



**HAL**  
open science

## **Exposure assessment of fruit contaminated with pesticide residues from Valencia, 2001-2003**

Houda Berrada, Mónica Fernández, Maria Jose Ruiz, Juan Carlos Moltó, Jordi Mañez

### ► **To cite this version:**

Houda Berrada, Mónica Fernández, Maria Jose Ruiz, Juan Carlos Moltó, Jordi Mañez. Exposure assessment of fruit contaminated with pesticide residues from Valencia, 2001-2003. *Food Additives and Contaminants*, 2006, 23 (07), pp.674-682. <10.1080/02652030600599132>. <hal-00577588>

**HAL Id: hal-00577588**

**<https://hal.science/hal-00577588v1>**

Submitted on 17 Mar 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization



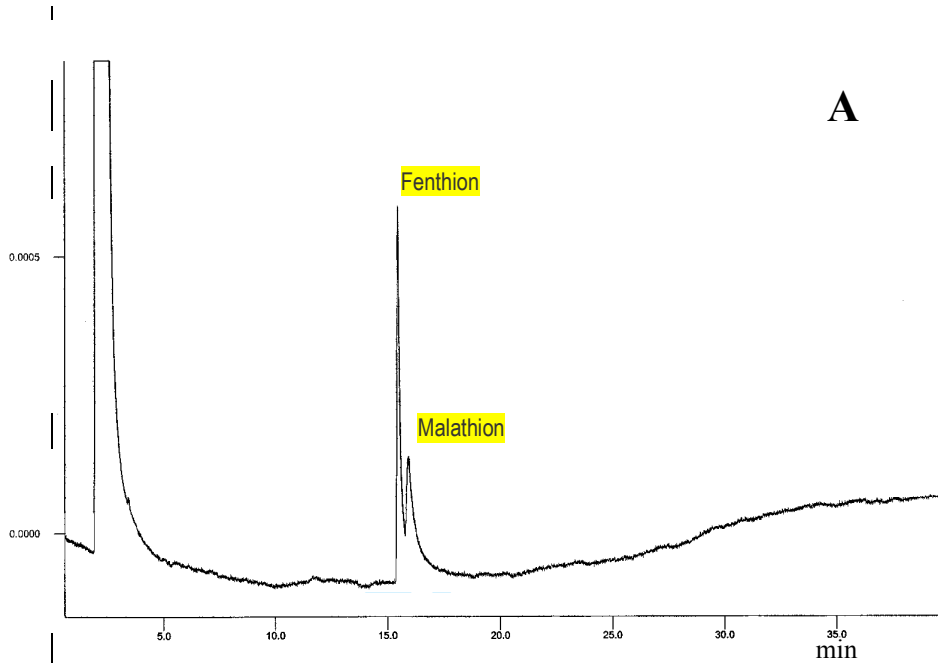
**Exposure assessment of fruit contaminated with pesticide residues from Valencia, 2001-2003**

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2005-399.R2
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	23-Jan-2006
Complete List of Authors:	Berrada, Houda; University, Toxicology Fernández, Mónica; University, Toxicology Ruiz, Maria Jose; University, Toxicology Moltó, Juan Carlos; University, Bromatology Mañez, Jordi; University, Bromatology
Methods/Techniques:	Total diet studies, Chromatography - GC/MS
Additives/Contaminants:	Pesticide residues
Food Types:	Fruit

