation of long-term risk assessment in fruit and vegetable samples, HQ and HI ratios were calculated. If the ratio was observed to be less than unity (1), the consumer was considered to be adequately protected. The HQ was calculated (Eq. (2)) by dividing EDI with relevant acceptable daily intake:

$$HQ = EDI/ADI \times 100\% \quad (2)$$

where: ADI is acceptable daily intake.

The HI for a given diet was calculated (Eq. (3)) by summing the obtained hazard quotients (HQs) for each pesticide (p) in the particular commodity.

$$HI = \sum HQ \quad (3)$$

If HI exceeded a value of 1, there was a possibility of health risk associated with pesticide exposure. This evaluation method has been proven to deliver an indication regarding the commodities that contribute to health risk (EFSA, 2006).

3. Results and discussion

3.1. Quality control and quality assurance

Method performance was evaluated in terms of linearity, accuracy as well as precision. Matrix-matched calibration curves were constructed to minimize the matrix effect and also to compensate for analytical signals towards matrix interfering compounds. Thus, seven level matrix-matched calibration curves were used for the quantitation of pesticide residues in the samples. The values of correlation coefficient were reported to be greater than 0.99 for linearity range between 5–500 µg L⁻¹. With regard to LOD_m and LOQ_m of the method, obtained LOD_m ranged between 0.30–2.32 µg kg⁻¹, 3.74–7.25 µg kg⁻¹ and 1.0–3.0 µg kg⁻¹ for OCs, SPs and OPs, respectively in vegetables and fruit samples. The LOQ_m ranged between 0.95–7.20 µg kg⁻¹, 11.91–23.09 µg kg⁻¹ and 4.0–9.0 µg kg⁻¹ for OCs, SPs and OPs, respectively in the matrix. The obtained LOQ_m values were well within the MRL prescribed by Food safety and standard authority of India (FSSAI), European commission (EU) and Codex Alimentarius. The values for recovery of OCs, SPs and OPs ranged between 72–106%, 77–123% and 74–108% at spiked level of 10 µg kg⁻¹ and 25 µg kg⁻¹ for OCs, OPs and SPs, respectively. The percentage recovery range of all samples was within 70–120%, which is well within the accepted range (70–120%) for estimation of multi residues in the samples. The %RSD ranges were observed 1.1–8.7%, 1.0–6.8%, and 1.0–3% in the spiked samples, respectively. The obtained values were within the acceptable limits (≤20%) prescribed by SANTE/12682/2019. The obtained results are summarized in Tables 1 and 2. Overall, the method validation results were found to be excellent fulfilling the regulatory requirements as prescribed by the SANTE, (2021). The standard and spiked chromatograms of OCs described in Figures 2 and 3 and SPs are showed in Figures S1 and S2.

3.2. Distribution of pesticide residues in fruit and vegetable samples

Pesticide residues were analyzed in fruit and vegetable samples using UHPLC-HR/MS, GC-MS/SIM and GC-µECD. None of the samples analyzed showed OCs or SPs residues. OPs such as acephate, dichlorovos,

Table 1. GC- μ ECD method performances of pesticide residues in fruit and vegetable samples.

