

Original Research

Investigation of Multi-Pesticide Residues in *Prunus persica* L. (peach) Cultivars of District Swat Using Gas Chromatography-Mass Spectroscopy

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Abstract

Protection of agricultural crops from pests and diseases is very important to fulfill the needs of growing population. For this purpose, different types of chemicals are used which leads to the accumulation of toxic organic and inorganic compounds in agricultural cycle particularly in economically important fruits and vegetables. Pesticide residue analysis is fundamentally important to ensure the safety of foods, plant and animal origin, and to preserve the environment. It is therefore crucial to monitor fruits and vegetables for pesticide residues using available advanced analytical techniques. The current study was assigned to investigate pesticide residues in peach fruit. We selected six peach cultivars (Early Grand, Florida King, NJC (05), Elberta (06), Maria Delezia, and Indian blood) from four different locations of district Swat. The sampled fruit varieties were then analysed for pesticide residues using gas chromatography and mass spectroscopy (GC-MS). Results showed that Early Grand variety had pesticide residues with highest concentration of Cypermethrin ($16.7 \pm 1.38 \mu\text{g kg}^{-1}$) followed by Pyridaben ($7.425 \pm 0.11 \mu\text{g kg}^{-1}$). In Florida King, the highest concentration of Endosulfan ($32.78 \pm 0.9 \mu\text{g kg}^{-1}$) is detected followed by Metachlore ($17.36 \pm 0.44 \mu\text{g kg}^{-1}$). In variety NJC and Elberta, Pyredaben, Propachlor, Carbofuran, Cypermethrine, Endosulfan, and Cyhalothrine compound were found. In both varieties, Endosulfan was in the highest concentration ($21.27 \pm 1.20 \mu\text{g kg}^{-1}$ and $67.94 \pm 4.61 \mu\text{g kg}^{-1}$ respectively). As these two varieties had close harvesting time, both varieties showed a similar pattern of pesticide residues. In variety Maria, Difenazonazole was found in the highest concentration ($187.51 \mu\text{g kg}^{-1}$) while the Indian blood variety difenazonazole

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was noted with the highest concentration ($88.60 \pm 8.9 \mu\text{g kg}^{-1}$). The Chloropyrifos was not detected in any variety and the possible reason may be, it is applied at flowering stage before fruit initiation. Although all cultivars at different locations had pesticide residues, however it cannot be considered a serious public health problem because compounds and their residual levels were below critical concentration as defined by European Union regulations. Furthermore, judicious use of pesticides in fruit and vegetable would certainly ensure their minimal exposure in products.

Keywords: *Prunus persica* L., pesticides, mass spectrometry, gas chromatography

Introduction

Agriculture and horticulture sectors share more than 20% of its gross domestic product (GDP), providing an opportunity of employment to 67.5 % population of Pakistan [1]. These sectors help in improving the life styles of individual of rural areas linked to agriculture [2]. Vegetables and fruits are the important components of horticulture crops across the globe due to its consumption rate. Pakistan is an agriculture country and it exports different fruits (Apple, Peach, Mango, Oranges, etc.), vegetables (Turnips, Carrots, Radish, Cabbages etc.) to United Arab Emirates, India, Afghanistan, Saudi Arabia, United Kingdom and China etc. to earn valuable foreign exchange [3]. Apart from nutritional and economic value, fruits also provide important antioxidants to reduce toxic substances produced as a result of metabolic activities in cell [4]. These antioxidants offers resistance to certain human diseases like cardiac disorders, diabetes mellitus, neurodegenerative diseases and cancer etc. [5].