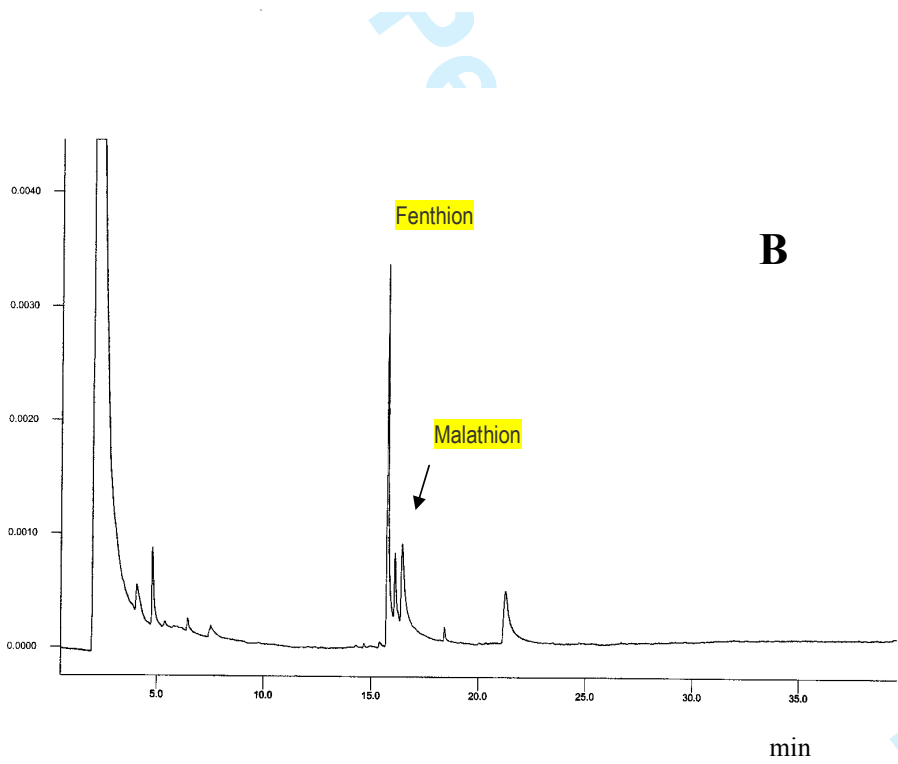
SCHOLARONE™  
Manuscripts

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

Formatted: Right: 70.9 pt, Bottom: 69.45 pt, Width: 595.3 pt, Height: 841.9 pt

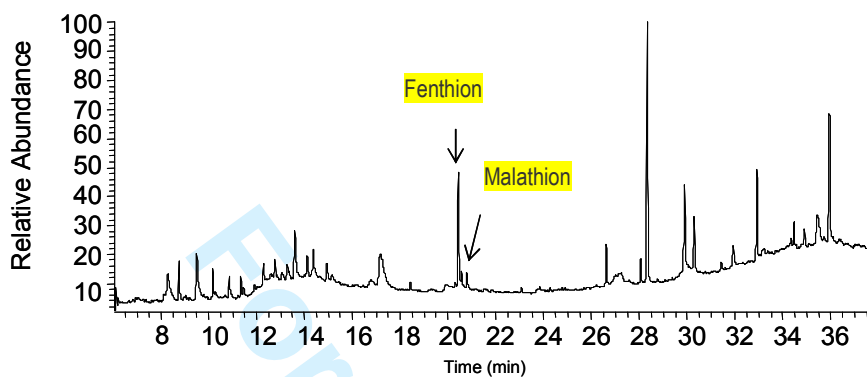


A

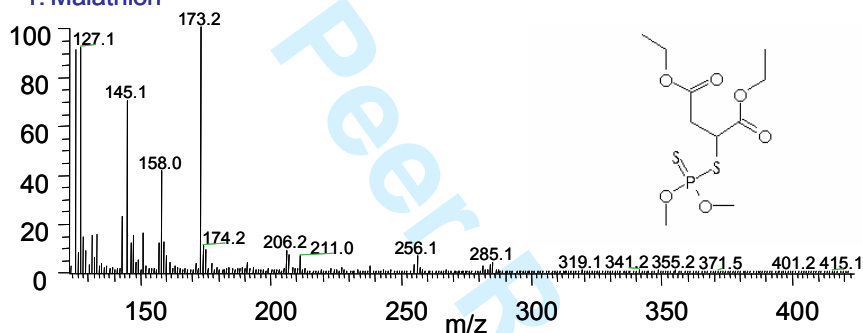


B

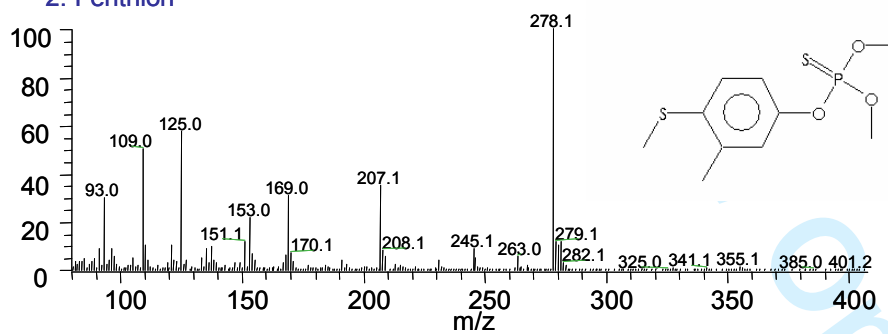
Formatted: Right: 0 pt



1. Malathion

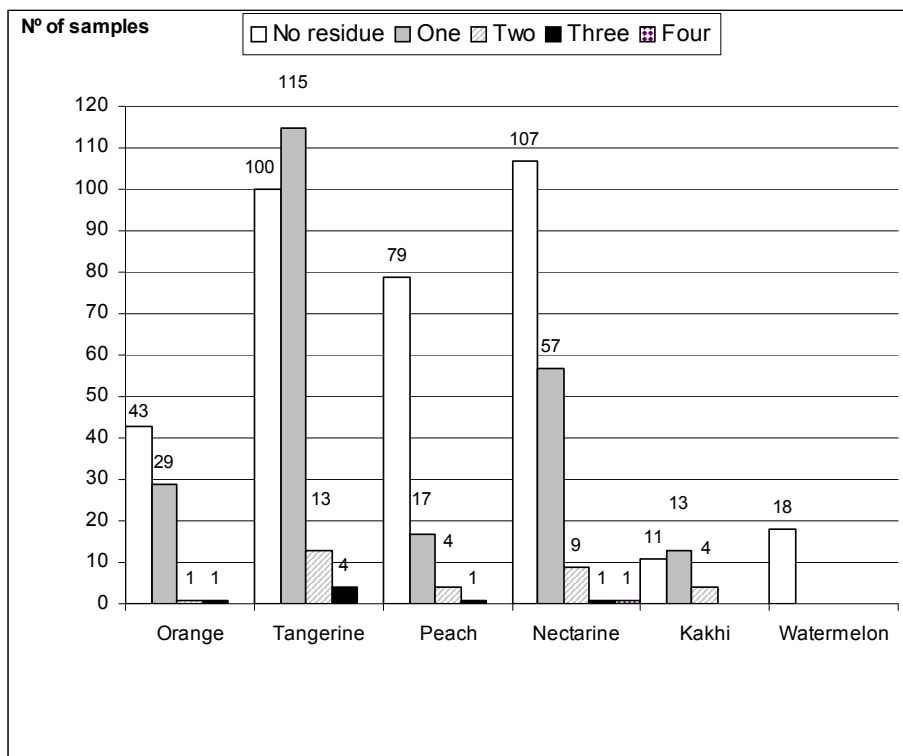


2. Fenthion



Formatted: Right: 0 pt

2



Formatted: Left, Adjust space between Latin and Asian text, Adjust space between Asian text and numbers

Review Only

Formatted: Right: 0 pt

3

1  
2  
3  
4  
5 **Exposure assessment of fruits contaminated with pesticide**  
6 **residues from Valencia, 2001-2003**  
7  
8  
9

