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Investigation of Pesticide Persistence on *Berberis vulgaris* L. in Iran

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ABSTRACT

Pesticide residues and their derivatives in agricultural products are a serious threat to consumer's health. Due to the use of barberry in the raw state, determination of the residual common pesticide residue is essential, which has not been done so far. This study aimed to evaluate the pesticide residues in the *Berberis vulgaris* by QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction, and Gas chromatographic-mass spectrometry (GCMS) in Iran. In general, barberry fruit samples from *Berberis vulgaris* gardens from 6 different regions have been studied, in which Diazinon, Phosalone and Oxydemeton-methyl pesticides have been used, the durability of the effects of Diazinon, Oxydemeton-methyl and Phosalone pesticides on barberry extract was investigated within 15 days daily with three replicates. In this study, Diazinon has the least duration, until the 12th day. Oxydemeton-methyl has a weak downtrend in Barberry, and the Phosalone pesticide has more stability in this product during this investigation.

Keywords: Pesticide persistence, *Berberis vulgaris*, QuEChERS, Extraction.

INTRODUCTION

Pesticides are chemical substances that are very toxic and persistent in the environment. Although their use for plant protection products in agriculture result in benefits, they can be harmful both to the environment and as residue in particular products and consequently to human and animals (Jallow *et al.*, 2017). There may be allergic and carcinogenic effects that can come from digestive organs. Small amounts even can be harmful if they accumulate as a result of long intake (Cakici and Akat, 2013).

A maximum residue level (MRL) is the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly in Good Agricultural Practice (Yadegarian *et al.*, 2013).

Berberis vulgaris, the common Barberry, produce edible berries that people in many countries eat as a refreshing fruit. The shrub is native to central and southern Europe, northwest Africa and western Asia (Othman *et al.*, 2014). In Iran and Southwest Asia, berries used in cooking in rice, and production of jam and barberry juice. Zereshk, a dried fruit that is

widely cultivated in Iran is a Persian name for Berberis. The Southern Khorasan province in Iran is the main area of common barberry production in the world, especially around Birjand and Qaen (85% of production is in Qaen and about 15% in Birjand). There is evidence of cultivation of seedless barberry in South Khorasan two hundred years ago (Hermenean *et al.*, 2015). The use of the plant in traditional medicine has been limited by the bitter taste of the bark and root. However, numerous folk medicinal uses for barberry exist. Other reported medical applications include the treatment of fever, gout, renal and biliary diseases, rheumatic symptoms, diarrhea, gastric indigestion, and dermatitis. Many studies have been reported barberry's beneficial effect on the liver (Ashraf and Zare, 2016).

Diazinon, functions as an acetylcholinesterase (AChE) inhibitor. It is a thiophosphoric acid ester, colorless to dark brown liquid. When it enters in to the body, it is oxidatively degenerated to diazoxon. Diazoxon is an organophosphate compound that is much more poisoning than diazinon and causes mainly the inhibition of AChE. The activation of diazinon is located in the liver microsomal enzyme system and requires NADPH. It might cause adverse effects to other organisms (Saraei *et al.*, 2016).

Phosalone is an organophosphate chemical commonly used as an insecticide. It is a weak acetylcholinesterase inhibitor (Ye *et al.*, 2009). Using phosalone residues in milk may have unfavorable effects on the health of humans. When ewes fed on 280 mg phosalone per day for 63 consecutive days, pesticide residue found in milk, feces, and urine during both sampling periods. (Kazemi *et al.*, 2017)

The level of oxydemeton-methyl existing in cucumber in Kerman greenhouses were assessed that the median for oxydemeton-methyl was 1.910 mg/L (Ganjeizadeh Rohani, 2014). No studies exist on the measurement of residual pesticides in barberry. In this study, we detected three most common pesticides that used to control pests of barberry in Iran and checked their shelf life in barberry.

MATERIALS AND METHODS

To evaluate the pesticide residues in barberry products, some barberry gardens were selected in Qaen city (Zohan, Zirkooh and Haji-Abad areas) with no use of chemical pesticide and fertilizers, but only Diazinon, Oxydemeton-methyl and Phosalone pesticides were sprayed. At the time of harvesting barberry in the region (late October and November) clusters of fresh barberries were selected according to the international method recommended by Codex Alimentarius 2000, at intervals of 24 hours to the 15th day. Samplings were carried out daily, and placed in a cold condition (4°C) and transferred to the laboratory away from light. Each sample was identified and tested according to the code. First, the barberry seeds were separated from the barbed branches and thoroughly crushed and keep in suitable containers (Eppendorf Tubes®) and kept refrigerated until injected into the Gas Chromatograph.

For the extraction and purification method, QuEChERS Extraction (quick, easy, cheap, effective, rugged, and safe) method was used as AOAC Official Method 2007.01.

The level of Diazinon and Oxydemeton-methyl existing in cucumbers sampled from Kerman greenhouses were assessed in 2014. Due to high moisture content in cucumber compared to barberry, the pesticide residue was extracted by acetone and dichloromethane. The extracts were cleaned up according to the solid-phase extraction method. The pesticide residues were determined by capillary gas chromatography with nitrogen-phosphorus detection (Ganjeizadeh Rohani, 2014). In barberry due to low moisture, the QuEChERS Extraction method was used.

The gas chromatography method is effective for achieving low detection limits; however, samples need to be cleaned up. GC is accurate, sensitive, and very reliable; so it is suitable for

monitoring studies, For cleanup, before injecting samples into GC-MS, to ensure that the device is clean, all parts of the device especially the injector and detector (interface) increased to the maximum possible temperature for some minutes.