Agriculture revolution has increased the chemical burden on natural environment, of which, pesticides is widely used agrochemicals to protect crops [6]. On the other hand, these pesticides are very hazardous to environment due to their potential of causing adverse effects both to living and non-living components. Since several pesticides have been linked to health and environmental problems, they have been phased out of use [7]. Chemical pesticides have been related to a range of negative health effects, including dermatological, gastrointestinal, neurological, carcinogenic, respiratory, reproductive, and endocrine effects [8]. Pesticides enter to living system either through direct contact, ingestion, or inhalation. The type of pesticide, its duration, the route of exposure, and the individual's health status (e.g. nutritional deficits and healthy/damaged skin) all influence the risk of harmful health impacts [7]. Pesticide residues can be present in a wide range of daily foods and drinks, such as cooked meals, water, wine, fruit juices, snacks, and animal feeds [9].

Climatic condition of Pakistan favours growth (production) of vegetables, fruits and other ornamental plants [10]. The fruit sector had excellent development in the last few decades. Among which, peach is believed the "Queen" of fruits having very next position to apple in terms of popularity. Fresh peach is comprised of very healthy nutrients, good source of vitamins (A and C)

and also contains potassium and fibres. In Pakistan, atmosphere of Khyber Pakhtunkhwa (KP) favours the peach cultivation. Land over 950 meters above the sea level is an ideal for nurturing of peach plant. It is grown in northern areas of KP, of which Swat, Peshawar, Parachinar, Chitral, and Hazara are very prominent. District Swat of KP yields high quality of peach fruit in Pakistan [11].

Pesticide residues in food are rapidly increasing causing significant health implications and therefore, attract global attention [12]. The resurgence of pests, soil, water and air pollution, annihilation of predators, parasites and other non-target species exposes the adverse effects on ecological systems inextricably linked to human health [13]. In Pakistan, over 108 insecticides types, 30 fungicides, 39 weedicides, 5 acaricides, and 6 rodenticides are currently in use [14]. Misuse of pesticides leads to financial losses as well as health risks. The current level of pesticides in the environment (soil, water, and air) helps to measure its impact on human health [15, 16]. The present work was designed, to provide base-line data on status of pesticide residues level in the peach fruit samples from different locations of district Swat. This study will also help in determination of toxicity level of pesticides in fruits.

Materials and Methods

In Pakistan, district Swat is very popular due to its greenery producing a number of edible fruits. In the current study, peach cultivars from 4 of sub-divisions of district Swat (i.e. Matta, Khwaza Khela, Kabal, and Barikot) (Fig. 1) were selected for determination of pesticide residues. 6 peach cultivars were selected from each sub division namely: Early Grand (EG), Florida King (FK), NJC (05), Elberta (06), Maria Delezia (MD), and Indian Blood (IB). Each variety was collected from individual sub division during 2018. A total of 24 fresh fruits composite samples were collected from different peach orchards in district Swat for pesticide residues analysis. We evaluate pesticides residues in the collected mature fresh peach fruit samples from farmer's orchards.