10  
11  
12  
13  
14 Houda Berrada, Mónica Fernández\*, Maria José Ruiz, Juan Carlos Moltó, Jordi  
15

16  
17 Mañes  
18  
19

20  
21  
22  
23  
24 Laboratory of Food Chemistry and Toxicology, Faculty of Pharmacy, University of  
25  
26 Valencia, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Spain  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53

54  
55 \_\_\_\_\_  
56 \* Corresponding author. Tel: +34-963543056; fax: +34-963544954  
57 *E-mail address:* monica.fernandez@uv.es  
58  
59  
60

## Abstract

A total of 634 samples of oranges, tangerines, peaches, nectarines, khakis, and watermelons were collected from an Agricultural Valencia Community Cooperative during May 2001 to April 2003 campaigns and analyzed for fifteen pesticides among those recommended for their pest treatment. A conventional multi-residue analytical procedure based on ethyl acetate extraction was used followed by gas chromatography coupled to nitrogen phosphorus detector for routine analysis and mass spectrometry for confirmation. Recovery studies with spiked samples at 0.5 mg kg<sup>-1</sup> for each pesticide ranged from 52 % for acephate to 87 % for fenthion with standard deviation below 20 %. Limits of quantification ranged from 0.1 to 100 µg kg<sup>-1</sup>. A total of 43 % of samples contained pesticide residues and 5 % exceeded the Maximum Residue Levels (MRLs). Nine of the pesticides studied were found. Malathion, which was the most frequently detected, was found in 121 samples (19 %) at 0.002-4.25 mg kg<sup>-1</sup>, followed by fenthion in 104 samples (16 %) at 0.005-2.3 mg kg<sup>-1</sup> and methidation in 68 samples (10 %) at 0.008-1.3 mg kg<sup>-1</sup>. Khaki showed the highest contamination rates with 60% of contaminated samples which exceeded more often the MRLs and fenthion was the pesticide more frequently detected in all the commodities studied at levels above the European MRLs. The Estimated Daily Intakes of each pesticide calculated from the results obtained were much lower than the Acceptable Daily Intakes.

1  
2  
3  
4 **Keywords:** monitoring, multiresidue analysis, fruits, pesticides, gas  
5  
6 chromatography, mass spectrometry, Valencia, ADI and EDI.  
7  
8  
9

## 10 11 12 13 **Introduction**

14  
15  
16 Increasing public concern in recent years about possible health risks from pesticide  
17  
18 residues in food supply has led to establish strict regulation of pesticide tolerances  
19  
20 and to assess dietary intakes of pesticide residues in food commodities (Stenersen  
21  
22 2004, Ecobichon 2001, Nasreddine and Parent-Massin 2002). To ensure the  
23  
24 safety of food for consumers, the *Codex Alimentarius* Commission of the Food  
25  
26 Agriculture Organization (FAO/WHO 2004) have established Maximum Residue  
27  
28 Limits (MRLs) for pesticides in foodstuffs, which are also regulated by the  
29  
30 European Union (EU) and Spanish directives (European Commission, 2005,  
31  
32 Ministerio de Agricultura Pesca y Alimentación 2005.  
33  
34  
35  
36

37  
38 Monitoring programme for pesticide residues in food are a useful tool for ensuring  
39  
40 that consumers are not exposed to unacceptable pesticide residue levels,  
41  
42 authorised pesticides are correctly applied to food crops in terms of granted  
43  
44 authorizations and registrations (application rates and pre-harvested intervals) and  
45  
46 to permit the free circulation of pesticide-treated products as long as they comply  
47  
48 with the fixed MRLs (Dogheim *et al.* 1997, Fernández *et al.* 2001, Blasco *et al.*  
49  
50 2005).  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Monitoring programs are carried out by regulatory authorities to check regularly the  
5 compliance of foodstuffs with MRLs (Andersen and Poulsen 2001, JMPR 1999,  
6 European Commission 2001). However, these results are not representative of the  
7 situation on a particular area so monitoring of the locally produced commodities is  
8 relevant to have a complete view of the pest treatment making possible to take  
9 specific measures in the contaminated area.  
10  
11  
12  
13  
14  
15  
16  
17  
18

19  
20 The frequent application of different types of pesticides and the large number of  
21 samples makes necessary the determination of as many compounds as possible in  
22 a single analysis at levels below the MRL. Generally monitoring analysis are  
23 accomplished with gas chromatography (GC) in combination with different  
24 detectors, such nitrogen-phosphorus detector (NPD), electron-capture detectors  
25 (ECD) or mass spectrometry (MSD) which provides a fingerprint spectra by  
26 electron ionization and allows the possibility of confirming pesticide identity (Albero  
27 *et al.* 2003, Puglese *et al.* 2004, Lehotay and Hajlová 2002, Torres *et al.* 1997).  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38

39  
40 When assessing the impact on consumers of pesticide exposure through diet, it is  
41 important to consider the effects of both, chronic and acute exposure. Limiting  
42 chronic exposure to a pesticide residue is managed through establishing the  
43 Acceptable Daily Intake (ADI) for the pesticide, which is an estimate of the  
44 maximum level of intake over a lifetime, judged to result without appreciable health  
45 risk. Estimations include a safety factor to ensure that the elderly, infants, children,  
46 and those whose systems are under stress because of illness are protected  
47 (Leblanc *et al.* 2000, Caldas and Souza 2004, Chun and Kand 2003).  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Valencia is an important citrus growing area in Europe although other fruit  
5 commodities are also produced and exported, so assessing pesticide residues in  
6 fruit intended for human consumption is necessary. The aim of this work was to  
7 analyze fifteen pesticide residues in tangerines, oranges, peaches, nectarines and  
8 khakis from agricultural cooperative of Valencia during 2001-2003. The results of  
9 the monitoring program were taken into consideration to evaluate whether the  
10 Estimated Daily Intake (EDI) of pesticides through the fruit consumed by Spanish  
11 adult population is a cause for health concern according to the recommended  
12 intake of the FAO/WHO organization.  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24

