

Research Article

Analysis of Vegetables and Fruits Organophosphorus Pesticides Residual Detecting Results in Qingdao Market

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Abstract: In this study, organophosphorus pesticides residuals of vegetables and fruits in Qingdao market were detected and analyzed and the detecting results provide valuable data for food safety control and agriculture supervisions. Testing method in national standard NY/F761-2008 was applied to detect 16 kind of organophosphorus pesticides residuals in 350 vegetable and fruit samples. Detecting results showed that, in 350 samples, there were 52 positive in pesticide residuals and the qualified rate was 85.14% and in these samples, there were 39 samples in which 1 pesticide residual quantity was unqualified, 9 samples in which 2 pesticide residual quantity were unqualified, 3 samples in which 3 pesticide residual quantity were unqualified and 1 samples in which 4 pesticide residual quantity were unqualified. Pesticides residuals were all positive in the vegetables, fruits and grains sold in Qingdao market in 2014 and the situation is especially serious in leaf vegetables. This suggests that the food enterprises should pay more attention to this situation and should control more carefully in food materials safety.

Keywords: Fruits, organophosphorus pesticides, pesticides residual, vegetables

INTRODUCTION

Organophosphate pesticides degrade rapidly by hydrolysis on exposure to sunlight, air and soil, although small amounts can be detected in food and drinking water. Their ability to degrade made them an attractive alternative to the persistent organochloride pesticides, such as DDT, aldrin and dieldrin (Mo, 2014). Although organophosphates degrade faster than the organochlorides, they have greater acute toxicity, posing risks to people who may be exposed to large amounts (see the Toxicity section below).

Commonly used organophosphates have included parathion, malathion, methyl parathion, chlorpyrifos, diazinon, dichlorvos, phosmet, fenitrothion, (Sultatos, 1994) tetrachlorvinphos, azamethiphos and azinphos-methyl. Malathion is widely used in agriculture, residential landscaping, public recreation areas and in public health pest control programs such as mosquito eradication (Richins *et al.*, 1997). In the US, it is the most commonly used organophosphate insecticide. Forty organophosphate pesticides are registered in the U.S. (Bonner *et al.*, 2007), with at least 73 million pounds used in agricultural and residential settings (Simplicio and Boas, 1999). China was a large pesticides-use country. The annual used quantity of

pesticides was in the first place in the world. Among all the pesticides, the quantities of organophosphorus pesticides account for more than 70% of the total used pesticides. Organophosphorus pesticides were widely used on vegetables (Liu *et al.*, 2005), fruits and grains. The pesticides residuals on crops directly relate to the food safety (Wu *et al.*, 2007). In order to know the current situation of organophosphorus pesticides residuals on vegetables, fruits and grains in Qingdao, this study analyzed the test results of the organophosphorus pesticides residuals on vegetables, fruits and grains in Qingdao in 2012. It helped to grasp the organophosphorus pesticides residual levels and mainly-used pesticide kinds on the agricultural products in Qingdao, which will offer scientific basis for the prevention of food pollution and the control of food-source diseases.

MATERIALS AND METHODS

Experimental apparatus and reagents: Shimadzu GC-2010 gas chromatograph, Flame Photometric Detector (FPD), GC Solution chemical working station, AOC-20i automatic sample injector, distributary/non-distributary injection port, RTX-1 capillary

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chromatographic column (Huo *et al.*, 2014), Termovap Sample Concentrator, adjustable high-speed electric homogenizer, water-bath constant-temperature oscillator, swirl mixer, electronic balance.

Color-spectrum pure acetone, acetonitrile, spectrum pure sodium chloride (Guan *et al.*, 2014), 7 organophosphorus pesticides: methamidophos, omethoate, phorate, chlorpyrifos-methyl, fenitrothion, isocarbophos, profenofos (manufactured by Environmental- Protection Scientific- Research Monitoring Institution of Minwastry of Agriculture).

Sample collection: Combining the actual situation of daily consumption of the residents in Qingdao, we collected the local representative agricultural products as samples. In farmer' homes, farmer's markets and supermarkets in Shinan district, Shibei district, Pingdu county, Jimo county, Licang district and Huangdao district, we randomly bought 200 portions of vegetables and 150 portions of fruits; every portion weighed 500 g.

Test method and contents: We made test according to NY/F761-2008 the Test Method for the Residual of Organophosphorus, Organochlorine, Pyrethrum and Carbamates on Vegetables and Fruits. Gas chromatograph was used to test 16 kinds of pesticides which were DDVP, methamidophos, acetyl methamidophos, phorate, omethoate, monocrotophos, dimethoate, tolclofos-methyl, parathion-methyl, malathion, fenitrothion, parathion, ethion, triazoline, phosmet, phosalone.

