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

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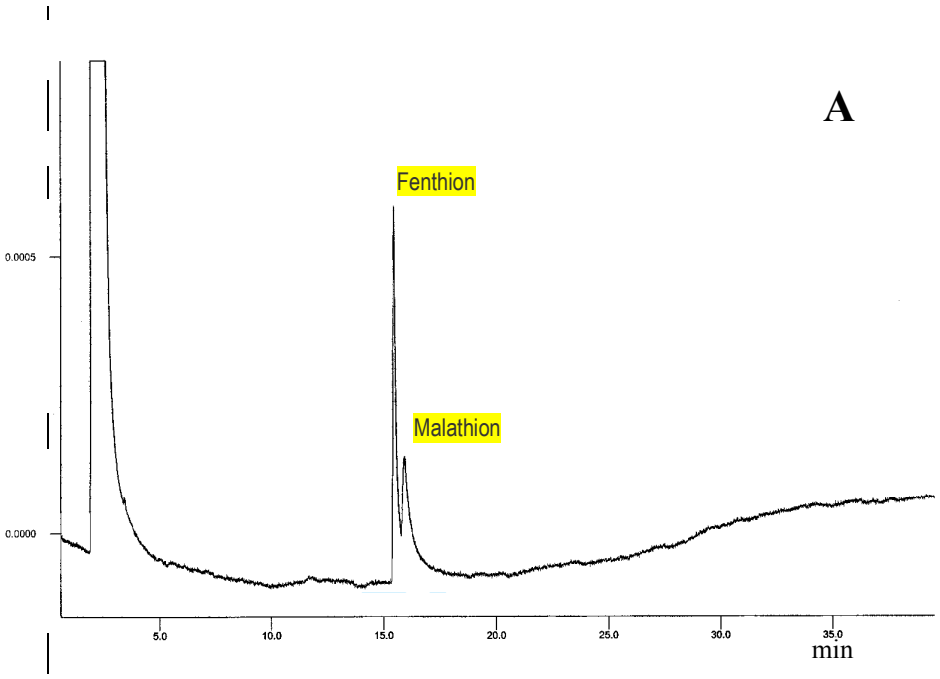
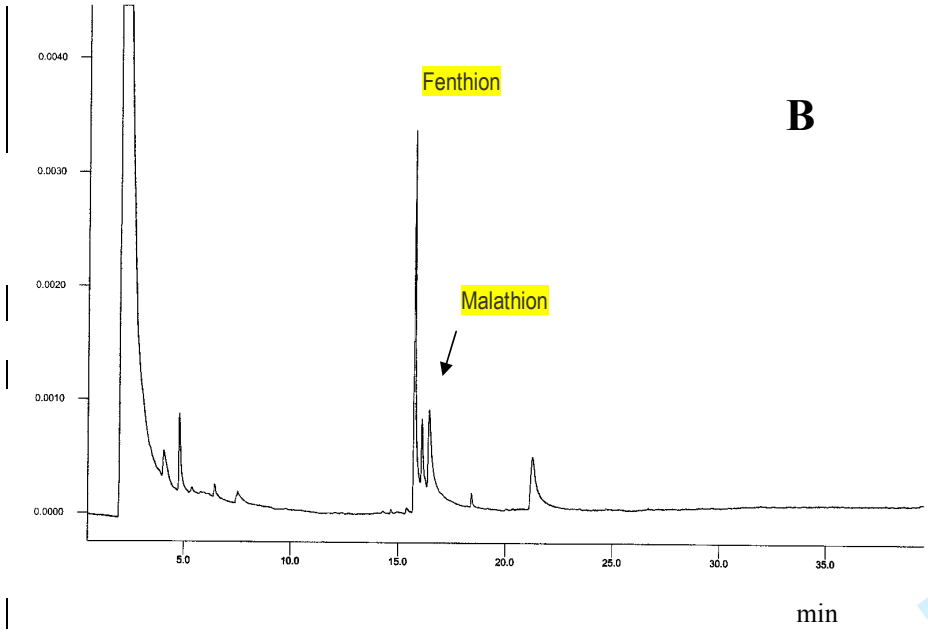
Methods/Techniques:	Total diet studies, Chromatography - GC/MS
Additives/Contaminants:	Pesticide residues
Food Types:	Fruit