## 25 26 **Material and methods**

### 27 28 *Samples and reagents*

29  
30  
31  
32  
33 Samples of 175 nectarines, 74 oranges, 107 peaches, 28 khakis, 232 tangerines  
34 and 18 watermelons were taken during May 2001 to April 2003 campaigns  
35 obtained from an agricultural cooperative which covers one of the main agricultural  
36 production areas of Valencia. Fruit samples were taken in accordance with the  
37 guidelines of the European Union (EU), they were taken at various places  
38 distributed throughout the lot (size ca. 50 kg), (European Commission, 1979).  
39 Samples were stored at 4°C and analyzed in 24h. Pesticides with purities up to  
40 98% were supplied by Riedel-de Haën (Seelze, Germany). Ethyl acetate for  
41 residue analysis was purchased from Merck (Darmstadt, Germany) and anhydrous  
42 sodium sulfate (analytical grade) was bought from Panreac (Barcelona, Spain).  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

### *Sample preparation*

The individual stock solutions were prepared by dissolving 100 mg of each compound in 100 ml of methanol. Standard working solutions at various concentrations were daily prepared by appropriate dilution of aliquots of the stock solutions in methanol. The recovery and precision were determined by adding 50  $\mu$ l of the appropriate working mixture to 50 g of chopped untreated samples. The spiked samples were allowed to stand for 1 h before the extraction to achieve the pesticide distribution in the sample.

### *Extraction Procedure*

Samples were extracted by an official procedure for routine analysis that allows the analysis of about 120 pesticides (Conselleria de Sanidad y Consumo de la Comunidad Valenciana 1995). A 50 g portion of sample previously homogenized was weighed in a 500 ml beaker, 100 ml of ethyl acetate and 75 g of anhydrous sodium sulphate were added and the mixture was blended using a stainless steel-armed blender for 5 min, the resulting mixture was filtered through 20 g of anhydrous sodium sulphate. The solid was washed with 50 ml of ethyl acetate and the organic extract was concentrated to less than 10 ml on a vacuum rotary evaporator using a water bath at 44-46°C and 250 mBar. Finally, the extract was reconstituted to 10 ml with ethyl acetate and 2  $\mu$ l was analyzed by GC.

### *Analysis of pesticide residues*

1  
2  
3  
4 Routine analyses were carried out on a Varian Star 3400CX gas chromatograph  
5 (Varian, Walnut Creek, CA, USA) equipped with an 8200CX autosampler, an on-  
6 column injector (SPI 1093), and NPD system. Identification of peaks was  
7 performed in a Trace GC gas chromatograph (Thermo Electron Corporation, San  
8 José, CA, USA) with a Thermo-Finnigan AS 2000 autosampler, a split/splitless  
9 injector, and a Trace MS quadrupole mass spectrometer. Compounds were  
10 separated on DB-5 ms (J&W Scientific, Folsom, CA USA) fused-silica capillary  
11 columns (30 m × 0.25 mm i.d., 0.25 µm film thickness).  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23

24 Varian gas chromatograph conditions: injector 280 °C, detector 300 °C. Oven  
25 temperature program: initial temperature, 140 °C; held for 1 min, programmed to  
26 280 °C, at 5 °C/min, and held for 11 min. Helium was used as carrier gas at a flow  
27 rate of 1.9 ml/min.  
28  
29  
30  
31  
32  
33

34 Trace gas chromatograph conditions: injector and transfer line 280 °C, source  
35 temperature 230 °C. Oven temperature program: the initial temperature (50 °C) was  
36 held for 1 min, programmed to 120 °C at 30 °C/min, held for 1 min, then  
37 programmed to 275 °C at 5 °C/min, and held for a further 5 min. The mass  
38 spectrometer was used with electron impact ionization (–70 eV) in full scan mode  
39 (65–365 amu). The carrier gas was helium at 1.5 ml/min. Splitless time was 0.9  
40 min.  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51

## 52 **Results and Discussion**

### 53 *Method performance*

54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Analytical parameters were calculated for the multi-residue method proposed using  
5 GC-NPD. Precision was calculated in terms of intra-day repeatability ( $n=5$ ) and  
6 inter-day reproducibility (5 different days). The intra-day repeatability evaluated as  
7 relative standard deviation (RSDs) ranged from 3 to 5%. The inter-day  
8 reproducibility was lower than 8% for all instances. Calibration curves prepared  
9 with standard in ethyl acetate were linear at the studied range as shown in Table 2  
10 with regression coefficients  $>0.99$ . Limits of quantification (LOQs) which were  
11 calculated as the lowest concentration of compound that gave a response that  
12 could be quantified as the minimum concentrations providing chromatographic  
13 signals 10 times higher than background noise ranged from 0.0001 to 0.1 mg kg<sup>-1</sup>  
14 and were lower than the MRLs established by the EU and Spanish legislations and  
15 those recommended by the FAO/WHO for each of the commodities studied (Table  
16 1). Accuracy of samples spiked at 0.5 mg kg<sup>-1</sup> and 5 mg kg<sup>-1</sup> were equivalent in the  
17 commodities studied. Except for some cases, principally at 5 mg kg<sup>-1</sup>, results of  
18 accuracy and precision fulfilled the criteria of the European guidelines indicating  
19 that a method can be considered accurate and precise when accuracy data are  
20 comprised between 70 and 110% with relative standard deviations not higher than  
21 20% (European Commission, 2000).  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47