Reagents Used

Sigma-Aldrich provided acetonitrile (HPLC grade),

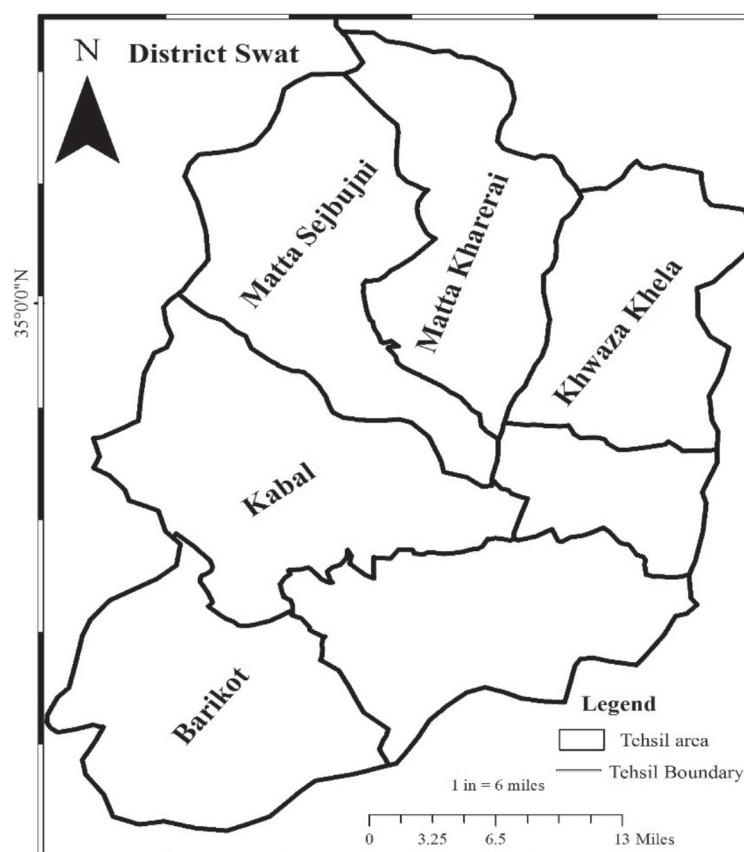


Fig. 1. Map of the study area.

anhydrous magnesium sulphate (99.5%), glacial acetic acid, anhydrous sodium acetate (99.5%), primary-secondary amine (PSA), and NaCl (Germany). All of the chemicals used in the experiment were analytical grade.

Samples Preparation

Collected fruit samples from the farmer's orchards were placed in polythene bags and labelled properly. Samples were then kept in ice box, and brought to the Pakistan Council of scientific and Industrial Research Complex, Peshawar. The samples were stored in 4°C, than chopped into smaller pieces for extraction of pesticides residues QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) following standard method of Albinet et al. [17].

Extraction

Aliquot (8 ml), 1.2 g of MgSO_4 and 50 mg sorbent (Primary secondary amine) were added to extract. The extract tube was then vortex and centrifuged for 1 minute at 3500 rpm.

Volume of extract was then reduced to 0.3 - 0.5 ml by removing the excess solvent using rotary evaporator (50°C and reduced pressure). Next toluene was added to make final volume 1 ml. For drying, 1.2 g anhydrous MgSO_4 were added to extract and then swirl to settle

down solid materials. The supernatant was filtered by 0.45 μm membrane and transferred the aliquot to GC vial for analysis on GC-MS.

GC-MS Analysis

A Shimadzu QP 2010 plus gas chromatography-mass spectrometry system (Kyoto, Japan) was used for the study. An SE 30 capillary column (50 m 0.25 mm ID at 0.25- μm film thickness) was used for separation. The temperature program for the column was set to begin at 50°C and hold for 1 minute, then gradually increase to 300°C and hold for 10 minutes. At a column flow of 1 ml min^{-1} , the carrier gas was helium (99.999 percent). The interface and injection were set to 250°C to break a 1 l injection into two sections. For the determination of selected pesticides, an ion monitoring mode with electron effect ionization was used.

Results and Discussion

The determination of pesticides residues in peach fruit was carried out Pakistan Council of Scientific and Industrial Research Laboratories, Peshawar. Information regarding extent of pesticide application for different varieties of peach samples was obtained from local farmers. The selection of peach varieties was based upon their popularity and high consumption

Table 1. Different Peach varieties containing pesticide residues (μgKg^{-1}).

