Residue Levels of Chlorpropham in Individual Tubers and Composite Samples of Postharvest-Treated Potatoes

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Chlorpropham, a herbicide and sprout suppressant, is used on stored potatoes to prolong the storage period without deterioration of produce quality. Data for residue concentrations on an individual tuber basis are required by WHO for the estimation of the variability factor. In this study, the levels of chlorpropham in individual tubers and in composite samples were determined. The distribution of chlorpropham between the peel and the tuber flesh was examined, and the fate during the cooking process (washing, boiling, frying) was studied. The concentrations in individual tubers ranged from 1.8 to 7.6 mg/kg 10 days postapplication (mean 3.8 mg/kg, RSD 39%), from 0.7 to 4.0 mg/kg 28 days postapplication (mean 2.9 mg/kg, RSD 28%), and from 0.8 to 3.8 mg/kg 65 days postapplication (mean 2.2 mg/kg, RSD 48%). The calculated residues in composite samples 10 days postapplication ranged from 4.3 to 6.1 mg/kg (mean 4.9 mg/kg, RSD 20%). Those in samples taken 28 days postapplication ranged from 3.1 to 4.2 mg/kg (mean 3.8 mg/kg, RSD 15%). The concentrations determined in composite samples of whole tubers 65 days postapplication ranged between 2.6 and 3.2 (mean 2.9 mg/kg, RSD 11%). Peeling removed 91−98% of the total residue; washing reduced residues by 33−47%. Detectable residues were found in boiled potatoes and the boiling water, and in french fries and the frying oil. Monitoring data on commercial prefried frozen french fries are reported.

Keywords: *Chlorpropham; residues; potatoes; variability factor; processing*

INTRODUCTION

Potatoes destined for storage require treatments with sprout inhibitors to prolong the storage period without deterioration of produce quality. Chlorpropham (CIPC) (Figure 1) is a residual phenylcarbamate herbicide and plant growth regulator used as a sprouting inhibitor for stored potatoes (*1*). It is formulated under several formulation types (granular, hot fogging solution, dust powder, etc). In Greece, only the dust powder (DP) formulation is registered. Data on the magnitude of residues on treated raw commodities are necessary for the establishment of maximum residue limits (MRLs). Consumption of potatoes is high, and, given that potatoes are consumed only as a cooked product, data on the fate of residues during the cooking process are important for the calculation of transfer factors, for the estimation of real residue intake, and for risk assessment. MRLs are based on composite samples, in which a number of individual commodity units are homogenized and the analysis is carried out on the mixed sample. Thus, they do not entirely reflect the variation in residue levels between the individual units. With recent attention being focused on the potential for acute exposure through diet, the possible risk associated with high residues in individual units has been highlighted (*2*). Since significant variation can occur in the residue levels in individual units comprising a single composite sample (*3*, *4*), the variability of residue concentration in bulk produce should be taken into consideration for the best estimate of intake. This is particularly important for cases when the cooking process leaves the commodity in the same form of individual consumable units (e.g., boiling of potatoes). Given that three or less potato tubers may comprise a large portion, potatoes are included in the WHO list of commodities for which residue data on an individual commodity basis are necessary for the estimation of the variability coefficient (variability factor) *v* to be used in risk assessment estimates (*2*). In this study, the levels of chlorpropham in individual tubers and in composite potato samples after post-harvest treatment were determined and the distribution and the fate of its residues during the potato cooking process were studied. Coxon and Filmer (*5*) showed that chlorpropham is the predominant residue on postharvest-treated potatoes; thus, in this study, the analysis was targeted only toward parent chlorpropham. Chlorpropham has not yet been cleared toxicologically by the FAO/WHO JMPR (joint meeting for pesticide residues), and an ADI (acceptable daily intake) has not yet been established. The Scientific Committee for Pesticides of the Commission of the European Union has reviewed in 1995 the toxicology of this compound and suggested a temporary ADI of 0.1

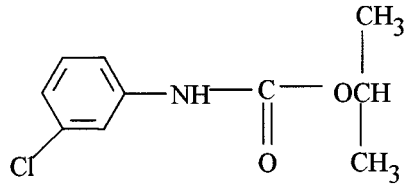

Figure 1. Chemical structure of chlorpropham (CIPC), isopropyl 3-chlorocarbanilate (IUPAC), 1-methylethyl (3-chlorophenyl) carbamate (CA).

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mg/kg b.w., based on a NOEL (no observable effect level) of 50 mg/kg b.w./day and a 500-fold safety factor, pending review of a complete up-to-date database to be generated (*6*). Maximum chlorpropham residue concentrations tolerated in several countries range between 0.5 mg/kg (for peeled potatoes in Italy) to 5 mg/kg (for washed or brushed potatoes in Belgium, Germany, The Netherlands, Spain), and 50 mg/kg (raw potatoes in the USA).