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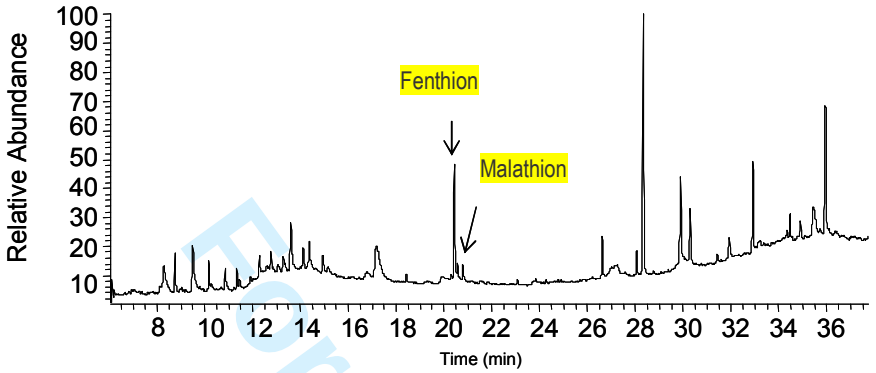

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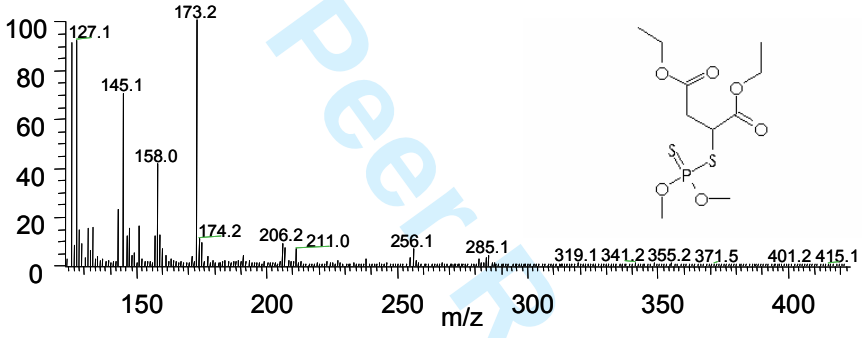

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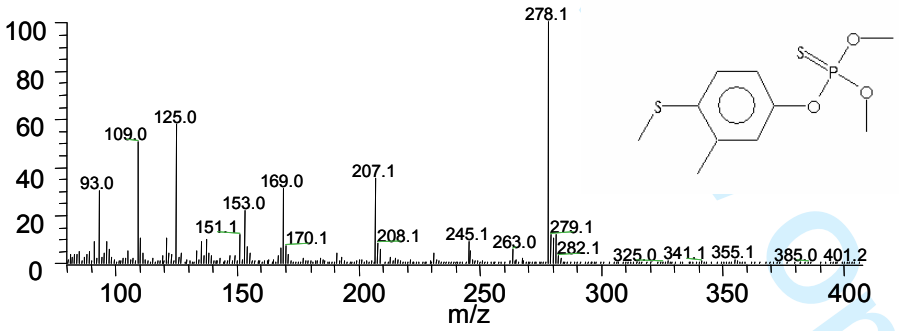

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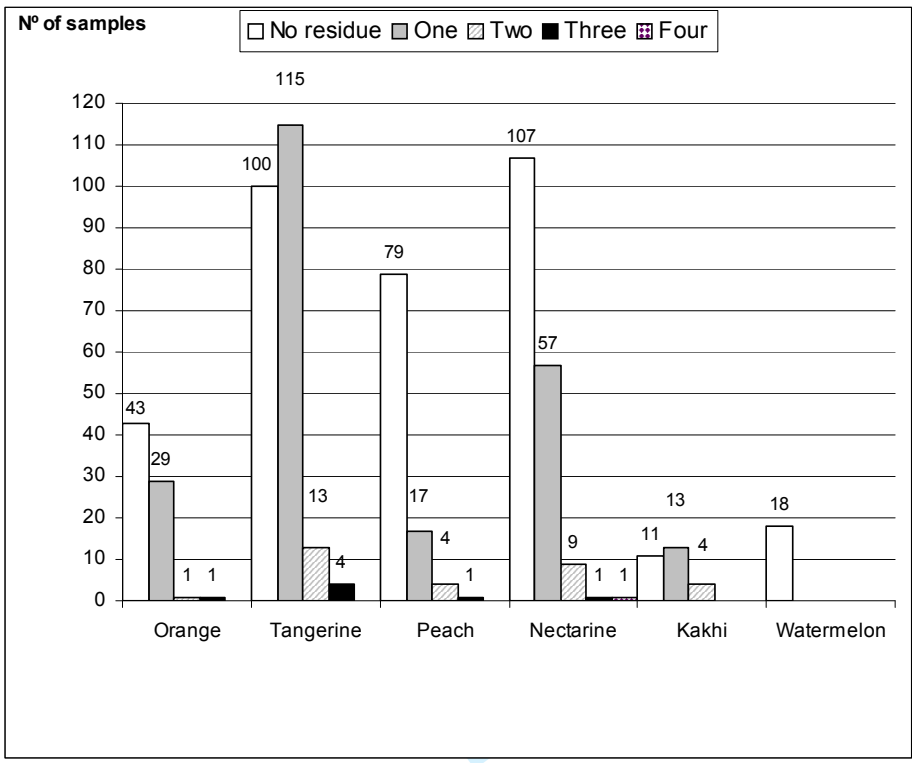