Varieties	Early grand	Florida King	NJC (05)	Elberta (06)	Maria Delezia	Indian blood
Compounds detected						
Pyridaben	7.425 \pm 0.11	13.8 \pm 2.5	24.25 \pm 2.15	22.3 \pm 0.82	28.50 \pm 4.06	11.29 \pm 3.12
Chlorpyrifos	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0
Propachlor	2.94 \pm 0.42	1.15 \pm 0.4	0.81 \pm 0.46	1.54 \pm 0.85	4.10 \pm 0.75	5.16 \pm 0.87
Carbofuran	1.74 \pm 0.12	12.39 \pm 1.06	0 \pm 0	15.21 \pm .01	4.21 \pm 0.09	17.45 \pm 0.81
Metachlore	0 \pm 0	17.36 \pm 0.44	0 \pm 0	0 \pm 0	0 \pm 0	18.0 \pm 0.77
Cypermethrine	16.7 \pm 1.38	4.47 \pm 2.01	4.14 \pm 1.49	3.56 \pm 0.55	2.28 \pm 0.32	1.85 \pm 0.52
Dichlorovos	2.27 \pm 0.29	2.11 \pm 0.91	0 \pm 0	0 \pm 0	0 \pm 0	2.31 \pm 0.05
Endosulfan	0 \pm 0	32.78 \pm 0.9	21.27 \pm 1.20	67.94 \pm 4.61	18.41 \pm 1.18	10.39 \pm 1.48
Cyhalothrine	0 \pm 0	15.32 \pm 1.13	14.51 \pm 0.11	0 \pm 0	0 \pm 0	34.8 \pm 1.03
Difenaconazole	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	88.60 \pm 8.9	107.4 \pm 4.2
Acetamprid	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	90.02 \pm 2.47

rates by indigenous population of KP. Different types of pesticides are being used in order to control pest infestation in food crops. The results of the current study indicate that toxins are absorbed in fruits, where metabolizing enzymes are responsible for their bio-activation and detoxification. The toxicity of different pesticides and insecticides like Chlorpyrifos (CPF) and diazinon (DZN) can be mediated through metabolism to CPF-oxon and DZN-oxon, respectively [18]. These toxic chemicals can also be detoxify to trichloropyridinol (TCP) and 2-isopropyl-4-methyl-6-hydroxypyrimidine

(IMHP) [19, 20]. Physiologically based pharmacokinetic/ pharmacodynamic (PBPK/PD) models have been developed for the Organophosphorus (OP) like Chlorpyrifos (CPF), Metolachlor (Met), Profenofos (Prfe) and Diazinon (DZN) etc. It is anticipated that these OPs could interact at a number of important metabolic steps including: CYP450 mediated activation/ detoxification, B-esterases carboxylesterase (CaE), butyrylcholinesterase (BuChE) and acetylcholinesterase (AChE) or PON-1 (A-esterase) oxon detoxification [21].