MATERIALS AND METHODS

Application and Storage. The commercial product NEOSTOP containing 1% w/w chlorpropham formulated as Dust Powder (DP) was used, manufactured by Chimac Agriphar S. A. Belgique. For the experiment, 230 untreated tubers of the Lizetta variety were used, analyzed before treatment, and found to be free from chlorpropham residues. The total weight of these tubers was 50 kg, and the estimated average weight of each tuber was 217 g. A number of tubers were weighed at several stages of the study, and data on the actual weight of each tuber are given in Table 2. The application mode, the application rate, and all the label instructions were very closely followed. First, the quantity of product to be used was estimated, taking into account the application rate recommended (1 kg of formulated material/tonne of potatoes, equivalent to 0.01 kg of active substance/tonne). After weighing of the amount needed, the exact quantity of chlorpropham was transferred into a container supplied by the manufacturer of the product, a kind of salt barrel. Two cartons (30 × 40 × 60 cm) were prepared by spreading a plastic sheet on the bottom, and applying a thin layer of product. The tubers were packed into the boxes in layers, and chlorpropham was applied on each layer. Then, the tubers were covered with a plastic sheet and were stored in a refrigerator at 5 °C in the dark for 65 days (recommended minimum time period between application and consumption of potatoes 28 days). Some tubers were left untreated to be used as controls for the preparation of fortified samples.

Samplings. Ten days after application of the chlorpropham the plastic sheet was removed, as recommended, and the first sampling was carried out. Eighty tubers in total were randomly taken from the two cartons and were subjected to the following procedures:

(i) 16 tubers were analyzed individually as whole raw potatoes.

(ii) 16 tubers were divided into three composite subsamples, consisting of 5 or 6 tubers and were handwashed individually under running cold tap water for 20 s. Each subsample was homogenized and analyzed as whole washed tubers.

(iii) 16 tubers were divided into three subsamples of 5 or 6 tubers and were peeled with a kitchen knife, in the way the peeling is usually carried out by consumers. The thickness of the peel removed in that way ranged between 4.0 and 8.5 mm (average 6.4 mm). The weights of the flesh and of the peel of each sample were recorded. The analysis was carried out on flesh and peel separately. The concentration in whole unwashed tubers was estimated taking into account the concentration in the flesh and the peel, and the respective weights.

(iv) 16 tubers were divided into three subsamples and were washed, peeled, and cut into pieces for french fries. The weights of the peel and the flesh were recorded. Each subsample was fried in a friteuse containing 3 L of prewarmed soybean oil for 15 min. The weight of fries after cooking was taken. The fries, as well as the oil, were analyzed.

(v) 16 tubers were divided into three subsamples, then washed and boiled for 15 min in a pressure kettle, containing 1 L of hot water. The weight of each subsample was recorded before and after boiling. (The above methods of cooking were chosen since they are among the most common cooking methods used around the world, and, also, these products are highly consumed by children).

The same procedures were repeated 28 days postapplication, and, in addition, three more composite samples were taken consisting of 5 tubers and analyzed as whole raw potatoes. The latter sampling procedure was repeated 65 days postapplication.

Method of Analysis. *Extraction and Cleanup. Potatoes (Whole, Flesh, Peel, French Fries, and Boiled).* For the extraction of chlorpropham residues, the extraction step of a multiresidue GLC with ECD detection method was used (*7*) slightly modified as to the sample size and solvent volumes used. Briefly, 25 g of chopped potatoes were homogenized with 25 mL of propan-2-ol and 50 mL of toluene for 3 min. After filtration through glass wool, the extract was purified twice by liquid−liquid partitioning with 125 mL of 2% Na_2SO_4 aqueous solution. The organic layer was dried over anhydrous sodium sulfate and directly injected into a gas chromatograph. The second cleanup step of the original method (use of an adsorbent mixture containing activated carbon and Celite) was omitted, since it was found to result in very low recoveries, apparently due to the retention of the compound by the adsorbents.

Frying Oil. The method routinely used in our laboratory for the determination of organochlorine and synthetic pyrethroid insecticides in olive oil was applied. This method consists of extraction of pesticide residues with *n*-hexane saturated with acetonitrile; a first cleanup by liquid−liquid partitioning with acetonitrile saturated with *n*-hexane and deionized water; and a further cleanup by solid-phase extraction (SFE) on Sep-Pak alumina N cartridges (method to be published). For NPD detection (see GLC determination), the SPE extraction cleanup step was omitted.

Boiling Water. Five hundred milliliters of water were extracted twice with 100 mL each time of *n*-hexane. The organic phase was concentrated to a volume that resulted in a residue concentration approximating that of the working standard solutions. The concentrated extract was filtered over filter paper containing anhydrous sodium sulfate and injected into the gas chromatograph.