Pesticides	t_r^a	Calibration range ^b	r^{2c}	LOD ^d	LOQ ^e	RSD ^f	Rec ^g	Uc ^h
α -HCH	12.05	5–100	0.997	1.52	4.85	7.5	64	10
β -HCH	12.94	5–100	0.998	0.33	1.06	1.1	96	11
γ -HCH	13.21	5–100	0.998	1.48	4.71	6.5	73	11
δ -HCH	13.99	5–100	0.997	1.64	5.21	5.6	93	11
Heptachlor	15.83	5–100	0.998	2.26	7.20	8.7	83	12
Aldrin	17.10	5–100	0.998	1.73	5.52	6.8	81	2
Heptaclor-b	18.66	5–100	0.997	1.58	5.04	5.8	86	2
Heptaclor-a	18.85	5–100	0.998	2.10	6.68	7.8	85	14
α -Endosulfan	20.35	5–100	0.998	1.46	4.65	4.4	106	11
pp'DDE	21.52	5–100	0.997	1.07	3.40	4.6	74	12
Dieldrin	21.75	5–100	0.998	1.00	3.20	4.4	72	11
Endrin	23.03	5–100	0.997	0.78	2.47	3.0	82	10
β -Endosulfan	23.56	5–100	0.999	1.15	3.66	4.6	80	13
pp'DDD	24.06	5–100	0.998	0.30	0.95	1.2	81	12
Endosulfan sulfate	26.30	5–100	0.999	0.97	3.09	3.3	95	20
pp'DDT	26.58	5–100	0.998	0.98	3.12	3.9	80	10
Methoxychlor	31.15	5–100	0.998	2.32	7.38	6.8	108	10
Fluchloraline	9.16	25–500	0.993	7.22	22.98	2.3	100	20
Alachlor	10.62	25–500	0.994	5.96	18.98	2.0	96	16
Pendimethaline	12.45	25–500	0.994	6.49	20.68	2.0	103	22
Butachlor	13.43	25–500	0.993	6.84	21.80	2.2	100	22
Bifenthrin	17.29	25–500	0.99	7.08	22.54	1.9	117	26
Fenprothrin	17.48	25–500	0.989	7.25	23.09	2.1	113	15
λ - Cyhalothrin	18.65	25–500	0.991	6.78	21.59	2.8	77	25
Cyfluthrin	21.10	25–500	0.994	3.74	11.91	1.0	115	19
a - Cypermethrin	22.73	25–500	0.996	6.66	21.22	2.0	107	25
Fenvalerate	23.89	25–500	0.999	6.79	21.62	1.7	123	20
Deltamethrin	25.32	25–500	0.999	7.18	22.88	2.0	114	19

^a Retention time of the compound.

^b Calibration range ($\mu\text{g L}^{-1}$).

^c Linearity of analytes.

^d Limit of detection ($\mu\text{g kg}^{-1}$) defined at 10 ng/mL for OCs and 50 for SPs, 3.14 x (s), Student's t value, 3.14 (t value at 99%).

^e Limit of quantification ($\mu\text{g kg}^{-1}$) 10 ng/mL¹⁰ ng/mL for OCs and 50 for SPs, seven replicates, 10 x (s).

^f % Relative standard deviation (Seven replicates, n = 7).

^g % Recovery (Seven replicates, n = 7).

^h Uncertainty estimated for a level of confidence 95% (k = 2) at a concentration 10 $\mu\text{g kg}^{-1}$.

edifenfos, monocrotophos, profenofos, chlorpyriofos, diazinon, dimethoate, ethion, malathion and triazophos were detected in most of the samples analysed whereas phorate sulfoxide, phosphamidon, chlorfenvinphos, omethoate, malaonox, quinalphos, edifenphos and phosalone were absent in the samples. The results of pesticide residues detected in fruit and vegetable samples are tabulated in Table 3. The results showed that potato (n = 3), tomato (n = 2), cabbage (n = 13) and cauliflower (n = 7) reported pesticide residues above the MRL. Overall, a total of n = 25 samples (2.3%) reported were above the MRLs. It was observed that the concentration of acephate, monocrotophos, profenofos ranged from 11–3348, 1–212 and 14–374 $\mu\text{g kg}^{-1}$, respectively were found in tomato, okra, cabbage, apple and grapes samples.

A summary of the total vegetable samples (n = 642) analysed and their corresponding locations are presented in Table-S6. The results indicate that acephate, monocrotophos, ethion and profenofos were found in majority of the vegetable samples irrespective of their locations. The concentration of these pesticide residues was observed to be in the range from 10–3348 $\mu\text{g kg}^{-1}$, with the maximum concentration being observed in samples from Porbandar district. Anand region reported presence of pesticide residues; however, these were observed to be below the MRL prescribed by FSSAI, 2011. Profenophos was chosen as a representative pesticide detected in cauliflower samples using UHPLC-HR/MS and respective chromatogram is illustrated in Figure 4. The overall results hinted that among the 642 vegetable samples

analysed, n = 200 samples (31%) reported presence of pesticide residues. A total of 4% (n = 25) of samples analysed reported exceedance of MRL.