48 Figure 1 illustrates a NPD chromatograms corresponding to a spiked nectarine and  
49 a contaminated nectarine with 0.5 mg kg<sup>-1</sup> of fenthion and 0.1 mg kg<sup>-1</sup> of malathion.  
50  
51 Due to the presence of some interfering peaks as the one between both peaks a  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 confirmatory method is necessary. In Figure 2 the total ion GC-MS chromatogram  
5  
6 and the two peaks spectra confirmed the identity of both pesticides.  
7  
8

### 9 10 *Monitoring data*

11  
12  
13 Table 3 outlines the data obtained after analyzed 634 samples of fruits in which  
14  
15 276 (43 %) of the analyzed samples were contaminated and 34 (5 %) exceeded  
16  
17 the MRLs. In terms of commodity groups, khakis was the fruit with the highest rate  
18  
19 of contaminated samples (61 %), followed by of tangerines (57 %), oranges (42  
20  
21 %), nectarines (39 %) and peaches (26 %). No residues were found in  
22  
23 watermelons.  
24  
25  
26

27  
28  
29 Most of the pesticides found were organophosphorus used as insecticides except  
30  
31 triazole fungicides (bitertanol and flusilazole) and a chloronitrile fungicide  
32  
33 (chlorothalonil). Malathion was the most frequently pesticide detected and at the  
34  
35 highest concentration, 121 (19 %) samples of the commodities studied except  
36  
37 watermelon were contaminated from 0.002 to 4.25 mg kg<sup>-1</sup> (0.282 mg kg<sup>-1</sup> average  
38  
39 level). This pesticide is a wide spectrum organophosphorous insecticide suitable  
40  
41 for the control of insects that shuck and chew on fruit and vegetables. Fenthion  
42  
43 was detected in 104 samples (16%) at levels ranging from 0.005 to 2.3 mg kg<sup>-1</sup>  
44  
45 (0.179 mg kg<sup>-1</sup> average level), this pesticide is a contact insecticide used against  
46  
47 many sucking, biting pests, especially fruit flies, stem borers and mosquitoes.  
48  
49 Methidathion was found in 68 samples (10%) at levels between 0.008 and 1.3 mg  
50  
51 kg<sup>-1</sup> (0.2 mg kg<sup>-1</sup> average level).  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Bitertanol was found in 12 samples (1.9 %) at levels that range from 0.14 and 1.9  
5 mg kg<sup>-1</sup> (0.52 mg kg<sup>-1</sup> average level). Fenitrothion was found in 6 (0.9%) at levels  
6  
7 between 0.01 to 0.53 mg kg<sup>-1</sup> (0.05 mg kg<sup>-1</sup> average level). Chlorpyrifos methyl and  
8  
9 flusilazole were detected in 3 samples, the first one with a range from 0.04 mg kg<sup>-1</sup>  
10  
11 to 0.37 mg kg<sup>-1</sup> (0.176 mg kg<sup>-1</sup> average level) and the second one from 0.06 to 0.1  
12  
13 mg kg<sup>-1</sup> (0.079 mg kg<sup>-1</sup> average level). Trichlorfon and Parathion methyl were found  
14  
15 only in one sample, both in peaches with a level around 0.02 mg kg<sup>-1</sup>.  
16  
17  
18  
19  
20

21  
22 The pesticides detected with levels above European MRLs were fenthion (22  
23  
24 samples), malathion (10 samples), bitertanol (3 samples), fenitrothion (1 sample)  
25  
26 and flusilazole (1 sample).  
27  
28

29  
30 The co-occurrence of pesticide residues are shown in Figure 3. A total of 231  
31  
32 samples (36% of the total) contained only one pesticide, 31 (4 %) samples of the  
33  
34 six commodities studied contained two residues of pesticides and 7 (1%) samples  
35  
36 of peach, tangerine, nectarine and orange were contaminated with three pesticide  
37  
38 residues and 1 samples of nectarine contained four pesticide residues.  
39  
40  
41

42  
43 Furthermore, earlier monitoring data conducted in fruits contaminated with  
44  
45 pesticide residues are similar with the levels and frequencies reported by other  
46  
47 authors (Andersen and Poulsen. 2001. Blasco *et al.* 2002, , European  
48  
49 Commission, 2001, FAO/UNEP/WHO, 1991, Fernández et al., 2001, Torres 1997).  
50  
51  
52

53  
54 *Daily intake*  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 The safety of fruit consumption was evaluated according to the toxicological  
5 significance of human exposure to these pesticides. The FAO/WHO have  
6 established ADIs in accordance with the evaluation of all available data relating to  
7 the substance studies conducted in human, experimental animals and *in vitro*  
8 system.  
9

10  
11 To evaluate this risk we have calculated the EDIs for a human being with a body  
12 weight of 60 kg, taking into consideration an inquire about the mean food  
13 consumption in Spain (Spanish Institute National of Statistic 2005). The average  
14 level of pesticide found, the ADIs and EDIs of each pesticide calculated for the  
15 main group of the commodities are shown in Table 4. The EDIs of pesticides is  
16 much lower than the ADIs established. The highest EDIs obtained for methidation in  
17 citrus fruits was 11 times lower than the ADIs. This organophosphorous is mainly  
18 used in citric fruits which are basically consumed in the Mediterranean area,  
19 therefore the combined intake of this pesticide residue from other food items is not  
20 significant and therefore, it is unlike to reach exposures above acceptable levels.  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40

