JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effect of Household Processing and Unit-to-Unit Variability of Pyrifenox, Pyridaben, and Tralomethrin Residues in Tomatoes

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Residue levels of pyrifenox, pyridaben, and tralomethrin were determined in unprocessed and processed tomatoes, grown in a experimental greenhouse, to evaluate the effect of three different household processes (washing, peeling, and cooking) and the "unit to unit" variability of these pesticides in tomatoes. The study was carried out on 11 greenhouse tomato samples collected during a 5 week period in which two successive treatments with the studied pesticides were applied. Residue levels in unprocessed and processed tomato samples were determined by means of ethyl acetate extraction and gas chromatography−electron capture detection determination. The washing processing factor results were 0.9 ± 0.3 for pyridaben, 1.1 ± 0.3 for pyrifenox, and 1.2 ± 0.5 for tralomethrin, whereas the peeling processing factors were 0.3 ± 0.2 for pyridaben and 0.0 ± 0.0 for both pyrifenox and tralomethrin. The average loss of water in the tomato pure samples during the cooking process was ∼50%; the cooking processing factors were 2.1 ± 0.8 for pyridaben, 3.0 ± 1.1 for pyrifenox, and 1.9 ± 0.8 for tralomethrin. The unit-to-unit variability factors were determined on three different greenhouse samples analyzing 10 different units of unprocessed tomatoes from each sample. In all cases, the unit-to-unit variability factor results were within the range of 1.3−2.2.

KEYWORDS: Pyrifenox; pyridaben; tralomethrin; tomatoes; household processing; residues variability

INTRODUCTION

Pyrifenox [2′,4′-dichloro-2-(3-pyridyl)acetophenone (*E*,*Z*)-*O*-methyloxime] is a systemic fungicide used for the control of powdery mildew, scab, and other pathogenic Ascomycetes, Basidiomycetes, and Deuteriomycetes on vines, fruits, vegetables, and ornamentals (*1*). Pyridaben, 2-*tert*-butyl-5-(4-*tert*-butylbenzylthio)-4-chloropyridazin-3(*2H*)-one, is the common name of the acaricide/insecticide developed by Nissan Chemical Ind., Ltd. (*2*), which is effective for the control of Acari, Aleyrodidae, Aphididae, Cicadellidae, and Thysanoptera on field crops, fruit trees, ornamentals, and vegetables (*1*). Tralomethrin, (*S*)-α-cyano-phenoxybenzyl-(1*R*,3*S*)-2,2-dimethyl-3-[(*RS*)-1,2,2,2-tetrabromoethyl]cyclopropanecarboxylate, is a nonsystemic pyretroid insecticide discovered and introduced by Roussel Uclaf, which is effective for the control of a range of agronomic pests, particularly Lepidoptera in cereals, fruits, vegetables, and others crops, at application rates as low as 7.5−20 g (a.i.)/ha (*1*). The structures of pyrifenox, pyridaben, and tralomethrin are given in **Figure 1**.

In Spain, pyrifenox and pyridaben are commercialized by Novartis and BASF, respectively, under the tradenames of Dorado and Sanmite. Both pesticides are currently authorized in Spain to be used on different vegetable crops, including tomato, for which preharvest intervals (PHIs) and maximum residue limits (MRLs) have been established as follows: 3 days and 0.20 mg/kg for pyrifenox (sum of *E*-pyrifenox and *Z*-pyrifenox) and 7 days and 0.10 mg/kg for pyridaben (*3*, *4*). On the other hand, tralomethrin (commercialized by DuPont under the trade name Tracker) was authorized in Spain until July 2003 to be used on tomatoes and other vegetable crops (3 days PHI;

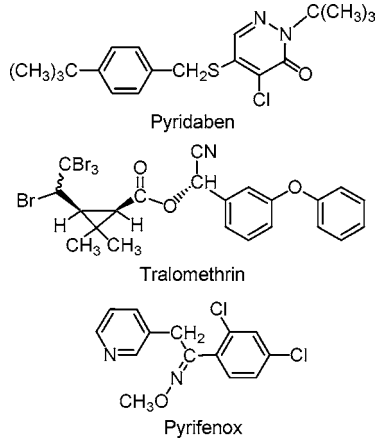

Figure 1. Molecular structures of pyridaben, tralomethrin, and pyrifenox.