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Exposure assessment of fruits contaminated with pesticide residues from Valencia, 2001-2003

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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^{-1} 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^{-1}. 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^{-1}, followed by fenthion in 104 samples (16 %) at 0.005-2.3 mg kg^{-1} and methidation in 68 samples (10 %) at 0.008-1.3 mg kg^{-1}. 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.

Keywords: monitoring, multiresidue analysis, fruits, pesticides, gas chromatography, mass spectrometry, Valencia, ADI and EDI.

Introduction

Increasing public concern in recent years about possible health risks from pesticide residues in food supply has led to establish strict regulation of pesticide tolerances and to assess dietary intakes of pesticide residues in food commodities (Stenersen 2004, Ecobichon 2001, Nasreddine and Parent-Massin 2002). To ensure the safety of food for consumers, the *Codex Alimentarius* Commission of the Food Agriculture Organization (FAO/WHO 2004) have established Maximum Residue Limits (MRLs) for pesticides in foodstuffs, which are also regulated by the European Union (EU) and Spanish directives (European Commission, 2005, Ministerio de Agricultura Pesca y Alimentación 2005.

Monitoring programme for pesticide residues in food are a useful tool for ensuring that consumers are not exposed to unacceptable pesticide residue levels, authorised pesticides are correctly applied to food crops in terms of granted authorizations and registrations (application rates and pre-harvested intervals) and to permit the free circulation of pesticide-treated products as long as they comply with the fixed MRLs (Dogheim *et al.* 1997, Fernández *et al.* 2001, Blasco *et al*. 2005).

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Monitoring programs are carried out by regulatory authorities to check regularly the compliance of foodstuffs with MRLs (Andersen and Poulsen 2001, JMPR 1999, European Commission 2001). However, these results are not representative of the situation on a particular area so monitoring of the locally produced commodities is relevant to have a complete view of the pest treatment making possible to take specific measures in the contaminated area.

The frequent application of different types of pesticides and the large number of samples makes necessary the determination of as many compounds as possible in a single analysis at levels below the MRL. Generally monitoring analysis are accomplished with gas chromatography (GC) in combination with different detectors, such nitrogen-phosphorus detector (NPD), electron-capture detectors (ECD) or mass spectrometry (MSD) which provides a fingerprint spectra by electron ionization and allows the possibility of confirming pesticide identity (Albero *et al.* 2003, Puglese *et al.* 2004, Lehotay and Hajlová 2002, Torres *et al.* 1997).

When assessing the impact on consumers of pesticide exposure through diet, it is important to consider the effects of both, chronic and acute exposure. Limiting chronic exposure to a pesticide residue is managed through establishing the Acceptable Daily Intake (ADI) for the pesticide, which is an estimate of the maximum level of intake over a lifetime, judged to result without appreciable health risk. Estimations include a safety factor to ensure that the elderly, infants, children, and those whose systems are under stress because of illness are protected (Leblanc *et al.* 2000, Caldas and Souza 2004, Chun and Kand 2003).

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Valencia is an important citrus growing area in Europe although other fruit commodities are also produced and exported, so assessing pesticide residues in fruit intended for human consumption is necessary. The aim of this work was to analyze fifteen pesticide residues in tangerines, oranges, peaches, nectarines and khakis from agricultural cooperative of Valencia during 2001-2003. The results of the monitoring program were taken into consideration to evaluate whether the Estimated Daily Intake (EDI) of pesticides through the fruit consumed by Spanish adult population is a cause for health concern according to the recommended intake of the FAO/WHO organization.

Material and methods

Samples and reagents

Samples of 175 nectarines, 74 oranges, 107 peaches, 28 khakis, 232 tangerines and 18 watermelons were taken during May 2001 to April 2003 campaigns obtained from an agricultural cooperative which covers one of the main agricultural production areas of Valencia. Fruit samples were taken in accordance with the guidelines of the European Union (EU), they were taken at various places distributed throughout the lot (size ca. 50 kg), (European Commission, 1979). Samples were stored at 4ºC and analyzed in 24h. Pesticides with purities up to 98% were supplied by Riedel-de Haën (Seelze, Germany). Ethyl acetate for residue analysis was purchased from Merck (Darmstadt, Germany) and anhydrous sodium sulfate (analytical grade) was bought from Panreac (Barcelona, Spain).