## 41 **Conclusions**

42  
43 Results show that most of the pesticide levels detected were below than the MRLs  
44 established by the EU. Pesticide residue monitoring programmes should be  
45 recommended to be implanted for ensuring minimal residue levels in fruit  
46 commodities. Moreover, the calculation of the EDI of each pesticide from these  
47 data showed that the contribution of the fruits studied to dietary intake was much  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 lower than the ADIs published. The EDIs for calculated in this way were higher  
5  
6 than the real values because khaki was the fruit with proportionally more  
7  
8 contaminated samples, but their contribution of this fruit to the Spanish population  
9  
10 diet is less than 1 kg. In general, the dietary intake of these pesticide residues  
11  
12 through the diet for the mean adult Spanish consumer does not seem to pose a  
13  
14 relevant risk.  
15  
16  
17  
18

### 19 **Acknowledgements**

20  
21  
22  
23 This work has been financially supported by the Spanish Ministry of Science and  
24  
25 Technology together with the European Regional Developments Funds (ERDF)  
26  
27 (project No. AGL2003-01407).  
28  
29  
30

### 31 **References**

32  
33  
34 Albero B, Sanchez-Brunete C, Tadeo JL. 2003. Determination of  
35  
36 organophosphorus pesticides in fruit juices by matrix solid-phase dispersion and  
37  
38 gas chromatography. *Journal of Agricultural Food Chemistry* 51:6915-21.  
39  
40  
41

42 Andersen JH, Poulsen ME. 2001. Results from the monitoring of pesticide residues  
43  
44 in fruit and vegetables on the Danish market, 1998–99. *Food Additives and*  
45  
46 *Contaminants* 18:906-931.  
47  
48  
49

50 Blasco C, Fernández M, Picó Y, Font G, Mañes J. 2002. Simultaneous  
51  
52 determination of imidacloprid, carbendazim, methiocarb and hexythiazox in  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 peaches and nectarines by liquid chromatography–mass spectrometry. *Analytica*  
5  
6  
7 *Chimica Acta* 461:109-116.

8  
9  
10 Blasco C, Font G, Mañes J, Picó Y. 2005. Screening and evaluation of fruit  
11  
12 samples for four pesticide residues. *Journal of AOAC International* 88:847-53.

13  
14  
15  
16 Caldas ED, Souza LC. 2004. Related chronic dietary risk for pesticide residues in  
17  
18 food in Brazil: an update. *Food Additives and Contaminants* 21:1057-64.

19  
20  
21  
22 Chun OK, Kang HG. 2003. Estimation of risks of pesticide exposure, by food  
23  
24 intake, to Koreans. *Food and Chemical Toxicology* 41:1063-1076.

25  
26  
27  
28 Consellería de Sanidad y consumo de la Comunidad Valenciana (Spain) 1995.  
29  
30 *Diario oficial de la Generalitat Valenciana*. Num. 2546, 07/07/1995.

31  
32  
33  
34 Dogheim SM, El-Marsafy AM, Salama EY, Gadalla SA, Nabil YM. 2002.  
35  
36 Monitoring of pesticide residues in Egyptian fruits and vegetables during 1997.  
37  
38 *Food Additives and Contaminants* 19:1015-27.

39  
40  
41  
42 Ecobichon DJ. 2001. Toxic effect of pesticides. In: Klaasen, CD editors *Cassarett*  
43  
44 *and Doull's Toxicology*. New York: MacGraw Hill pp.763-810.

45  
46  
47  
48 European Commission, *Monitoring of Pesticide Residues in Products of Plant*  
49  
50 *Origin in the European Union, Norway and Iceland*. Report 2001. Available from:  
51  
52 [http://europa.eu.int/comm/food/fvo/specialreports/pesticides\\_index\\_en.htm](http://europa.eu.int/comm/food/fvo/specialreports/pesticides_index_en.htm).

53  
54 [Accessed 2005 October 30](#).

1  
2  
3  
4 European Commission, Commission Directive 79/700/EEC of 24 July 1979  
5  
6 establishing Community methods of sampling for the official control of pesticide  
7  
8 residues in and on fruit and vegetables.  
9

10  
11  
12 European Commission, Directorate General Health and Consumer Protection,  
13  
14 Residue analytical methods for post-registration control and monitoring,  
15  
16 SANCO/825/00 (rev. 7) 17 March 2004.  
17  
18

19  
20 European Commission Pesticide residue. Available from:  
21  
22 <http://europa.eu.int/comm/food/fs/ph-ps/pest/index-en.htm>. Accessed 2005  
23  
24 October 30.  
25  
26

27  
28  
29 FAO/UNEP/WHO. 1991. Food Contamination Monitoring Program, Summary of  
30  
31 1986–1988 Monitoring Data. WHO, Geneva, Switzerland.  
32  
33

34  
35 FAO/WHO. 2004. Available from: <http://www.codexalimentarius.net>. Accessed  
36  
37 2005 October 30.  
38  
39

40  
41 Fernández M, Picó Y, Mañes J. 2001. Pesticide residues in oranges from Valencia  
42  
43 (Spain). Food Additives and Contaminants 18:615-624.  
44  
45

46  
47 JMPR. 1999. Pesticides Residues in Food: Report of the 1999 Joint FAO/WHO  
48  
49 Meeting of Experts. Geneva, World Health Organization.  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Leblanc LC, Malmauret L, Guerin T, Bordet F, Boursier B, Verger P. 2000.  
5  
6 Estimation of the dietary intake of pesticide residues, lead, cadmium, arsenic and  
7  
8 radionuclides in France. Food Additives and Contaminants 17:1-8.  
9  
10

11  
12 Lehotay SJ, Hajlová J, 2002. Application of gas chromatography in food analysis.  
13  
14 TrAC Trends in Analytical Chemistry 21:686-697.  
15  
16