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10.1021/jf040455y CCC: $30.25
Published on Web 04/15/2005

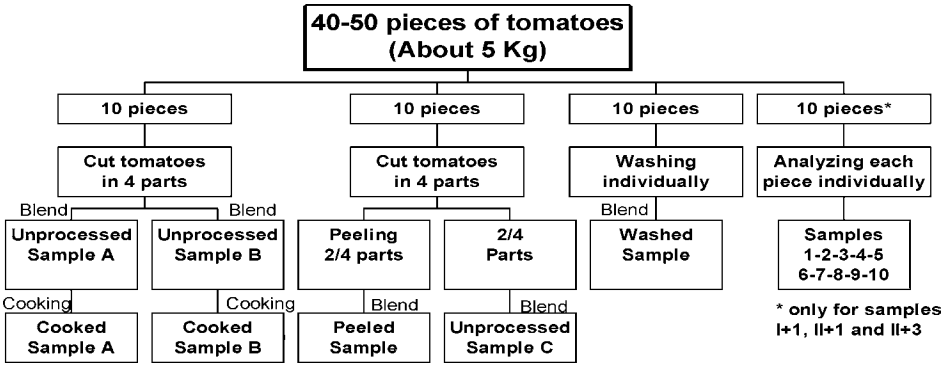

Figure 2. Sample preparation and processing scheme.

0.01 mg/kg MRL) (*3*, *4*). Since that date, and as a consequence of the implementation of the European Council Directive 91/414/EEC concerning the placing of plant protection products on the European market, tralomethrin is not authorized in the European Union (*5*).

At the present time, the literature on pyrifenox, pyridaben, and tralomethrin residues in foods is very sparse, but some papers describing analytical methods have been published (*6*−*9*). The only papers found in the open literature studying the behavior of some of these three pesticides in fruits and vegetables are those published by Cabras et al. (*7*) and Valverde et al. (*10*), in which some data for pyridaben in clementine citrus and for pyridaben and tralomethrin in peppers are given.

The aims of this study were to evaluate the residue levels of pyrifenox, pyridaben, and tralomethrin in tomatoes grown in a plastic greenhouse and to assess the influence on these residues of some household processes (washing, peeling, and cooking). Another important objective of this work was to study the variation of the residue levels of these pesticides in individual tomato units vs composite samples and to compare the calculated "variability factors" with the default values usually considered for consumer risk assessment (*11*, *12*).

EXPERIMENTAL PROCEDURES

Chemicals and Apparatus. Acetone, ethyl acetate, cyclohexane, and anhydrous sodium sulfate (pesticide residue grade) were obtained from Panreac (Barcelona, Spain). Certified standards of pyrifenox (96.7% purity as a sum of *E*-pyrifenox and *Z*-pyrifenox) and tralomethrin (90.0% purity) were supplied by Dr. Ehrenstorfer (Augsburg, Germany), and a certified standard of pyridaben (99.6% purity) was supplied by Riedel-de Haën (Seelze, Germany). Individual stock standard solutions of pyrifenox, pyridaben, and tralomethrin were prepared in acetone. Standard solutions for gas chromatographic (GC) analysis were prepared by suitable dilution of the stock standard solutions with blank tomato extracts.

The GC was a Varian model 3800 (Walnut Creek, CA) equipped with a model 1079 injection port, a model 8200 Cx autosampler, an electron capture detector (ECD), and a DB-5MS fused silica capillary GC column (J&W, Folsom, CA) of 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness. The chromatographic conditions were as follows: detector temperature, 300 °C; injector temperature, 250 °C; oven temperature program, 1 min at 60 °C, 25 °C/min to 180 °C, 5 °C/min to 260 °C, and hold for 29 min; carrier gas, helium; flow rate, 1.2 mL/min; makeup gas, nitrogen; flow rate, 30 mL/min; injection volume, 1 μL; and splitless time, 0.75 min. The retention times of *Z*-pyrifenox, *E*-pyrifenox, pyridaben, and tralomethrin in this column under these GC conditions were 15.2, 16.0, 25.8, and 36.3 min, respectively. The retention times of *Z*-pyrifenox and *E*-pyrifenox were previously confirmed by using individual reference standard solutions of each isomer (supplied by Dr. Ehrenstorfer). Pyrifenox was always determined as a sum of *Z*-pyrifenox and *E*-pyrifenox. A Varian Star 4.5 Chromatography Workstation was used for chromatographic data processing.