Gas chromatography machine conditions have been set as follows:

Column: (column of the type: non-polar) Restec-Rxi-1ms

Column oven: 120-270°C 3 min Hold Pressure: 80 KPa Injector: 250°C Start time: 3min Column flow: 1mL/min Carrier gas: Helium 99.999%

Detector settings (MS) in SIM Mode; Interface: 300°C Ion Source: 200°C

For Analysis the Schimatzu Gas chromatography (GC-MS QP 2010 PLUS) was used, the barrel was splitless and the 30-meter Restek column -1ms®Rxi, with External diameter 0.25mm and internal diameter 0.25µm. The carrier gas was Helium, with 99.9999 purity and 1ml per minute flowed, and the Pressure was 80kPa. The Injector temperature was 250°C, and Detector was 300°C. The Detector voltage was 70 eV. The Oven temperature at first 120°C within 3min, then up to 170°C with 5min/c speed. Then raise to 250°C with 2 min/c speed, then up to 300°C with 5min/c speed and 3min stop in this temperature. One microliter of sample was injected in splitless mode, the device tuned in SIM (Selected Ion Monitoring) and by Electron Ionization analyzed. (Table1) To calculate Relative Standard Deviation (RSD), first, the standard deviation and standard error for each sample calculated and then RSD amount in each sample was determined for each pesticide. The Detection limit (LOD) and Limit of quantitation (LOQ) from standard solutions of each pesticide were determined. (Pesticides Standards were from Sigma-Aldrich)**.**

Table1. Number of Ionic pesticides

Pesticides	Ion No. (m^{-1})		
Diazinon	179	304	199
Oxidemethon methyl	88	169	60
Phosalone	367	182	-

Table2.Persistence of tracking Pesticides (mg/L)

Sample	Pesticides	24h	5D	7D	10D	11D	12D	13D	14D	15D
Barberry	Oxydemeton-methyl	870.13	14.02	12.50	0.019	0.07	0.07	0.017	0.01	0.011
		910	17.08	15	0.098	0.019	0.018	0.015	0.015	0.085
		805/88	15	11.90	0.062	0.019	0.011	0.01	0.016	0.03
	Diazinon	120.12	9.5	0.05	0.095	0.01	<LOQ	<LOQ	<LOQ	<LOQ
		102.49	10.14	0.07	0.048	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		105.85	10.14	0.039	0.056	0.04	<LOQ	<LOQ	<LOQ	<LOQ
	Phosalone	610.48	199	190.50	10.54	8.5	2.01	1.95	0.99	1.13
		699.10	245	210	10.99	8.1	2.55	1.5	1.1	0.99
		577.8	223	135	10.721	6.5	1.99	0.85	0.5	0.43

RESULTS AND DISCUSSION

All barberries were collected from Qaen city (Zohan, Zirkooh and Haji-Abad areas) in south Khorasan Province with no use of chemical pesticide and fertilizers. The durability of the effects of Diazinon, Oxydemeton-methyl and Phosalone pesticides, spiked on barberry extract was investigated within 15 days daily with three replicates (Table 2).

A significant amount of Diazinon in barberry extract reaches 0.05 mg/L after 7 days. In the meantime, the use of diazinon pesticides is of the least duration, until the 12th day is completely unidentifiable. And the Phosalone pesticide has more stability in this product. So, on the twelfth day remain about 1 mg/L in the Barberry. Oxydemeton-methyl has a weak downtrend in Barberry. It has a significant residue until the tenth day after harvest and then weakening.

The residue amount of Oxydemeton-methyl on third day was more than the amount of doses that have been sprayed. While the pesticide Phosalone has very little useful life on the third day. This can be due to the potential effects of the pesticide and the chemical nature of barberry on the duration of the residue and pesticide effects. The Diazinon pesticide has the least period of residue, so it is completely unidentifiable until the 12th day.

Many of the fruit and vegetable samples are contaminated with pesticide residues, with concentrations above the MRL (Maximum Residue Level) the amount of pesticide residue that can be accumulated in foods, depends on factors such as the chemical itself, soil type, moisture, soil Ph, temperature and cultivation (Talekar *et al.*, 1977).

Darko and Akoto (2008) analyzed 350 local fruits and vegetables that were purchased from markets in Kumasi in Ghana. The results showed that 37.5% of samples contained no detectable levels of the studied pesticide residue.

From the public health point of view, any tracked levels of pesticide residues pose a potential health risk for consumers. MRL levels for Barberries have not yet been reported in Iran. Therefore, in order to reduce this risk, in addition to being aware of the need for farmers to properly use pesticides, pesticide residue monitoring is constantly recommended (Ramachandran *et al.*, 2009). Actually, there isn't many data on long-term persistence in soil under field conditions and real application practices exist for polar and more degradable pesticides, (Aurea, *et al.*, 2017).

Kazemi *et al.* (2017) proclaimed the remains of Phosalone and Diazinon until the fifteenth day with a slowdown in alfalfa. However, Phosalone, in contrast to Diazinon, had a longer shelf life in alfalfa, and was further degraded over time. Talebi, (2006) noted that the decreasing trend of Phosalone and Diazinon residues in the fresh alfalfa forms an exponential curve that contradicts our results.

Understanding pesticide behavior in plants is important for effectively applying pesticides and in reducing pesticide exposures from ingestion (Tianxi, *et al.*, 2017).

The findings of this study might help in extending awareness in farmers and local people about pesticides and their hazardous effects on humans. Repeated spraying of farms and early harvesting after spraying, and failure to comply with the residue level period and bringing it to the market and consuming these products seriously threatens the health of consumers. So surely in March, when aphid's eggs were observed abundantly, it is the best time to fight them. Even in the event of chemical warfare, the residue level of pesticides is also observed, and the aphid damage is also prevented. However, the information obtained from Qaen city farms seems inadequate. Due to possible indirect exposure, the results pose a high risk to human health.

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