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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 µl 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 44-46ºC and 250 mBar. Finally, the extract was reconstituted to 10 ml with ethyl acetate and 2 µl was analyzed by GC.

Analysis of pesticide residues

Routine analyses were carried out on a Varian Star 3400CX gas chromatograph (Varian, Walnut Creek, CA, USA) equipped with an 8200CX autosampler, an on-column injector (SPI 1093), and NPD system. Identification of peaks was performed in a Trace GC gas chromatograph (Thermo Electron Corporation, San José, CA, USA) with a Thermo-Finnigan AS 2000 autosampler, a split/splitless injector, and a Trace MS quadrupole mass spectrometer. Compounds were separated on DB-5 ms (J&W Scientific, Folsom, CA USA) fused-silica capillary columns (30 m × 0.25 mm i.d., 0.25 µm film thickness).

Varian gas chromatograph conditions: Injector 280°C, detector 300°C. Oven temperature program: initial temperature, 140ºC; held for 1 min, programmed to 280°C, at 5ºC/min, and held for 11 min. Helium was used as carrier gas at a flow rate of 1.9 ml/min.

Trace gas chromatograph conditions: injector and transfer line 280ºC, source temperature 230ºC. Oven temperature program: the initial temperature (50ºC) was held for 1 min, programmed to 120ºC at 30ºC/min, held for 1 min, then programmed to 275ºC at 5ºC/min, and held for a further 5 min. The mass spectrometer was used with electron impact ionization (–70 eV) in full scan mode (65–365 amu). The carrier gas was helium at 1.5 ml/min. Splitless time was 0.9 min.

Results and Discussion

Method performance

Analytical parameters were calculated for the multi-residue method proposed using GC-NPD. Precision was calculated in terms of intra-day repeatability (*n*=5) and inter-day reproducibility (5 different days). The intra-day repeatability evaluated as relative standard deviation (RSDs) ranged from 3 to 5%. The inter-day reproducibility was lower than 8% for all instances. Calibration curves prepared with standard in ethyl acetate were linear at the studied range as shown in Table 2 with regression coefficients >0.99. Limits of quantification (LOQs) which were calculated as the lowest concentration of compound that gave a response that could be quantified as the minimum concentrations providing chromatographic signals 10 times higher than background noise ranged from 0.0001 to 0.1 mg kg^{-1} and were lower than the MRLs established by the EU and Spanish legislations and those recommended by the FAO/WHO for each of the commodities studied (Table 1). Accuracy of samples spiked at 0.5 mg kg^{-1} and 5 mg kg^{-1} were equivalent in the commodities studied. Except for some cases, principally at 5 mg kg^{-1}, results of accuracy and precision fulfilled the criteria of the European guidelines indicating that a method can be considered accurate and precise when accuracy data are comprised between 70 and 110% with relative standard deviations not higher than 20% (European Commission, 2000).

Figure 1 illustrates a NPD chromatograms corresponding to a spiked nectarine and a contaminated nectarine with 0.5 mg kg^{-1} of fenthion and 0.1 mg kg^{-1} of malathion. Due to the presence of some interfering peaks as the one between both peaks a

confirmatory method is necessary. In Figure 2 the total ion GC-MS chromatogram and the two peaks spectra confirmed the identity of both pesticides.

Monitoring data

Table 3 outlines the data obtained after analyzed 634 samples of fruits in which 276 (43 %) of the analyzed samples were contaminated and 34 (5 %) exceeded the MRLs. In terms of commodity groups, khakis was the fruit with the highest rate of contaminated samples (61 %), followed by of tangerines (57 %), oranges (42 %), nectarines (39 %) and peaches (26 %). No residues were found in watermelons.

Most of the pesticides found were organophosphorus used as insecticides except triazole fungicides (bitertanol and flusilazole) and a chloronitrile fungicide (chlorothalonil). Malathion was the most frequently pesticide detected and at the highest concentration, 121 (19 %) samples of the commodities studied except watermelon were contaminated from 0.002 to 4.25 mg kg^{-1} (0.282 mg kg^{-1} average level). This pesticide is a wide spectrum organophosphorous insecticide suitable for the control of insects that shuck and chew on fruit and vegetables. Fenthion was detected in 104 samples (16%) at levels ranging from 0.005 to 2.3 mg kg^{-1} (0.179 mg kg^{-1} average level), this pesticide is a contact insecticide used against many sucking, biting pests, especially fruit flies, stem borers and mosquitoes. Methidathion was found in 68 samples (10%) at levels between 0.008 and 1.3 mg kg^{-1} (0.2 mg kg^{-1} average level).