Greenhouse Plantation, Treatments, and Sampling. The study was conducted in a 500 m^2 experimental plot, inside a commercial greenhouse belonging to CampoNix S. L., located in Nijar (Almeria, Spain). The tomato plantation density (variety Daniela) was around 2 plants/m^2. Residue levels of pyrifenox, pyridaben, and tralomethrin were determined in tomatoes of commercial size (90−110 g), during a period of 5 weeks in which two different treatments with the three pesticides were applied to the plantation (treatments I and II). Tomato plants, receiving routine horticultural treatment, were first sprayed with an application mixture containing 0.5 mL/L Dorado (20% pyrifenox), 1 g/L Sanmite (20% pyridaben), and 1 mL/L Tracker (3.6% tralomethrin) at the recommended application rates of 160 g of pyrifenox/ha, 320 g of pyridaben/ha, and 58 g of tralomethrin/ha. After 3 weeks, treatment II was applied by spraying a mixture of 2 mL/L Dorado, 2 g/L Sanmite, and 2 mL/L Tracker at exaggerated application rates of 800 g of pyrifenox/ha, 800 g of pyridaben/ha, and 144 g of tralomethrin/ha. Samples were collected at 1, 2, 3, 7, 14, and 21 days after treatment I (samples I + 1, I + 2, I + 3, I + 7, I + 14, and I + 21) and at 1, 2, 3, 7, and 14 days after treatment II (samples II + 1, II + 2, II + 3, II + 7, and II + 14). Also, a number of blank tomato samples were collected just before applying treatment I. In all cases, the greenhouse samples consisted of 40−50 pieces of tomatoes taken at random from the experimental plot.

The daily maximum/minimum/medium temperatures inside the greenhouse throughout the study ranged between 19/8/15 and 35/18/24 °C, whereas the daily maximum/minimum/medium relative humidity inside the greenhouse ranged between 92/33/62 and 99/72/88%.

Sample Preparation, Processing, and Analysis. Inmediately after picking, the greenhouse samples were put into polyethylene bags and transported to the laboratory. From these samples, four identical subsamples were prepared, each containing 10 pieces of tomatoes. The 10 pieces of tomatoes from one of these four subsamples were cut in four identical parts, and the two opposite parts from each tomato were mixed and chopped to obtain the "unprocessed" sample A. The other two opposite parts from these tomatoes were also mixed and chopped to obtain the unprocessed sample B. The 10 pieces of tomatoes from the second subsample were prepared in the same way, but two opposite parts from each tomato were peeled before mixing and chopping to obtain, in this case, the unprocessed sample C and the "peeled" sample. On the other hand, before they were chopped and mixed, the 10 pieces of tomatoes from the third subsample were intensively washed with tap water and further dried with absorbent paper obtaining the "washed" sample. In addition, inmediately after the unprocessed samples A and B were prepared, a 250 g aliquot of each one was cooked to obtain the corresponding "cooked" samples A and B. The cooking process was carried out in 1 L glass jars by heating at 100 °C for 30 min (after a period of 30 min, aproximately, from room temperature to 100 °C) with continuous magnetic agitation. In all cases, the loss of water produced during the cooking process was determined; water was reconstituted in the cooked samples before analysis. Finally, just for the greenhouse samples I + 1, II + 1, and II + 3, each piece of tomato from the fourth subsample was chopped and analyzed separately to carry out the unit-to-unit variability study. A scheme of the preparation and processing procedure applied to each greenhouse sample is showed in **Figure 2**. Immediately after chopping or cooking, all of these samples

Table 1. Pesticide Recoveries from Spiked Blank Tomato Samples

pesticide	spike level (mg/kg)	*n*	recovery (%)	RSD (%)
pyrifenox	0.022	5	111	22
	0.054	6	106	23
	0.54	5	102	17
pyridaben	0.046	5	117	17
	0.46	8	98	12
tralomethrin	0.011	5	91	25
	0.11	8	92	14

were kept deep-frozen until analysis. In all cases, <72 h passed between sampling and analysis.