Evaluation basis and judgment standard: We made sample classification according to Chinese Food Composition Table (2010 edition) and GB2763-2012 Food Classification Method. There were three categories of sample which were vegetables, fruits and grains. The test results were analyzed and evaluated according to European Union (EC No. 396/2005) pesticides residual standard system. If the residual quantity of pesticides exceeded the "detection limit", the result would be judged to be "detected"; if the residual quantity of pesticides exceeded the maximum limit, the result would be judged to be "out of limits".

RESULTS AND DISCUSSION

Results: Among the 350 sample portions of vegetables, fruits and grains, there were 298 sample portions whose residuals of the 16 kinds of organophosphorus pesticides were qualified. The qualified rate was 85.14%. Among the 52 portions which were not qualified, there were 39 portions whose residuals of one kind of organophosphorus pesticides were unqualified; there were 9 portions whose residuals of two kinds of organophosphorus pesticides were unqualified; there were 3 portions whose residuals of three kinds of

organophosphorus pesticides were unqualified; there was 1 portion whose residuals of four kinds of organophosphorus pesticides were unqualified.

Residual pesticides varieties: Among the 350 sample portions, the 16 kinds of organophosphorus pesticides were all detected (above the "detection limit"). There were 14 portions whose residuals of triazoline were out of limit, 14 portions whose residuals of phorate were out of limit, 12 portions whose residuals of parathion-methyl were out of limit, 8 portions whose residuals of parathion were out of limit, 5 portions whose residual of DDVP were out of limit and 5 portions whose residuals of methamidophos were out of limit; the residual of acetyl methamidophos, omethoate, monocrotophos and phosmet was respectively out of limit in three portions. The residual of dimethoate, tolclofos-methyl, malathion, fenitrothion, ethion and phosalone was, respectively not out of limit.

The pesticides residuals of vegetable samples: As for the 200 portions of vegetable sample, there were 37 portions of root vegetable, 37 portions of fresh beans vegetable, 43 portions of eggplant-fruit-melon vegetable, 44 portions of stem-leaf-flower vegetable and 39 portions of onion-garlic vegetable. The number of the portions of root vegetable, fresh beans vegetable, eggplant-fruit-melon vegetable, stem-leaf-flower vegetable and onion-garlic vegetable which were detected was 24, 15, 26, 35 and 14, respectively; the detected rate was 64.8, 40.5, 66.2, 79.5 and 35.9%, respectively; the out-of-limit number was 11, 2, 3, 16 and 2, respectively; the out-of-limit rate was 29.7, 5.4, 6.82, 41.0 and 4.54%, respectively. The detected rate and out-of-limit rate of pesticides residuals on stem-leaf-flower vegetable were both highest. Through chi-square test, the detected rate ($\chi^2 = 11.296$, $p < 0.05$) and out-of-limit rate ($\chi^2 = 11.452$, $p < 0.05$) of different kinds of vegetable were not all same; the difference had statistics significance.

The pesticides residuals of fruit samples: As for the 150 portions of fruit sample, there were 50 portions of nutlets, 50 portions of berry and small-sized fruits and 50 portions of oranges and tangerines. The number of the portions of nutlets, berry and small-sized fruits and oranges and tangerines which were detected was 20, 15 and 15, respectively; the detected rate was 40.0, 30.0 and 30.0%, respectively; the out-of-limit number was 10, 5 and 10, respectively; the out-of-limit rate was 20.0, 10.0 and 20.0%, respectively. Through chi-square test, the difference of the detected rate ($\chi^2 = 0.300$, $p > 0.05$) and out-of-limit rate ($\chi^2 = 0.480$, $p > 0.05$) of pesticides residual of the three kinds of fruit had no statistics significance.

The pesticides residuals of the samples in different season: In the whole year of 2014, 350 sample portions

in the season of summer and autumn and the season of winter and spring were collected. Among the sample portions, there were 193 portions in the season of summer and autumn and 157 portions in the season of winter and spring. The number of the portions in the season of summer and autumn and the season of winter and spring which were detected was 110 and 50, respectively; the detected rate was 57.0 and 32.7%, respectively; the out-of-limit number was 43 and 15, respectively; the out-of-limit rate was 22.0 and 8.18%, respectively. There were 55 portions of out-of-limit sample in the whole year; the out-of-limit rate was 15.8%. The difference of detected rate ($\chi^2 = 8.119$, $p < 0.05$) and out-of-limit rate ($\chi^2 = 4.894$, $p < 0.05$) of pesticides residuals of samples in different season had statistics significance. The detected rate and out-of-limit rate of organophosphorus pesticides residuals of samples in summer and autumn (namely the second season and the third season) were both higher relatively.