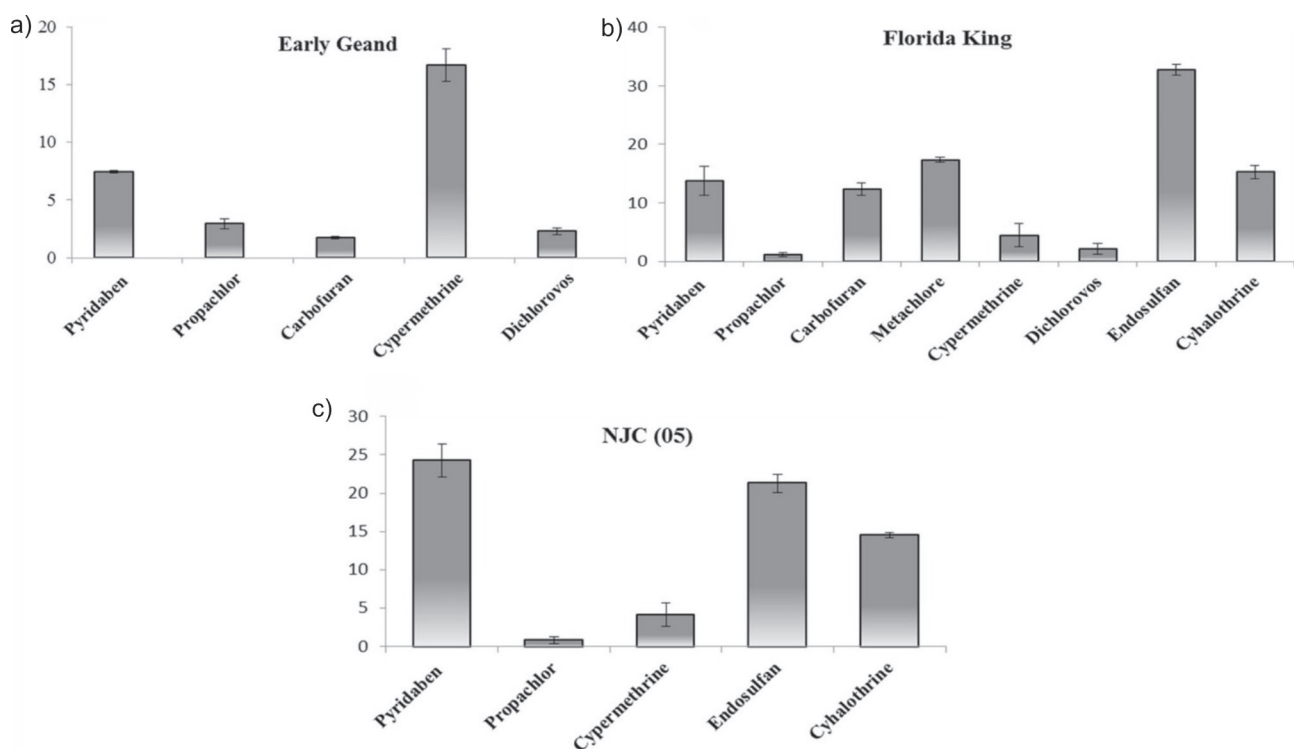


Fig. 2. Pesticides residues in various cultivars of peach: Early Grand a), Florida King b), and NJC-05 c).

Table 2. GC-MS instrument calibration with the standard pesticides.

Name of the compound	Retention time	Area	LOD	LOQ	R ²	Y= a+bx
Aldicarb deg	3.46	303263	0.09	0.31	0.997	6545X-295
Methamidophos	6.40	740971	0.07	0.25	0.998	15699X-519
Dichlorovos	6.46	800123	0.04	0.14	0.999	14042X-446
Carbofuran deg.	7.06	22574	0.19	0.65	0.990	604X-10
Metolcarb	8.82	1059299	0.04	0.13	0.999	20807X+232
Propachlor	10.41	997615	0.01	0.06	0.999	19635X+212
Carbofuran	11.85	118382	0.07	0.23	0.998	2182X-141
Atrazine	11.99	187875	0.10	0.33	0.997	4045X-167.67
Acetochlor	13.45	262899	0.27	0.89	0.982	6779X-961.67
Metribuzin	13.57	132571	0.26	0.87	0.983	3385X-460
Methiocarb Sulfoxide	13.94	4755	0.02	0.06	0.999	114X+4.33
Metolachlor	14.63	1453128	0.24	0.81	0.985	36570X-4929.33
Chloropyrifos	14.68	190666	0.30	1.01	0.978	4855X-621.67
Aldrine	14.80	145268	0.20	0.67	0.989	3694X-567.67
Pendimethalin	15.58	123348	0.24	0.82	0.984	3901X-550
Alpha endosulfan	16.92	46174	0.29	0.98	0.978	1221X-192.33
Profenofos	17.45	295149	0.20	0.68	0.989	7640X-1276
p, p' DDE	17.57	317812	0.24	0.81	0.984	8340X-1398
Beta Endosulfan	18.77	24757	0.28	0.93	0.980	675X-125
Acetamiprid	21.65	70817	0.13	0.45	0.995	2245X-258.33
Cyhalothrine I	23.18	60776	0.24	0.81	0.985	1905X-209.67
Cyhalothrine II	23.51	206316	0.25	0.84	0.983	4691X-799.67
Pyridaben	25.28	770168	0.23	0.76	0.986	19155X2406.7
Cypermethrine I	26.66	41545	0.24	0.82	0.984	1389X-218.33
Cypermethrine II	26.96	123198	0.31	1.05	0.976	2550X-275.33
Fenvalerate I	28.36	71844	0.23	0.78	0.986	1542X-226
Fenvalerate II	28.76	49303	0.17	0.58	0.991	1318X-277
Difenaconazole I	29.22	116223	0.18	0.63	0.990	2881X-329.33
Difenaconazole II	29.347	122589	0.075	0.250	0.998	2476X+29.667