Extraction of pyrifenox, pyridaben, and tralomethrin residues in tomato samples was carried out according to a modification of the ethyl acetate/GC multiresidue extraction method developed by the Swedish National Food Administration for fruits and vegetables (*10*, *13*). A brief description of the extraction procedure is as follows: 37.5 g of thoroughly homogenized sample was weighed and blended with 100 mL of ethyl acetate and 20 g of anhydrous sodium sulfate for 5 min. The solvent phase was filtered through a glass fiber filter with a 10 g sodium sulfate layer, and the filtrate was dried by shaking with 5 g of sodium sulfate. Twenty-five milliliters of the ethyl acetate layer was transferred to a 100 mL round-bottomed flask and concentrated to approximately 2 mL on rotary vacuum evaporator at 37 °C. The concentrate was transferred quantitatively to a graduated test tube, and the volume was adjusted to 5 mL with ethyl acetate and then to 10 mL with cyclohexane. The extract was filtered through a 0.45 μm microfilter by suction with a 10 mL syringe. The extracts so obtained, which contained 0.94 g sample/mL, were analyzed by GC-ECD using the operating conditions described above. A dilution factor of 100/(100 − % water lost) was taken into account to determine pesticide levels in the cooked samples.

Previous validation studies included the evaluation of the linearity and limits of quantification (LOQs) of the analytical method. The linearity of the method (peak area vs concentration of matrix matched standard solutions) was evaluated in the range of 0.020−0.50 mg/kg for pyrifenox, 0.040−1.0 mg/kg for pyridaben, and 0.010−0.40 mg/kg for tralomethrin. In all cases, good linearities were achieved over the assessed concentration ranges, with correlation coeffients >0.99, and both the relative standard deviation (RSD) of the mean responses from quadrupiclate injections of standard solutions and the RSD from five-point calibration injections were <12%. LOQs of 0.020 mg/kg for pyrifenox, 0.040 mg/kg for pyridaben, and 0.010 mg/kg for tralomethrin were established. In all cases, the signal-to-noise ratio obtained for these standard solutions was >10.

During the study, a number of quality control recovery tests were conducted on tomato samples previously analyzed and demonstrated not to contain any residues of pyrifenox, pyridaben, or tralomethrin. In total, 13 recovery tests (16 in the case of pyrifenox) were performed on blank tomato samples at spiking levels ranging from 0.022 to 0.54 mg/kg for pyrifenox, from 0.046 to 0.46 mg/kg for pyridaben, and from 0.011 to 0.11 mg/kg for tralomethrin.

RESULTS AND DISCUSSION

Recovery Tests. Mean recovery values and the corresponding RSDs obtained for pyrifenox, pyridaben, and tralomethrin in the recovery tests performed during the study are indicated in **Table 1**. These values can be considered acceptable according to the validation and quality control criteria recently established for pesticide residue analysis (*14*, *15*).

Unprocessed Tomatoes. Figure 3 shows a typical chromatogram of the analysis of an unprocessed tomato sample (II + 1, A) and a control (a blank of tomato). Pyrifenox, pyridaben, and tralomethrin residue levels determined in the unprocessed samples A and unprocessed samples B (which were prepared from the same fruits) were not significantly different according to the paired *t* statistical test. Likewise, the application of this test to both the unprocessed samples A and C and the unprocessed samples B and C demonstrated that the residue levels of the three pesticides in the unprocessed samples prepared from different fruits were also not significantly different.

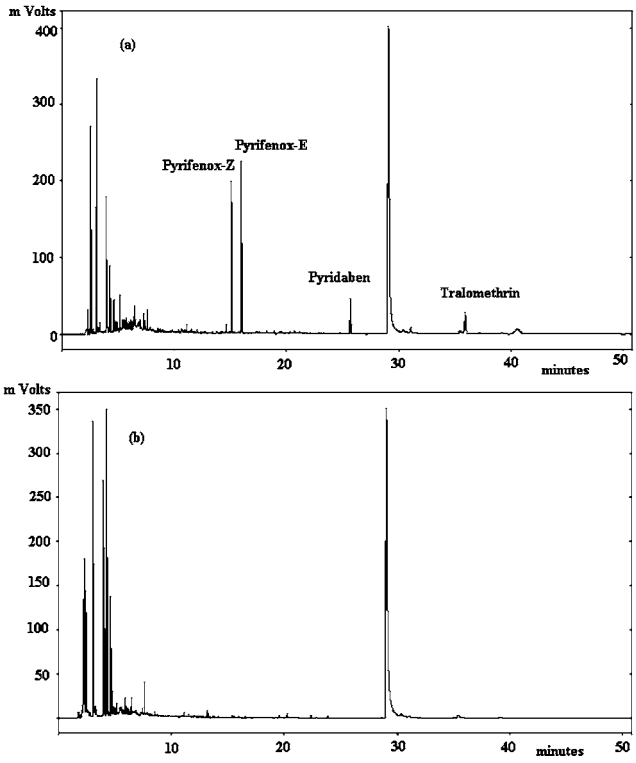

Figure 3. (**a**) Chromatogram of the analysis of the unprocessed sample II + 1; (**b**) chromatogram of the analysis of a blank of tomato.