17  
18 Ministerio de Agricultura Pesca y Alimentación (2005). Available from  
19  
20 <http://www.mcx.es/plaguicidas/espanol.asp>  
21  
22 [http://www.mcx.es/plaguicidas/espanol.](http://www.mcx.es/plaguicidas/espanol.asp)  
23  
24 asp Official maximum residue limits (MRLs).  
25

26  
27 Nasreddine L, Parent-Massin D. 2002. Food contamination by metals and  
28  
29 pesticides in the European Union. Should we worry? Toxicology Letters 127:29-  
30  
31 41.  
32  
33

34  
35 Pugliese P, Moltó JC, Damiani P, Marín RL, Cossignani L, Mañes J. 2004. Gas  
36  
37 chromatographic evaluation of pesticide residue contents in nectarines after non-  
38  
39 toxic washing treatment. Journal of Chromatography A 1050: 185-191.  
40  
41

42  
43 Spanish Institute National of Estadistic (2005). Available from <http://www.ine.es>.  
44  
45 Accessed 2005 October 30.  
46  
47

48  
49 Stenersen J. 2004. Chemical Pesticides: Mode of Action and Toxicology.  
50  
51 CRC Press  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 Torres CM, Picó Y, Mañes J. 1997. Evaluation of organophosphorus pesticide  
5 residues in citrus fruits from the Valencian Community (Spain). Journal of AOAC  
6  
7 International 80:1122-1128.  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

For Peer Review Only

**FIGURES:**

**Figure 1.** NPD chromatograms corresponding to: A) spiked nectarine sample with 0.5 mg kg<sup>-1</sup> of fenthion and 0.1 mg kg<sup>-1</sup> of malathion; B) field treated nectarine sample contaminated with 0.25 mg kg<sup>-1</sup> of fenthion and 0.05 mg kg<sup>-1</sup> of malathion.

**Figure 2.** Total ion chromatogram profile of the same nectarine sample of Figure 1 contained fenthion and malathion and their corresponding mass spectra.

**Figure 3.** Number of pesticide residues found in each commodities.

**Table 1.** Limit of quantifications (LOQs) and Maximum Residue Limits (MRLs) set by the European Union (EU), Food and Agricultural Organisation (FAO) and Spanish government for selected pesticides in the studied commodities.

Pesticides	LOQs (mg kg <sup>-1</sup> )	MRLs (mg kg <sup>-1</sup> )											
		Peaches and nectarines			Oranges and tangerines			Khakis			Watermelons		
		EU	Spain	FAO	EU	Spain	FAO	EU	Spain	FAO	EU	Spain	FAO
Acephate (OPP)	0.100		0.02			1			1.00			0.02	0.5
Bitertanol (triazole)	0.010		1	1		0.05			0.05			0.05	0.5
Cyproconazole (triazole)	0.015			0.05		0.05			0.05				0.05
Chlorotalonil (chloronitrile)	0.001	1		1	0.01	0.01		0.01	0.01		1	1	0.1
Chlorpyrifos methyl (OPP)	0.025	0.5	0.5	0.5	0.5(1) <sup>1</sup>	1		0.05	0.5	0.5		0.05	0.05
Diazinon (OPP)	0.018	0.02	0.02	0.2	1(0.02) <sup>1</sup>	1(0.02) <sup>1</sup>		0.02	0.02		0.02	0.02	0.05
Fenitrothion (OPP)	0.001	0.5	0.5	1	2	2	2	0.5	0.5		0.5	0.5	
Fenthion (OPP)	0.0001		1			0.5	2		0.05			0.05	
Flusilazole (triazole)	0.012		0.1	0.5		0.01			0.01			0.01	
Malathion (OPP)	0.0001	0.5	3	6	2	3	4	0.5	0.5		3	0.5	
Methamidophos (OPP)	0.036	0.05	0.05		0.2	0.2		0.01	0.01		0.01	0.01	0.5
Methidathion (OPP)	0.0001		0.2	0.5	2	2	2	0.05	0.3			0.02	0.05
Parathion methyl (OPP)	0.0001	0.2	0.2		0.2	0.2		0.2	0.2		0.2	0.2	
Pyroproxyfen (pyridine)	0.03		0.05			0.5			0.05			0.05	
Trichlorfon (OPP)	0.05	0.5	0.5			0.5	0.5	0.5	0.5		0.5	0.5	

<sup>1</sup> MRL for tangerine, OPPs: organophosphorous

**Table 2.** Range studied for linearity, correlation coefficients, recoveries and R.S.D.s at 0.5 and 5 mg kg<sup>-1</sup> levels (*n* = 10) of the different commodities studied.