Study along similar research lines in different vegetables have been reported by other authors from varied parts of India. Sinha et al. (2012) carried out a dietary exposure assessment to varied OPs residues in vegetables using liquid chromatography–mass spectrometry of urban population in Hyderabad, India. Presence of chlorpyriphos was reported in eggplant, cabbage and cauliflower with observed concentration as 24.02, 10.55 and 2.85 $\mu\text{g kg}^{-1}$, respectively. Same samples also showed the presence of triazophos and phosalone with mean concentrations observed to be 0.863, 2.21, 0.491 $\mu\text{g kg}^{-1}$ and 50.85, 27.43 and 4.51 $\mu\text{g kg}^{-1}$ respectively. Baig et al. (2009) confirmed the presence of three OPs in 33 % of vegetable samples studied, with 8% of the samples reporting residues above prescribed MRLs. These samples included okra, pumpkins, and eggplant collected from Southern Punjab, Pakistan. Similarly, in West Bengal, a monitoring study conducted for estimation of pesticide residues in vegetable samples (n = 149) reported pesticide residues in concentration range from 1–2230 $\mu\text{g kg}^{-1}$. A total of 16 % of the samples had pesticide residues above MRL (Kole et al., 2002). Likewise, estimation of pesticide residues in fruits (1423) and vegetable (850) carried out in Turkey reported exceedance above MRLs of 8.4% and 9.8% of fruits and vegetables, respectively.

In the present study, fruit samples (n = 433) collected from varied districts of Gujarat were analysed for residues of pesticides. The

Table 2. Mass measurement of organophosphorus pesticide residues by *UHPLC-HR-MS*.

Analytes	M ^a	RT ^b	Ion ^c	m/z ^d	LODm ^e	LOQm ^f	% RSD ^g	Rec ^h	Uc ⁱ
Acephate	C ₄ H ₁₀ NO ₃ PS	1.04	[M + Na] ⁺	206.0024	3	8	3	83	30
Monocrotophos	C ₇ H ₁₄ NO ₅ P	1.60	[M + Na] ⁺	246.0515	2	8	1	76	30
Dimethoate	C ₅ H ₁₂ NO ₃ PS ₂	1.88	[M + Na] ⁺	251.9896	2	7	2	86	25
Phosphamidon	C ₁₀ H ₁₉ ClNO ₅ P	2.82	[M + H] ⁺	300.0769	3	8	2	118	10
Dichlorovos	C ₄ H ₇ Cl ₂ O ₄ P	2.94	[M + H] ⁺	220.9539	3	9	3	93	30
Malaoxon	C ₁₀ H ₁₉ O ₇ PS	3.03	[M + Na] ⁺	337.0479	2	5	1	108	25
Phorate Sulfoxide	C ₇ H ₁₇ O ₃ PS ₃	2.43	[M + Na] ⁺	298.9972	3	8	3	91	28
Edifenphos	C ₁₄ H ₁₅ O ₂ PS ₂	3.67	[M + H] ⁺	311.0328	3	9	4	84	30
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	3.71	[M + Na] ⁺	353.0246	2	7	2	108	35
Chlorfenvinphos	C ₁₂ H ₁₄ Cl ₃ O ₄ P	3.75	[M + H] ⁺	358.9773	1	4	3	104	30
Triazophos	C ₁₂ H ₁₆ N ₃ O ₃ PS	3.78	[M + H] ⁺	314.0730	3	9	2	107	31
Phosalone	C ₁₂ H ₁₅ ClNO ₄ PS ₂	3.80	[M + Na] ⁺	389.9765	2	6	3	90	30
Profenophos	C ₁₁ H ₁₅ BrClO ₃ PS	3.96	[M + Na] ⁺	394.9250	3	8	2	80	40
Quinalphos	C ₁₂ H ₁₅ N ₂ O ₃ PS	4.03	[M + H] ⁺	299.0621	2	7	2	106	28
Chlorpyrifos	C ₉ H ₁₁ Cl ₃ NO ₃ PS	4.18	[M + Na] ⁺	371.9157	3	8	2	74	20
Ethion	C ₉ H ₂₂ O ₄ P ₂ S ₄	4.38	[M + Na] ⁺	406.9769	2	6	2	83	38

^a Molecular formula of the analytes.

^b Retention time of the compound.

^c Molecular ion with sodium and hydrogen adduct ions.

^d Experimental mass of analytes.

^e Method detection limit ($\mu\text{g kg}^{-1}$) 10 ng/mL, 3.14 x (s), Student's t value, 3.14 (t value at 99%).