Gas chromatography-electron capture detection recorded 0.04-0.25 µg/kg of 11 pesticides residues. The recoveries of the 11 pesticides in the vegetable and fruit samples were 81.5-111% with the relative standard deviations less than 11.2% [22]. Similarly pesticides residues detection in 85 fruits and vegetables shows recovery 81 % of pesticides through GC-MS [23]. Linear calibration curves for studied pesticides were obtained with correlation coefficients (r²) between 0.985 and 0.999. The LOD were ranges from 0.018 to 0.317 mg kg⁻¹ while the level of quantification ranged from 0.060 to 1.058 mg kg⁻¹. The levels of pesticide residues found in collected samples are presented

in Table 1. Eleven pesticides i.e. Pyridaben (Pyr), Chlorpyrifos (CPF), Propachlor (Pro), Carbofuran (Car), Metachlore (Met), Cypermethrine (Cyp), Dichlorovos (Dic), Endosulfan (End), Cyhalothrine (Cyh), Difenaconazole (Dif), and Acetamiprid (Ace) were found at levels between 0.81 µg kg⁻¹ and 107.4 µg kg⁻¹ (Table 1). The transport behaviour of Propachlor in the presence of thiosulfate was found to be relatively complex compared to traditional conservative or single-constituent tracers. Using thiosulfate to reduce the emissions of pesticides at the soil surface and as a soil remediation methodology [24].