Table 2. Mean Residue Levels, in mg/kg, and RSDs of Pyrifenox, Pyridaben, and Tralomethrin of the Unprocessed Tomato Samples A–C

	mean (RSD, %)		
sample	pyrifenox	pyridaben	tralomethrin
I + 1	0.073 (12)	0.189 (26)	0.032 (29)
I + 2	0.034 (21)	0.159 (18)	0.018 (17)
I + 3	0.039 (37)	0.282 (15)	0.037 (26)
I + 7	nd[a]	0.315 (17)	0.036 (19)
I + 14	nd	0.254 (19)	nd
I + 21	nd	0.185 (21)	nd
II + 1	0.340 (9)	0.415 (28)	0.123 (28)
II + 2	0.362 (11)	0.639 (22)	0.124 (26)
II + 3	0.107 (43)	0.404 (22)	0.092 (20)
II + 7	0.048 (33)	0.494 (14)	0.118 (27)
II + 14	nd	0.256 (16)	0.085 (27)

[a] Not detected.

As indicated in **Table 2**, residue levels in the tomato plantation (means of unprocessed samples A−C) ranged between not detected (<LOQ) and 0.37 mg/kg for pyrifenox, 0.16 and 0.64 mg/kg for pyridaben, and between not detected (<LOQ) and 0.12 mg/kg for tralomethrin. Pyrifenox residue levels in the tomato plantation were always below the Spanish MRL (0.20 mg/kg), except 1 and 2 days after the treatment with exaggerated application rates. However, pyridaben residue levels in the plantation were always above the Spanish MRL (0.10 mg/kg), including 21 days after the application of the treatment with the recommended application rates, and tralomethrin residue levels only were below the MRL (0.01 mg/kg)

Table 3. Mean Processing Factors and SDs Obtained for Pyrifenox, Pyridaben, and Tralomethrin in Tomatoes

	mean ± SD		
process	pyrifenox	pyridaben	tralomethrin
washing[a]	1.1 ± 0.3	0.9 ± 0.3	1.2 ± 0.5
peeling[a]	0.0 ± 0.0	0.3 ± 0.2	0.0 ± 0.0
cooking[b]	3.0 ± 1.1	2.1 ± 0.8	1.9 ± 0.8

[a] $n = 7$ for pyrifenox, 11 for pyridaben, and 9 for tralomethrin. [b] $n = 14$ for pyrifenox, 22 for pyridaben, and 18 for tralomethrin.

14 and 21 days after the application of treatment I. The results obtained for pyridaben indicate that the Spanish MRL for this pesticide in tomatoes should be revised, at least for greenhouse tomatoes. At this point, it is important to note that the Spanish MRL for pyridaben in peppers is 0.50 mg/kg, and this MRL has been demonstrated to be compatible with the use of this pesticide on peppers grown in a greenhouse (*10*).

Effect of Household Processing on Residue Levels. Processing factors (pesticide level in processed fruits/pesticide level in unprocessed fruits) were determined by applying the methodology above-described (see **Figure 2**) to the 11 greenhouse tomato samples. Washing factors were calculated as the ratio between the pesticide level in the washed sample and the mean value of the pesticide levels in the unprocessed samples A−C, whereas the peeling factors were calulated as the ratio between the pesticide levels in the peeled sample and the unprocessed sample C. Likewise, cooking factors were calculated as the ratio between the pesticide levels in the cooked sample (A or B) and the corresponding unprocessed sample (A or B). The means and standard deviation (SD) values obtained for the processing factors are indicated in **Table 3**.

The mean washing factors calculated for pyrifenox, pyridaben, and tralomethrin in tomatoes were 1.1, 0.9, and 1.2, respectively. Therefore, the application of an intensive washing to the tomatoes does not seem to reduce the residue levels of these three pesticides. These results could be justified by the high K_{ow} (octanol/water partition coefficient) values presented by these three pesticides, which are around 10^4-10^6 (*1*). Because of their high liposolubility, pyrifenox, pyridaben, and tralomethrin can be quickly absorbed and strongly retained by the waxes of the tomato skin, making their elimination by washing negligible. Washing factors of ∼1 can be found in the literature for pyridaben and tralomethrin in peppers (*10*) and for other pesticide/crop combinations (*16*−*20*).