^f Limit of quantification ($\mu\text{g kg}^{-1}$) 10 ng/mL¹⁰ ng/mL.

^g % Relative standard deviation, Seven replicates (n = 7).

^h % Recovery, Seven replicates (n = 7).

ⁱ Uncertainty estimated for a level of confidence 95% (k = 2) at a concentration 10 $\mu\text{g kg}^{-1}$.

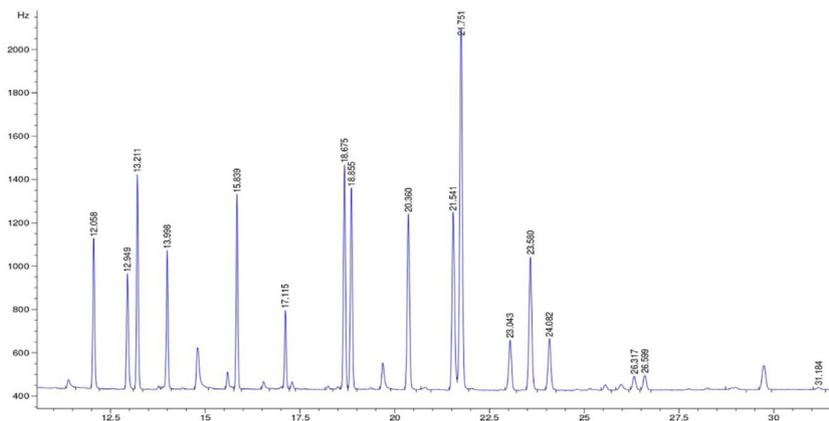


Figure 2. GC- μ ECD typical standard chromatogram of organochlorine pesticides at 10 $\mu\text{g/L}$.

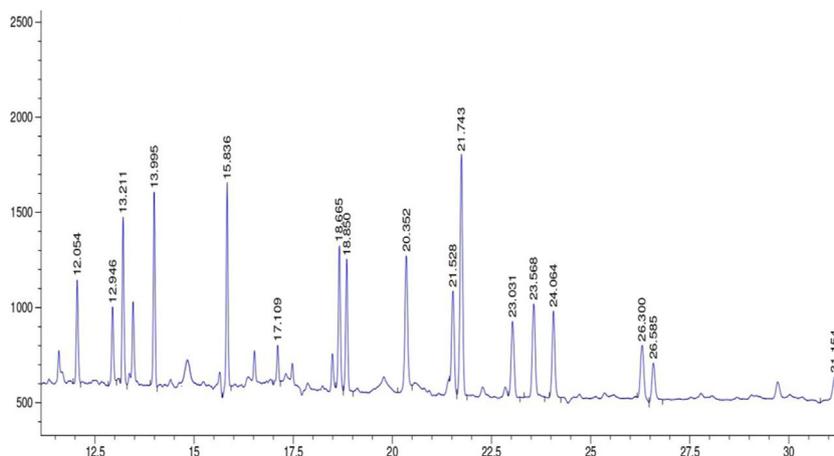


Figure 3. GC- μ ECD typical spiked chromatogram of organochlorine pesticides in sample at 10 $\mu\text{g kg}^{-1}$.

Table 3. Pesticide residues in vegetable and fruit samples collected from various locations in Gujarat, India.