Discussion: Organophosphorus pesticides are cheap and it is the pesticides whose sale quantity and used quantity are both largest in markets currently. The abuse of pesticides was very severe because the supervision was not strict and farmers didn't use them in accordance with corresponding norms. That caused the unceasing appearance of food poisoning and health injury owing to pesticides. From the test results, we can see that different detected rates of organophosphorus pesticides residuals exist in vegetables, fruits and grains; in addition, the out-of-limit phenomenon of organophosphorus pesticides residual existed in the three kinds of sample. This phenomenon prompts Qingdao that organophosphorus pesticides residual supervision is still the focal task in the pesticides residual supervision work.

The test results of 2012 indicated that the detected rate of pesticides residuals on stem-leaf-flower vegetable was higher than that of other kinds of vegetable; the out-of-limit situation was severest and the out-of-limit rate reached 35.0%. The secondary one was the kind of root vegetables; the out-of-limit rate was 29.4%. Comparing with the data of 2010, the out-of-limit rate of organophosphorus pesticides residuals on vegetables was obviously decreased. The out-of-limit rates of organophosphorus pesticides residuals on stem-leaf-flower vegetable, fresh beans vegetable and eggplant-fruit-melon vegetable were obviously decreased. The reason may be: related departments analyzed the monitoring data of the latest years, strengthened the management and cooperated with other related departments to improve the local pesticides residual situation. However, the out-of-limit rate of organophosphorus pesticides residuals on roots vegetable of 2013 was higher than that of 2012. The reason may be: the tested samples of 2013 were mostly

collected from summer and autumn. The using difference of seasonal pesticides caused the higher out-of-limit rate in 2013. After we made comparison about the data of 2012, we found that the out-of-limit rate of organophosphorus pesticides residuals on different kinds of vegetable was different, the reason of which should be analyzed further.

CONCLUSION

Organophosphorus Pesticides is one of the pesticides whose used quantity is largest currently. The use of it guarantees the harvest of vegetables, fruits and grains. However, pesticides residuals have become the potential killers on the diet table and they influence the diet safety and health of people. The population of Qingdao is more than 8 million. The residents in Qingdao need to consume large quantity of vegetables, which most come from Qingdao and the surrounding areas. The pesticides residual situation of vegetables relates to the food safety of residents in Qingdao. There is rare report about the survey of organophosphorus pesticides residuals on vegetables in Qingdao and surrounding regions and counties. The writer of this study made survey about the organophosphorus pesticides residuals on vegetables and expected to offer theoretical directions to the safe production of the vegetables in Qingdao.

After we made the survey about the local people's using situation of pesticides, we found that farmers had lack of pesticides knowledge and they tended to use excessive pesticides and paid little attention to the pesticides-safety interval before putting the agricultural products into markets (Bajwa and Sandhu, 2014). That might be one of the reasons which caused high out-of-limit rate of pesticides residuals. In the test, we found that residuals of several kinds of pesticide could be detected in one sample portion. For example, as for one portion of cabbage, the residuals of acetyl methamidophos, phorate, omethoate, monocrotophos and parathion could be all detected (Hu and Shi, 2015). At present, the potential influence of the exposure of the mixture of pesticides residual to the health of people is not clear. This problem should be paid enough attention to.

As for above problems, the propositions are in the following: The function departments should carry out the clearance of high-poison pesticides production enterprises, strictly normalize the circulating behavior of pesticides operation and strength the supervision of circulating behavior of pesticides operation. Agricultural departments should strength the technical direction to farmers and the agricultural-products production enterprises, further facilitate the enterprises to perfect the production records of agricultural products and detect the produced agricultural products by themselves or authorize other units to detect them to

prevent unqualified agricultural products going into the markets. Agricultural departments should also propagandize related national laws and regulations and the harms of the pesticides, which will strengthen the legal consciousness in the production process and sale process of pesticides. The legal consciousness of farmers will also be promoted. Media propaganda should be widely used to attract people's attention to the pesticides residuals in food, which will improve the food safety consciousness of people. The media propaganda can lead people to buy the foods with low pesticides residual and to use simple and practical method to decrease the pesticides residuals on vegetables and fruits before eating them. In the pest-elimination process on vegetables and fruits, it is proposed to popularize the high-efficiency, broad-spectrum and low-poison pesticides, strengthen the research of new pesticides which have high safety, low residual, no public hazard, good biological activity and low using cost, establish and perfect the network system of pollution monitoring for the local pesticides residuals, analyze and master the pollution situation of pesticides residuals in food and offer scientific basis for the development of effective preventive measures.

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