Residues of pyrifenox and tralomethrin were not detected in any of the peeled tomato samples, resulting in peeling factors of zero for these two pesticides. In the opposite, pyridaben residues were determined in all of the peeled samples at levels ranging between 0.065 and 0.17 mg/kg, resulting in a mean peeling factor for pyridaben of 0.3. These results could indicate that pyridaben, despite being a nonsystemic pesticide, enters into the tomato flesh more easily than pyrifenox and tralomethrin, whose residues practically remain in the peel. However, pyridaben levels in the unprocessed samples were much higher than the levels of pyrifenox and tralomethrin, and the small amounts of pyridaben determined in the peeled samples could be in part the result of contamination during the peeling process, such as it has been already reported for other nonsystemic pesticides/fruits combinations (*21*).

The mean cooking factors obtained for pyridaben and tralomethrin in tomatoes were 2.1 and 1.9, respectively. These results indicate that the cooking process applied to the tomatoes does not reduce, significantly, the residue levels of pyridaben and tralomethrin, since the obtained value of ∼2 for the cooking factors is justified by the concentration of the tomato puree in a factor of ∼2 as a consequence of a water loss of ∼50%. Specifically, the water loss determined in the 22 cooked tomato samples was 53.8 ± 8.8%. On the other hand, the mean cooking factor obtained for pyrifenox in tomatoes was 3.0. This unexpected value for the cooking factor could be justified assuming that incurred residues of pyrifenox are more efficiently extracted from the tomato puree after applying the cooking process. Therefore, we can conclude that the household washing or cooking usually applied to the tomatoes does not reduce, significantly, the residue levels of pyrifenox, pyridaben, and tralomethrin and that the amount of residues removed by peeling is ∼70% for pyridaben and ∼100% for pyrifenox and tralomethrin.

Table 4. Residue Variability among Individual Tomatoes and Minimum, Maximum, and Mean Residue Levels, in mg/kg, Obtained in the Analysis of 10 Individual Units of Tomato from Samples I + 1, II + 1, and II + 3

pesticide	sample	min/max values	mean	variability factor[a]
pyrifenox	I + 1	0.030/0.203	0.105	1.9
	II + 1	0.173/0.652	0.496	1.3
	II + 3	nd[b]/0.124	0.055	2.2
pyridaben	I + 1	0.123/0.389	0.263	1.5
	II + 1	0.394/1.038	0.706	1.5
	II + 3	0.151/0.680	0.322	2.1
tralomethrin	I + 1	0.018/0.083	0.047	1.8
	II + 1	0.094/0.297	0.182	1.6
	II + 3	0.027/0.164	0.074	2.2

[a] Max value/mean. [b] Not detected.

Residue Variability among Individual Tomatoes. The minimum, maximum, and mean residue levels of pyrifenox, pyridaben, and tralomethrin determined in the 10 individual units of tomato analyzed from the samples I + 1, II + 1, and II + 3 are reported in **Table 4**. Residues of the three pesticides were determined in all of the tomato units analyzed, except in three tomato units from sample II + 3, in which pyrifenox residues were not detected (in these cases, a residue level of zero was used to calculate the variability factor). The obtained unit-to-unit variability factors, which are also indicated in **Table 4**, ranged from 1.3 to 2.2, with an average of 1.8 for pyrifenox, 1.7 for pyridaben, and 1.9 for tralomethrin. Finally, unit-to unit variability factors obtained in this work are much lower than the variability factor recommended by the World Health Organization (WHO) to be used as a default value for consumer risk assessment (acute exposure through diet) of pesticide residues in tomatoes (*11*). These results are consistent with those obtained by other authors, who have also reported that variability factors estimated for different pesticides in oranges (*22*), potatoes (*23*), or kaki fruits (*21*) were lower than those recommended by the WHO and used by default for risk assessment.

ACKNOWLEDGMENT

We thank Francisco Montoya, from CampoNix, S.L., for collaboration in this work.

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Received for review November 9, 2004. Revised manuscript received February 19, 2005. Accepted February 21, 2005. This study was supported by the Spanish Ministry of Education and Culture (Project AGL2000-1485).

JF040455Y