Matrix	No. of detectable samples (%)	No. of samples > MRL (%)	Pesticide residues	Frequency of detection	Concentration range, mg kg ⁻¹	No. of samples > MRL			
Potato	16 (17)	3 (3.2)	Acephate	3	0.013–0.084	-			
			Monocrotophos	4	0.041–0.130	2			
			Dimethoate	2	0.046–0.046	-			
			Chlorpyrifos	1	0.013	1			
			Profenofos	2	0.037–0.164	-			
			Ethion	4	0.055–0.064	-			
Tomato	35 (38)	2 (2.1)	Acephate	9	0.020–1.219	-			
			Monocrotophos	10	0.029–0.207	2			
			Dimethoate	2	0.031–0.047	-			
			Profenofos	6	0.016–0.161	-			
			Ethion	8	0.052–0.59	-			
			Onion	9 (10)	-	Monocrotophos	2	0.036	-
Onion	9 (10)	-	Dimethoate	3	0.037–0.146	-			
			Profenofos	4	0.244–0.331	-			
			Okra	61 (65)	-	Acephate	27	0.011–3.348	-
Okra	61 (65)	-	Monocrotophos	11	0.010–0.094	-			
			Dimethoate	1	0.010	-			
			Chlorpyrifos	2	0.020	-			
			Profenofos	14	0.014–0.374	-			
			Ethion	5	0.026–0.057	-			
			Triazophos	1	0.012	-			
Brinjal	14 (15)	-	Acephate	9	0.123–1.197	-			
			Monocrotophos	2	0.046–0.159	-			
			Dimethoate	2	0.142	-			
Brinjal	14 (15)	-	Profenofos	1	0.025	-			
			Cabbage	40 (43)	13 (13.8)	Acephate	15	0.122–1.169	-
			Cabbage	40 (43)	13 (13.8)	Monocrotophos	4	0.055–0.090	-
Chlorpyrifos	13	0.019–0.291				13			
Profenofos	4	0.029–0.157				-			
Ethion	4	0.055–0.061				-			
Cauliflower	25 (27)	7 (7.6)				Acephate	14	0.122–1.555	-
Cauliflower	25 (27)	7 (7.6)	Monocrotophos	3	0.010–0.145	-			
			Chlorpyrifos	7	0.029–0.300	7			
			Profenofos	1	0.037	-			
Apple	49 (49)	-	Acephate	10	0.013–0.891	-			
			Monocrotophos	14	0.032–0.209	-			
			Dimethoate	5	0.033–0.146	-			
			Diazinon	1	1.467	-			
			Chlorpyrifos	8	0.013–0.090	-			
			Profenofos	4	0.029–0.032	-			
Apple	49 (49)	-	Ethion	7	0.059–0.071	-			
			Profenofos	7	0.018–0.248	-			
			Banana	10 (12)	-	Acephate	2	0.132–0.904	-
Banana	10 (12)	-	Monocrotophos	2	0.049–0.167	-			
			Dimethoate	3	0.143–0.147	-			
			Profenofos	1	0.155	-			
			Ethion	1	0.058	-			
			Edifenfos	1	0.021	-			
Mango	7 (10)	-	Acephate	2	0.022–0.100	-			
			Monocrotophos	3	0.027–0.212	-			
			Chlorpyrifos	1	0.025	-			
			Ethion	1	0.063	-			
Grapes	24 (25)	-	Acephate	11	0.068–1.588	-			
			Monocrotophos	2	0.153	-			
			Dimethoate	2	0.144	-			
			Chlorpyrifos	8	0.016–0.290	-			
			Profenofos	1	0.023	-			

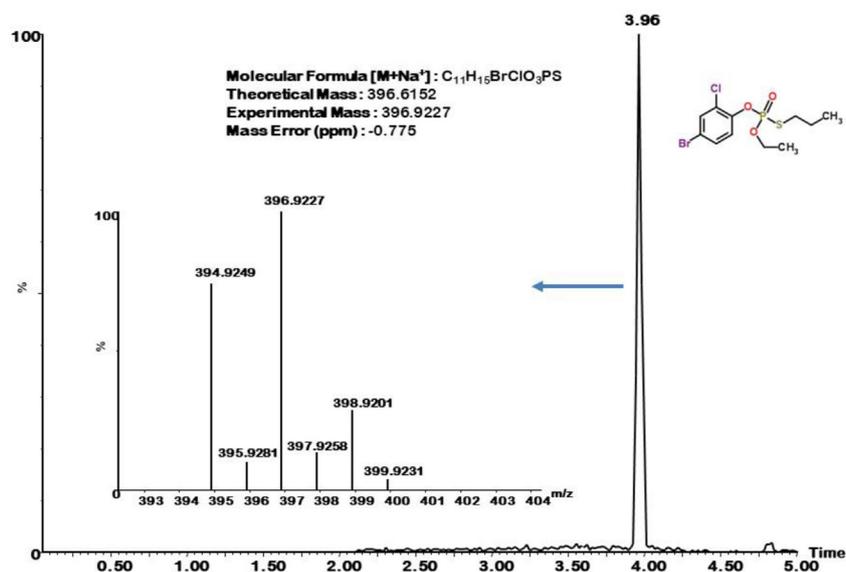


Figure 4. Profenophos detected in cauliflower by UPLC-QTOF-MS; Extracted ion chromatogram of profenophos (RT 3.96; m/z 394.9249); Accurate mass spectrum of profenophos.

