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EVALUATION OF METHYL PARATHION RESIDUES IN APPLE SAMPLES OBTAINED FROM DIFFERENT REGIONS OF TURKEY

TÜRKİYE'NİN FARKLI BÖLGELERİNDEN SAĞLANAN ELMA ÖRNEKLERİNDE METİL PARATİYON KALINTILARININ DEĞERLENDİRMESİ

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In this study, the levels of methyl parathion (MP) residue in apples collected by Market-Basket method were evaluated. A multiresidual analysis method recommended by AOAC for organophosphorus insecticides has been applied for MP analysis. A Hewlett-Packard 5890-II gas-chromatograph equipped with nitrogen-phosphor detector and SE-30 column was used. MP residues in 18 samples were found at levels below the maximum residue limits registered both in Turkey (0.1 ppm) and by Codex Alimentarius Commission (0.2 ppm) while no detectable levels were found in the rest.

Bu çalışmada Market-Basket çalışması ile toplanan elma örneklerinde metil paratiyon (MP) kalıntı düzeyleri değerlendirildi. MP analizi için AOAC tarafından organofosfatlı insektisidler için önerilen çok-kalıntılı analiz yöntemi uygulandı. Azot-fosfor detektörü ve SE-30 kolonu olan Hewlett-Packard 5890-II gaz kromatografisi kullanıldı. 18 örnekte MP kalıntısı Türkiye'de (0.1 ppm) ve Codex Alimentarius Komisyonu tarafından kabul edilen (0.2 ppm) maksimum kalıntı sınırlarının altında bulundu, kalan örneklerde ise saptanabilir düzeyde bulunmadı.

Keywords : *Methyl parathion; organophosphorus insecticide; apple samples*

Anahtar kelimeler: *Metil paratiyon; organofosfatlı insektisid; elma örnekleri*

Introduction

Pesticide residues in foods have been a focus of attention in recent years due to increased use of pesticides in agriculture. MP is an organophosphorus pesticide used in a wide variety of agricultural application in Turkey as well as other countries because of the selectivity and less persistency in environment (1-4). In several studies, it has been shown that MP is highly toxic to mammals, humans, aquatic invertebrates, birds and that it has genotoxic activity in mammalian somatic cells (5,6).

MP is not stored in tissues of animals when consumed as residue on feed crops, but the exposure to high amount of residues and/or interaction with other pesticide residues or certain drugs may increase toxicity risk (3,7,8). Climate conditions such as temperature, light, precipitation and the duration between stopping of pesticide spraying and harvesting period and the frequent and/or high amount of pesticide application, particularly done by uneducated farmers, are the main factors effecting the pesticide residue levels in crops (9,10). Therefore, routine analysis of pesticide residues is getting more important for safety of foods.

In present study, we aimed to determine the levels of MP residues in apples that form a major part of the diet of children as well as adult foods.

Materials and Methods

All chemicals used were analytical grade and as follow: Acetonitrile, anhydrous sodium sulphate, acetone, diethyl ether (Merck: Darmstadt, GFR); Petroleum ether (40°C-60°C) and MP standard (Riedel-de-Haen AG; Seelze, Hannover, GFR); sodium chloride (Atabay, Istanbul, Turkey); Florisil (60/100 mesh; Sigma; St. Louis, MO, USA).

A Hewlett-Packard Model HP 5890-II type gas chromatograph (GC) equipped with nitrogen-phosphorus detector and a computer which was connected with a printer, was used. Operating conditions as follow: Temperatures were 180°C in oven, 230°C in detector, and 200°C in injector port; flow rates of gases were 3.5 ml min^{-1} for air and hydrogen, 15 ml min^{-1} for helium (carrier gas); GC column was a SE-30 fused-silica column (5 m x 0.53 mm i.d., 2.6 µm film thickness).
Detection limit was 0.1 ppb.

Other instruments used were chopper and high speed blender (Arçelik; Istanbul, Turkey), rotary evaporator (Buchi, Switzerland), several glassware, etc.

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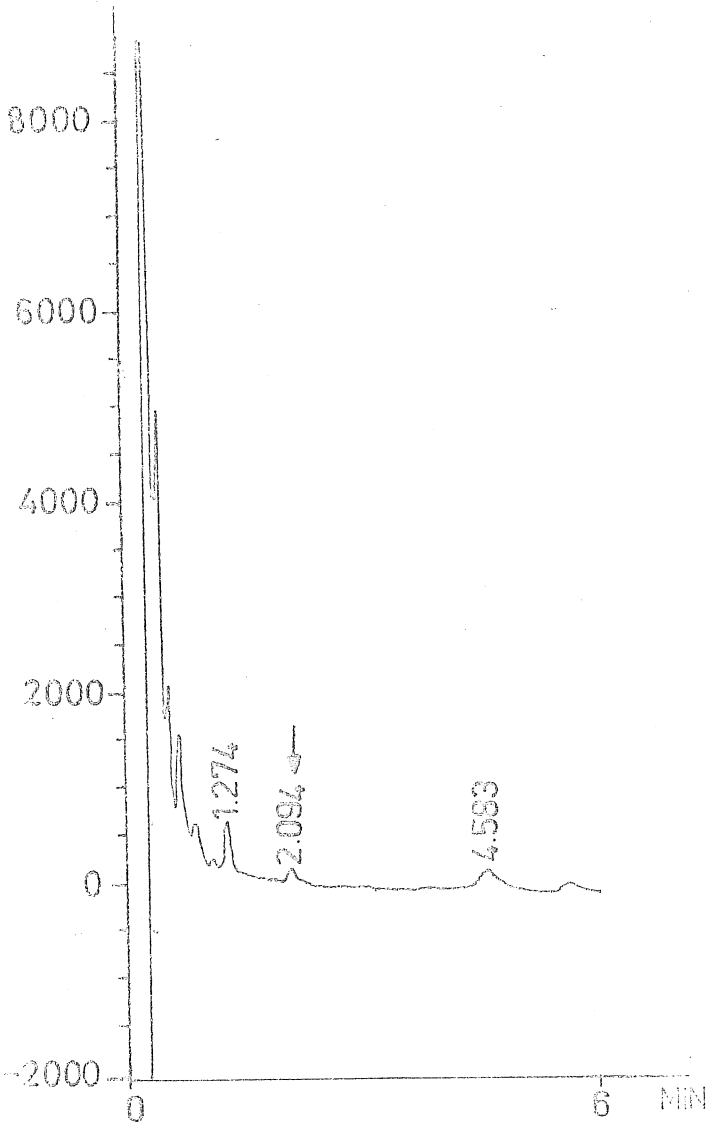