Pesticide	Conc. range (mg kg <sup>-1</sup> )	R <sup>2</sup>	Recovery (%) ± RSD							
			Peaches and nectarines		Oranges and tangerines		Khakis		Watermelons	
			0.5	5	0.5	5	0.5	5	0.5	5
Acephate	0.3-30	0.9988	54 ± 14	67 ± 9	62 ± 15	69 ± 6	57 ± 12	67 ± 11	52 ± 15	69 ± 12
Bitertanol	0.03-10	0.9985	62 ± 15	78 ± 6	60 ± 17	85 ± 7	64 ± 16	80 ± 8	60 ± 14	80 ± 10
Chlorothalonil	0.03-10	0.9900	80 ± 10	85 ± 5	78 ± 12	80 ± 9	75 ± 12	78 ± 8	77 ± 12	80 ± 9
Chlorpyrifos methyl	0.01-10	0.9997	83 ± 8	88 ± 3	86 ± 15	89 ± 10	80 ± 11	83 ± 7	80 ± 12	84 ± 9
Cyproconazole	0.03-10	0.9979	70 ± 18	72 ± 17	75 ± 13	79 ± 10	68 ± 16	72 ± 10	65 ± 14	68 ± 8
Diazinon	0.03-10	0.9984	65 ± 20	68 ± 15	71 ± 14	73 ± 14	68 ± 18	70 ± 15	67 ± 18	65 ± 12
Fenitrothion	0.003-5	0.9989	85 ± 8	87 ± 6	83 ± 9	88 ± 7	80 ± 12	83 ± 9	81 ± 8	83 ± 5
Fenthion	0.001-5	0.9999	87 ± 6	89 ± 3	85 ± 6	87 ± 5	83 ± 9	88 ± 7	81 ± 10	85 ± 5
Flusilazole	0.03-30	0.9965	63 ± 15	68 ± 12	69 ± 15	72 ± 10	57 ± 18	58 ± 15	57 ± 12	58 ± 9
Malathion	0.001-5	0.9978	75 ± 9	77 ± 6	73 ± 12	81 ± 6	70 ± 15	77 ± 9	68 ± 9	75 ± 8
Methamidophos	0.03-10	0.9934	57 ± 15	73 ± 12	58 ± 18	71 ± 8	62 ± 20	72 ± 18	65 ± 9	69 ± 5
Methidathion	0.001-5	0.9995	83 ± 6	85 ± 5	81 ± 7	84 ± 7	78 ± 12	80 ± 9	75 ± 12	81 ± 9
Parathion methyl	0.001-5	0.9992	84 ± 8	86 ± 5	82 ± 7	84 ± 6	81 ± 9	83 ± 8	79 ± 10	82 ± 8
Pyroproxyfen	0.1-10	0.9928	58 ± 17	63 ± 12	56 ± 15	62 ± 9	58 ± 18	57 ± 15	59 ± 14	57 ± 11
Trichlorfon	0.1-10	0.9937	57 ± 16	68 ± 12	58 ± 19	68 ± 12	58 ± 20	58 ± 20	56 ± 18	59 ± 12

**Table 3.** Occurrence of the studied pesticide residues in nectarines, peaches, khaki, tangerine and watermelon

Commodity	Total	Contaminated samples	>MRL	Pesticide found	Fr.	Range (min-max)	> MRL <sup>1</sup>
Nectarine	175	68	10	Bitertanol	7	0.14-1.90	1
				Fenitrothion	2	0.02-0.53	1
				Fenthion	60	0.005-1.44	5
				Flusilazole	1	0.07	-
				Malathion	9	0.002-2.80	3
				Methidathion	3	0.008-0.04	-
				Chlorpyriphos methyl	1	0.37	-
Peach	107	28	5	Bitertanol	5	0.3-1.41	2
				Chlorpyriphos methyl	1	0.37	-
				Fenitrothion	2	0.01-0.60	-
				Fenthion	8	0.03-0.43	-
				Flusilazole	1	0.06	-
				Malathion	8	0.02-4.25	3
				Methidathion	1	0.02	-
				Parathion-Methyl	1	0.02	-
Khaki	28	17	16	Fenthion	17	0.25-0.73	14
				Flusilazole	1	0.10	1
				Malathion	4	1.86-3.50	4
Orange	74	31		Fenthion	3	0.05-0.10	-
				Malathion	18	0.02-1.00	-
				Methidathion	12	0.1-1.10	-
				Fenitrothion	1	0.10	-
Tangerine	232	132	3	Chlorpyrifos methyl	1	0.04	-
				Fenitrothion	1	0.05	-
				Fenthion	16	0.05-2.30	3
				Malathion	82	0.05-1.60	-
				Methidathion	52	0.06-1.30	-

Fr: Frequency

<sup>1</sup>The MRL are the EU MRLs and when they are not stabilised, the Spanish MRLs were selected.

**Table 4.** Estimated daily intakes (EDIs) ( $\mu\text{g kg}^{-1}$  b.w./day) and admissible dairy intakes (ADIs) for pesticide residues found in stone fruit (peaches and nectarines), citrus fruit (tangerines and oranges) and other fruits (khakis and watermelons) collected during 2001-2003.

Commodities	ADI ( $\mu\text{g kg}^{-1}$ b.w. per day)	Citrus Fruit (n=306)			Stone Fruit (n=282)			Khaki (n=28)		
		Mean ( $\mu\text{g/kg}$ )	EDI <sup>a</sup>	EDI (as %ADI)	Mean ( $\mu\text{g/kg}$ )	EDI	EDI (as %ADI)	Mean ( $\mu\text{g/kg}$ )	EDI	EDI (as %ADI)
Bitertanol	12				30	0.011	0.094			
Chlorpyrifos methyl	10	0.2	0.0001	0.0015	2	0.0009	0.009			
Fenitrothion	5	0.92	0.0005	0.011	2	0.0008	0.016			
Fenthion	1	49	0.031	3.1	78	0.028	2.8	266	0.14	0.72
Flusilazole	1				0.4	0.0001	0.016	3	0.0019	0.19
Malathion	20	281	0.177	0.88	43	0.015	0.079	153	0.084	8.4
Methidathion	1	136	0.086	8.61	0.2	0.0001	0.01			
Parathion										
Methyl	4				0.07	$2.60 \times 10^{-5}$	0.0006			
Trichlorfos	10				0.7	0.00026	0.0026			

<sup>a</sup> EDI was calculated by the equation:  $EDI = (\sum c) (C M I D I K I)$ ;  $\sum c$  is the sum of the pesticide residues concentrations in the analyzed samples ( $\mu\text{g kg}^{-1}$ );  $C$  the mean annual intake per person. The value of the annual intake per person of stone fruit (nectarines and peaches) was 8.2 kg/person. of citrus fruit (tangerines and oranges) was 26 kg/person and of other fruit (khaki and watermelon) was 12 kg/person according with the National Inquiry of Consumption of Food, Drinks, and Tobacco performed in the years 2001-2002.