concentration range and distribution pattern are tabulated in Table S7. The results of the analysis indicated that residues of acephate, monocrotophos, dimethoate, chlorpyrifos, ethion and profenofos were detected in samples collected from most of the locations. The detected pesticide residue concentration ranged from 10–1588 $\mu\text{g kg}^{-1}$ with the maximum concentration observed in Narmada district. Location wise results indicated that out of 433 samples studied, 22% ($n = 97$) of the samples had pesticide residues below MRL (FSSAI, 2011). Dimethoate was chosen as the representative pesticide which was detected in fruit (apple) samples and its chromatogram is described in Figure 5. Similar studies on pesticide residues comprising various fruits of India and other countries too have been reported. Srivastava et al. (2011) carried out a study for determination and quantitation of pesticide residues in fruits and vegetables and the study included different classes of pesticides viz., thirteen OCs, seventeen OPs, ten SPs and eight herbicides. The outcomes depict the presence of twenty-three pesticides with the concentration being in range from 5–12350 $\mu\text{g kg}^{-1}$. Some vegetables samples such as radish, cauliflower, cucumber, okra and cabbage showed the presence of pesticide (α -BHC, dichlorvos, permethrin and chlorfenvinfos) residues

and were above MRL (FSSAI, 2011) limits. However, the levels of pesticide residues in other samples were observed to be below MRL. Likewise, Yuan et al., 2014 estimated presence of chlorpyrifos in celery, cowpea, Chinese cabbage and celuce with detection rates observed to be 22.8, 18.7, 15 and 10.6 % respectively. A similar study was conducted in fruits and vegetables by Knezevic et al., (2012), wherein the results showed that chlorpyrifos was found in orange, potato and lettuce with the highest residue levels being 67, 37 and 71 $\mu\text{g kg}^{-1}$, respectively. Diazinon was estimated in apple, orange and pear with peak concentration levels being 9, 28 and 8 $\mu\text{g kg}^{-1}$, respectively. The same study also evaluated presence of dimethoate in lettuce, pepper, and eggplant; wherein the highest concentration was observed to be 0.24, 0.05 and 0.10 $\mu\text{g kg}^{-1}$, respectively.

3.3. Co-occurrence of pesticide residues in food samples

Post evaluation for occurrence of pesticide residues, these food samples were further evaluated for presence of single and multiple pesticide residues. The presence of multiple pesticides was detected in

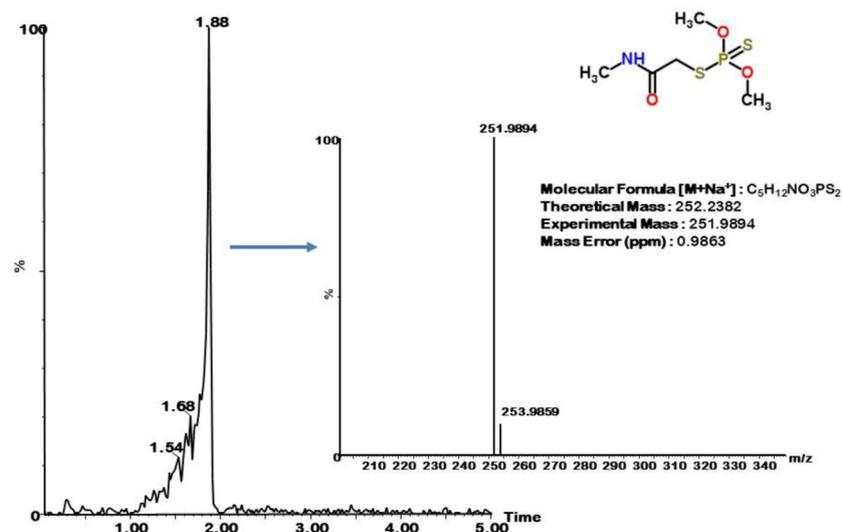


Figure 5. Dimethoate detected in apple by UPLC-QTOF-MS; Extracted ion chromatogram of dimethoate (RT 1.88; m/z 251.9895); Accurate mass spectrum of dimethoate.