Bitertanol was found in 12 samples (1.9 %) at levels that range from 0.14 and 1.9 mg kg^{-1} (0.52 mg kg^{-1} average level). Fenitrothion was found in 6 (0.9%) at levels between 0.01 to 0.53 mg kg^{-1} (0.05 mg kg^{-1} average level). Chlorpyrifos methyl and flusilazole were detected in 3 samples, the first one with a range from 0.04 mg kg^{-1} to 0.37 mg kg^{-1} (0.176 mg kg^{-1} average level) and the second one from 0.06 to 0.1 mg kg^{-1} (0.079 mg kg^{-1} average level). Trichlorfon and Parathion methyl were found only in one sample, both in peaches with a level around 0.02 mg kg^{-1}.

The pesticides detected with levels above European MRLs were fenthion (22 samples), malathion (10 samples), bitertanol (3 samples), fenitrothion (1 sample) and flusilazole (1 sample).

The co-ocurrence of pesticide residues are shown in Figure 3. A total of 231 samples (36% of the total) contained only one pesticide, 31 (4 %) samples of the six commodities studied contained two residues of pesticides and 7 (1%) samples of peach, tangerine, nectarine and orange were contaminated with three pesticide residues and 1 samples of nectarine contained four pesticide residues.

Furthermore, earlier monitoring data conducted in fruits contaminated with pesticide residues are similar with the levels and frequencies reported by other authors (Andersen and Poulsen. 2001. Blasco *et al.* 2002, , European Commission, 2001, FAO/UNEP/WHO, 1991, Fernández et al., 2001, Torres 1997).

Daily intake

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

To evaluate this risk we have calculated the EDIs for a human being with a body weight of 60 kg, taking into consideration an inquire about the mean food consumption in Spain (Spanish Institute National of Statistic 2005). The average level of pesticide found, the ADIs and EDIs of each pesticide calculated for the main group of the commodities are shown in Table 4. The EDIs of pesticides is much lower than the ADIs stablished. The highest EDIs obtained for methidation in citrus fruits was 11 times lower than the ADIs. This organophosphorous is mainly used in citric fruits which are basically consumed in the Mediterranean area, therefore the combined intake of this pesticide residue from other food items is not significant and therefore, it is unlike to reach exposures above acceptable levels.

Conclusions

Results show that most of the pesticide levels detected were below than the MRLs established by the EU. Pesticide residue monitoring programmes should be recommended to be implanted for ensuring minimal residue levels in fruit commodities. Moreover, the calculation of the EDI of each pesticide from these data showed that the contribution of the fruits studied to dietary intake was much

lower than the ADIs published. The EDIs for calculated in this way were higher than the real values because khaki was the fruit with proportionally more contaminated samples, but their contribution of this fruit to the Spanish population diet is less than 1 kg. In general, the dietary intake of these pesticide residues through the diet for the mean adult Spanish consumer does not seem to pose a relevant risk.

Acknowledgements

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FIGURES:

Figure 1. NPD chromatograms corresponding to: A) spiked nectarine sample with 0.5 mg kg^{-1} of fenthion and 0.1 mg kg^{-1} of malathion; B) field treated nectarine sample contaminated with 0.25 mg kg^{-1} of fenthion and 0.05 mg kg^{-1} 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^{-1})	MRLs (mg kg^{-1})											
		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)[1]	1		0.05	0.5	0.5		0.05	0.05
Diazinon (OPP)	0.018	0.02	0.02	0.2	1(0.02)[1]	1(0.02)[1]		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	

[1] 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^{-1} levels (n = 10) of the different commodities studied.

Pesticide	Conc. range (mg kg^{-1})	R^2	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[1]
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	-
				Trichlorfon	1	0.20	-
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

[1]The MRL are the EU MRLs and when they are not stabilised, the Spanish MRLs were selected.

Table 4. Estimated daily intakes (EDIs) (μg 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 (μg kg^{-1} b.w. per day)	Citrus Fruit (n=306)			Stone Fruit (n=282)			Khaki (n=28)		
		Mean (μg/kg)	EDI [a]	EDI (as %ADI)	Mean (μg/kg)	EDI	EDI (as %ADI)	Mean (μg/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	2.60×10^{-5}	0.0006			
Trichlorfos	10				0.7	0.00026	0.0026			

[a] EDI was calculated by the equation: EDI = *(∑c)* (*C N*1 *D*1 *K*1): ∑*c* is the sum of the pesticide residues concentrations in the analyzed samples (μg 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.