Fig.1. A chromatogram of MP residue in an apple sample (MP peak is indicated by an arrow; Retention time: 2.094 min)

Activation of Florisil Column

Florisil was heated at 675°C for 8 hours. After cooling in a desicator, florisil was kept in an air and light resistant glass container and heated at 130°C, at least 5 hours before using (11,12).

Samples preparation and extraction

Apple samples were obtained from different regions of certain cities of Turkey, namely İzmir, Kastamonu, Elazığ and Bursa, by Market-Basket method (13). 500 g from each sample without any processing were kept at-20°C, until analysis.

For the analysis of MP residues in samples, a multiresidual analysis method suggested by AOAC (1990; 970.52-970.52 BB) was used (12). Briefly, chopped material (500 g) transferred into the blender and homogenised. 200 ml acetonitrile and 50 ml distilled water were added to 100 g of homogenised material and mixed in a blender at high speed for 2 min. The mixture was filtered through a Buchner funnel; filtrate transferred to a separatory funnel and partitioned into petroleum ether by addition of 100 ml petroleum ether and 10 ml saturated sodium chloride and 600 ml distilled water, respectively. After washing 2 times whit distilled water, petroleum ether layer was dried over sodium sulphate anhydrate and evaporated to 5 ml in a rotary evaporator at 30-40°C. Concentrated samples were applied to activated florisil columns (12,14,15). For

Table 1. Total methyl parathion levels in samples in regards to the regions obtained

Region	Total MP (ppm)
Sasalı/İZMİR	0.0069
Emiralem/İZMİR	0.0029
Emiralem/İZMİR	0.0038
Bağarası/İZMİR	0.0084
Bağarası/İZMİR	0.0027
Foça /İZMİR	0.0089
Foça/İZMİR	0.0078
Taşköprü/KASTAMONU	undetectable
Taşköprü/KASTAMONU	undetectable
Taşköprü/KASTAMONU	0.0078
Merkez/KASTAMONU	0.0075
Kayalı/KASTAMONU	0.0074
Hatip/KASTAMONU	undetectable
Çayırcık/KASTAMONU	0.0039
Harput eteği /ELAZIĞ	0.0313
Harput eteği/ELAZIĞ	0.0032
Harput eteği /ELAZIĞ	0.0056
Karakoçan/ELAZIĞ	0.0076
Palu/ELAZIĞ	0.0070
İznik/BURSA	0.0030
İznik/BURSA	0.0059
İznik/BURSA	undetectable
İznik/BURSA	undetectable

cleaning-up the florisil column, a glass column (30 cm length, 2.2 cm i.d.) with a small glass wool plug in bottom was packed with florisil (up to 10 cm) and sodium sulphate (1 cm). Column was washed with 40-50 ml petoleum ether and flow rate was adjusted to 5 ml min^{-1}. Samples were loaded onto column and eluted with 200 ml of either 15% and 50% diethyl ether solutions in petroleum ether, respectively (12). Eluates mixture was concentrated in rotary evaporator to 5 ml and transferred into the glass tubes with tightened caps. Samples were kept at -20°C until analysis.

Identification and Quantification of MP

The identification and quantification of MP residues in samples were carried out automatically by a computer connected with GC, and based on retention time and peak height measurement which were determined by a calibration table obtained daily from solution of known concentrations of authentic MP compound. For the analysis, 1 µl of each, sample was injected into GC and concentrations of MP residues were expressed as ppm (16).

Recovery rate was determined as 90 ± 3.5 %. For the accuracy of the analyse, duplicate assays were performed in 6 apple samples. Method precision was acceptable, because the coefficient of variation of the assays was ± 5%.

Results and Discussion

A chromatogram of MP residue in an apple sample was shown in Fig.1 Table 1. shows the total MP amounts in apple samples in regard to the regions obtained.

As it is shown in Table 1., MP residues were detected in 18 samples and levels were below the maximum residue limits registered both in Turkey (0.1 ppm) and by Codex Alimentarius Commission (0.2 ppm) (17.18). Because they were analysed as the whole, unwashed and unpeeled product, the residue levels will also be lower in apples as consumed. Therefore, our results indicate the safety of the apples, in regard to the MP content. However, we did not determine the residues of other pesticides, yet. Therefore it will be more reliable to evaluate the safety of this fruit for children and adults after determination of other widely used pesticide residues.

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