12.4% of samples while 7.1% (n = 52) of the samples contained two different residues, 3.1% (n = 15) of the samples contained three pesticide residues and 2.2% (n = 8) of the samples were observed to be contaminated with four pesticide residues. Okra, cauliflower, tomato, cabbage and apple were found to contain more than one pesticide residue in a single sample. In recent years, it has been commonly observed to find two or more pesticide residues in vegetable samples. Wu et al. (2017) carried out exposure risk assessment and reported the presence of about 19 pesticide residues in a single garlic sprout. Some cultivated vegetable and fruit samples highly sensitive to pests have been observed to contain more than one pesticide residue since these often require multiple successive pesticide applications.

3.4. Evaluation of risk assessment in fruit and vegetable samples

3.4.1. Estimated daily intake

The EDI was calculated for detected vegetable and fruit samples and the results obtained are summarized in Table 4. The contribution of dietary intake of pesticide residues by consuming vegetable samples are in the following order: potato > tomato > brinjal > cabbage > okra > cauliflower > onion. The calculated EDI values were compared with the recommended ADI values to predict the exposure of pesticide residues in vegetable samples. The outcomes reveal that none of the samples exceeded the ADI.

With regard to contribution of dietary intake of pesticide residues in fruit samples, the following order was observed: Banana > grapes > apple > mango > orange. The calculated EDI values did not exceed ADI for any of the studied samples. A study carried out by Lozowicka et al. (2016) among adults and children exposed to residues of insecticides having a common mode of action (MoA) in pome, stone berries and other fruits reported that group of pesticides with highest contribution to ADI were found to be OPs viz. dimethoate and diazinon with 48% and 66% of ADI for adults and 144% and 294% of ADI for infants respectively.

3.4.2. Hazard quotient (HQ)

The HQ of pesticide residues through consumption of vegetables and fruits has been calculated and same have been tabulated in Table 4. None of the vegetable and fruit samples reported HQ values >1 thereby indicating that daily intake of these did not possess health risk. Overall results exhibited that vegetable and fruit samples do not possess risk and hence can be considered safe for human consumption. In Urmia city, health risk assessment was conducted on Iranian apple and grape where the results revealed HI value <1. Hence, consumers are not exposed to

high risk due to pesticide residue detected in the sample (Mahdavi et al., 2022). Pesticide residues were estimated in green-house cucumber, cantaloupe, and melon samples from markets in Iran by QuEChERS extraction method based on analysis with UHPLC-MS/MS. In the study, non-carcinogenic and carcinogenic probabilistic health risk assessments were evaluated by HQ, HI, and CR (Carcinogenic Risk). The results indicated HQ values where less than 1 in adult and children consumers for all pesticide residues. However, CR values were found to possess considerable carcinogenic risk in these commodities (Mahdavi et al., 2022a). Potential health risk assessment was evaluated in vegetables and fruits samples for pesticide residues. The results showed that consumers are not exposed to health risk because HIs values were <1 (Eslami et al., 2021; Hamid et al., 2017).

3.4.3. Hazard index (HI)

The HI values obtained from consumption of vegetables were evaluated for a mixture of pesticide residues in vegetable and fruit samples and results are portrayed in Table 4. HI values observed for acephate, dimethoate, profenofos and ethion were >1 and for rest of the pesticides it was found <1, respectively. Therefore, there is a possibility for health risk associated with consumption of these vegetables and fruits in long-term. An earlier study carried out by Wu et al. (2017) reported the target hazard quotient (THQ) of all pesticides (o-methoate, carbofuran, pyridaben, fipronil and difenoconazole) to be less than 1, when the hazard index (HI) was 0.0872. Liu et al. (2016) carried out a study on risk assessment of pesticides in nuts of China and they reported an insignificant Acute Health Index for consumption of nuts. However, in the course of a long term risk assessment, the risk indices were observed to be notably higher than the HIs, indicating chronic risk of pesticide exposure via nuts. Lehmann et al. (2017) carried out a dietary risk assessment for pesticides from drinking water and vegetables in Burkina Faso. The obtained results indicated that MRLs values had exceeded prescribed limits in 36% of analyzed samples. The exceedance above MRL values suggest a risk to consumers and therefore limits the export opportunities. Li et al. (2018) evaluated 15 pesticide residues in peach samples as also the associated dietary exposure risks for the Chinese population. They observed the presence of thirty-nine different pesticides, with 92.3% of analysed samples reporting presence of single and multiple pesticide residues. Likewise, eight pesticide residues in 3.2% of the analysed samples exceeded the MRLs with highest exceedance being 34.5%. Acute risks for children from chlorpyrifos, carbendazim, cyhalothrin, cypermethrin, pyridaben as well as triazophos; and for adults from exposure to triazophos exceeded acceptable levels in worst case scenarios. The authors (Sharma et al., 2022; Balkan and Yilmaz, 2022; Constantinou et al., 2021; Mozzaquatro et al., 2022) carried out various studies w.r.t to risk assessment and the results reveal that the consumers had no significant risk and also suggested that the study could be used for pesticide supervision and risk management programme. Likewise, the present study also showed no significant health risk to consumers in Gujarat state.