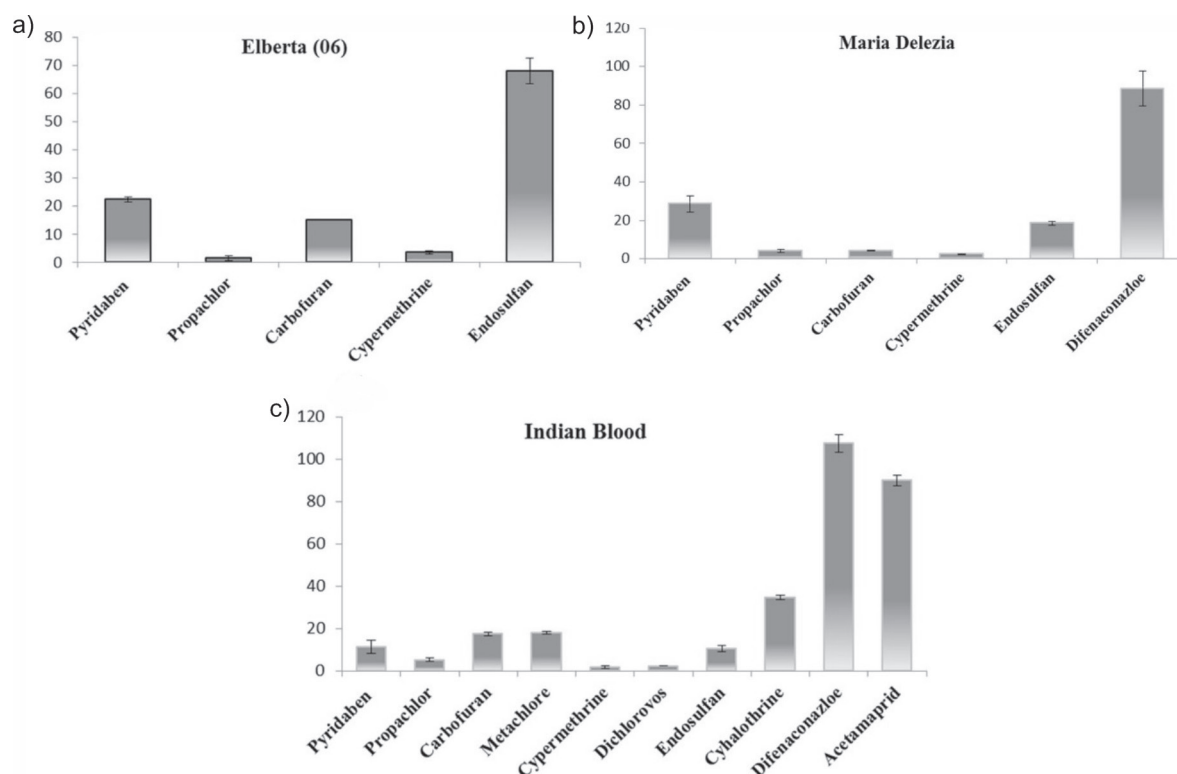


Fig. 3. Pesticides residues in various cultivars of peach: Elberta-06 a), Maria Delezia b), and Indian Blood c).

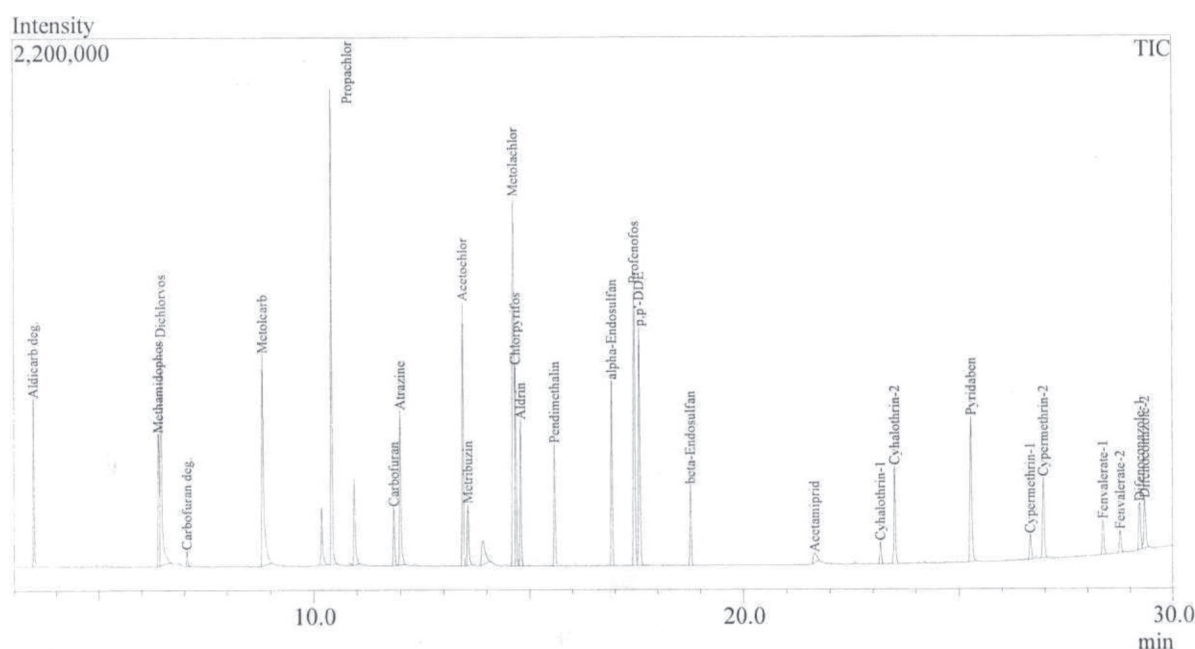


Fig. 4. GC-MS chromatogram of the Standard Pesticides.