4. Conclusion

The present work is a maiden attempt to explore the level of pesticide residues and their associated health risk in vegetable and fruit samples from different districts of Gujarat, India. The outcomes have potential to serve as a background reference data for generalized exposure of pesticides in the inhabitants of Gujarat. Overall, pesticide residues in vegetable and fruit samples may not be perceived as a serious problem since most of pesticides residues (97.67 %) did not exceed the MRLs. In case of EDI limits, none of the vegetable and fruit samples exceeded recommended acceptable daily intake (ADI) and none of the samples exceeded the HQ of 1, thereby indicating that consumption of these do not pose any health risk to humans. Some pesticides viz., acephate, dimethoate, profenofos and ethion reported HI to be greater than 1, thereby implying that these pesticides may have an associated risk factor. However, the possibility of risk can be reduced by employing systematic monitoring

Table 4. Estimated Daily Intake (EDI) and risk assessment for each pesticide.

Pesticide	EDI ($\mu\text{g kg}^{-1}$ bw day $^{-1}$)	Acceptable Daily Intake ^a ($\mu\text{g kg}^{-1}$ bw day $^{-1}$)	Hazard Quotient ΣHQ	Hazard Index (HI)
Vegetables				
Acephate	3.106	30 (JMPR, 2011)	0.104	10.355
Dimethoate	0.139	2 (JMPR, 2003)	0.069	6.936
Triazophos	0.002	1 (JMPR, 2002)	0.002	0.211
Chlorpyrifos	0.079	10 (JMPR, 2004)	0.008	0.788
Profenofos	0.350	30 (JMPR, 2007)	0.012	1.166
Ethion	0.102	2 (JMPR, 1990)	0.051	5.121
Fruits				
Acephate	0.235	30 (JMPR, 2011)	0.008	0.782
Dimethoate	0.064	2 (JMPR, 2003)	0.032	3.200
Chlorpyrifos	0.012	10 (JMPR, 2004)	0.001	0.122
Profenofos	0.064	30 (JMPR, 2007)	0.002	0.215
Ethion	0.033	2 (JMPR, 1990)	0.017	1.675

^a Acceptable daily intake prescribed for pesticides by JMPR-Codex Alimentarius (FAO/WHO, 2004).

and integrated pesticide management system/programme. The policy makers may create awareness among farmers to adopt good agricultural practices and follow integrated pesticide management system for prevention of pesticide exposure (Bhandari et al., 2019). Since dietary daily intake is a key factor for pesticide exposure assessment in humans, the overall assessment of human health risk still remains ambiguous and difficult in the general population due to differing dietary habits, metabolic activities and influence of several combined factors. Nevertheless, the dietary consumption of these samples does not possess risk to human health. Further studies as well as monitoring of toxic pollutants in different samples needs to be conducted for evaluating the cumulative exposure of toxic pollutants. Hence, continuous monitoring is suggested so that there is inclusion of wide range of pollutants in the samples.

Declarations

Author contribution statement

Sivaperumal P; Rupal Thasale; Dharendra Kumar; Tejal G Mehta; Riddhi Limbachiya: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This work was supported by the Indian Council of Medical Research [IRIS ID NO. 2011-02530].

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2022.e10876>.

Acknowledgment

The authors are greatly thankful to the Director in charge, ICMR-National Institute of Occupational Health (ICMR-NIOH) for guidance and support. We are also thankful to Mr. Chandrakant Parmar for his support during the sampling.

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