The detection area ranged from 0.78 mg/mL to 50.0 mg/mL was recommended fit for the demand of quantitative determination of Pro residue in plant productions [25]. Cross-reactivity indicated that the antiserum could only react with Metalaxyl and its acid, but not Met, Diethatyl-ethyl, Alachlor Pro, or Benzoylprop-ethyl, whose structures are similar to

Metalaxyl [26, 27]. Current data showed that majority of residues monitored were in concentrations below maximum residual limit (MRL). The increased selectivity of GC-MS reduces effect of matrix, and thus reduces limits of detection (LOD) ranged from $0.81 \mu\text{g kg}^{-1}$ – $107.4 \mu\text{g kg}^{-1}$ lower than MRL (Fig. 4). Sample preparation methods that have been proposed

to date for extraction of neonicotinoids might remain in a complicated sample matrix with lesser quantity for cleaning up, the interfering components that coexist in the sample extract [28]. In the present study, EG variety contained Pyr, Pro, Car, Cyp and Dic pesticide residues with highest concentration of Cyp $16.7 \pm 1.38 \mu\text{g kg}^{-1}$ followed by Prop $7.425 \pm 0.11 \mu\text{g kg}^{-1}$, while other pesticides residues were low and not hazardous to human health (Fig. 2a). In FK, Pyr, Pro, Car, Met, Cyp, Dic, End, and Cyh were detected. Among these, the highest concentration of End $32.78 \pm 0.9 \mu\text{g kg}^{-1}$ was detected followed by Cyh $15.32 \pm 1.13 \mu\text{g kg}^{-1}$ (Fig. 2b).

In variety NJC-05 and variety Elberta-06, Pyr, Pro, Car, Cyp, End and Cyh were detected. Pyr ($24.25 \pm 2.15 \mu\text{g kg}^{-1}$) was recorded maximum for NJC-05 followed by End ($21.27 \pm 1.20 \mu\text{g kg}^{-1}$), while the Pro was ranked the last with $0.81 \pm 0.46 \mu\text{g kg}^{-1}$ amount of residues (Fig. 2c). Unlike to NJC-05, the amount of End was ($67.94 \pm 4.61 \mu\text{g kg}^{-1}$) maximum for Elberta-06, while in same there was no residue of CPF, Met, Dic, Cyh, Dif and Ace (Fig. 3a). As these two varieties have similar harvesting time, therefore both varieties had a similar pattern of pesticide residues. Similar results for pesticides residues in peach fruits were reported by [29]. In variety MD, Pyridaben, Propachlor, Carbofuran, Metachlore, Cypermethrin, Endosulfan and Difenaconazole were detected. Among these compounds, Difenaconazole was detected in highest concentration ($88.60 \pm 8.9 \mu\text{g kg}^{-1}$) in comparison to other pesticides (Fig. 3b).

The Indian blood variety was contaminated with the Pyridaben, Propachlor, Carbofuran, Metachlore, Cypermethrine, Dichlorovos, Endosulfan, Cyhalothrine, Difenaconazole, and Acetamaprid except Chlorpyrifos (Fig. 3c). Generally, Chlorpyrifos was not detected among all the mentioned varieties because Chlorpyrifos was sprayed at dormant period when plants had no fruits. Similar results were reported for Chlorpyrifos in peaches in Pakistan [30]. Current study significantly correlates with results of [31]. Comparison of pesticides residues in different varieties showed that early varieties have less extent of pesticides residues as compared to late fruiting varieties. The present study showed that current contamination level cannot be considered as a serious public health problem according to EU regulations. To prevent pesticides exposure, it is necessary to reduce and monitor use of pesticides in fruit and vegetable products. Nevertheless, pesticide residue monitoring programs are appropriate to ensure minimal residue levels in products [32].

Conclusion

The present study was conducted to investigate the pesticides residues in different peach cultivars fresh fruits. The result revealed that the early fruiting

cultivars have less amount of pesticides residues as compared to the late fruit producing cultivars. All cultivars at different locations had pesticides residues; however, it cannot be considered a serious public health problem because the compounds and their residual levels were below critical concentrations as defined by European Union regulations. Furthermore, judicious use of pesticides in fruit and vegetable would certainly ensure their minimal exposure in products.

Conflict of Interest

The authors report no conflicts of interest.

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