GLC Determination. A Hewlett-Packard 5890 Plus series II gas chromatograph was used fitted with ECD operating at 290° C, a Hewlett-Packard 7673 autosampler, and a split-splitless injector operating in the splitless mode (60 s, 1 μL) at 170 °C. This relatively low injection-port temperature, as compared to that routinely used in our laboratory (250 °C), was found to be ideal, since at higher inlet temperatures the detector response was not reproducible, presumably due to decomposition of chlorpropham in the injector liner. The carrier gas was helium (110 kPa, 1.21 mL/min) and the makeup was nitrogen (30 mL/min). The column employed was Rtx-50 (50% diphenyl/50% dimethylpolysiloxane stationary phase, 30 m × 0.250 mm I. D., 0.25 μm film thickness). The following oven temperature program was used: Initial 80 °C hold 1 min; 15 °C/min to 190 °C; 3 °C/min to 260 °C, hold 3 min. Under these conditions, the retention time for chlorpropham was 13.35 min. The quantification was carried out using calibration curves of at least 3 calibration points of standards made up in toluene from an analytical standard of 99% purity. It was found that the linearity was excellent ($R^2 > 0.99$) over a wide range of concentrations (from 0.01 to 0.2; from 0.02 to 0.5 or to 1; from 0.05 and 0.2 to 1; and from 1 to 10 mg/kg). The lowest calibrated level, LCL (*8*) was estimated to be 0.02 mg/kg for potatoes, 0.06 mg/kg for oil, and 0.03 mg/L for water.

At a later stage, a new gas chromatograph (VARIAN 3600 CX equipped with TSD) was introduced in the laboratory and was used. The operating conditions were detector TSD operated at 300 °C, 8200 CX autosampler, and a temperature programmable injector in the splitless mode with initial temperature 140 °C and final temperature 250 °C, rate 100 °C/min, hold for 42.4 min. The carrier gas was helium (1.1 mL/min), and the make up gas was nitrogen. The column was a nonpolar Rtx-1 (100% dimethylpolysiloxane), and the following oven temperature program was used: Initial 75 °C, hold for 2 min; 12 °C/min to 170 °C hold for 2 min; 1.5 °C/min to 200 °C hold for 1 min; 15 °C/min to 260 °C hold for 6.59 min. Under these conditions, chlorpropham could be determined with sufficient sensitivity and reproducibility. The retention time

Table 1. Recoveries of Chlorpropham from Potatoes and Liquid Media

substrate	fortification level (mg/kg)	percent recovery[a]		%RSD[b]	
		ECD	TSD	ECD	TSD
whole fresh tubers	5	81	95	7	12
	1	85	94	8	15
	0.5	85	102	6	12
	0.25	73	85	10	10
	0.2	75	94	15	6
	0.05	80	120	10	8
peel	5	101	110	4	5
french fries	1	81	99	6	20
	0.5	90	93	9	9
	0.06	95	110	10	15
frying oil	1	81	86[c]	6	3
	0.5	90	87[c]	9	7
	0.06	95	104	10	5
boiling water	2	98	120	6	10
	1	85	100	10	7
	0.5	95	110	9	10
	0.03	93	101	13	10

[a] Mean of 3−6 replicate samples analyzed in duplicate. [b] Relative standard deviation. [c] Without SPE cleanup.

was 12.97 min. Fortified samples were run, and the quantification was carried out using calibration curves of 5 calibration points of standards made up in toluene at concentrations ranging between 0.1 and 2 mg/kg. Again the linearity was excellent ($R^2 > 0.99$). However, the recoveries, as compared to those obtained for the same samples using Hewlett-Packard/ECD, were generally higher (Table 1). The same was also observed for samples with incurred residues (prefried frozen potatoes from the supermarkets) (Table 4). This can be attributed to a possible matrix effect under the chromatographic conditions of the VARIAN chromatograph.

The above methods of analysis and chromatographic conditions gave satisfactory recoveries and repeatability, as shown in Table 1.

RESULTS AND DISCUSSION

The residues in individual raw tubers ranged from 1.8 to 7.6 mg/kg in the first sampling (mean 3.8 mg/kg, RSD 39%), from 0.7 to 4.0 mg/kg in the second sampling (mean 2.9 mg/kg, RSD 28%), and from 0.8 to 3.8 mg/kg in the third sampling (mean 2.2 mg/kg, RSD 48%) (Table 2). The residue concentrations in composite samples of whole raw potatoes taken 10 days postapplication (calculated from the concentrations determined in flesh and peel and the weight of samples) ranged from 6.1 to 4.3 mg/kg, with an average of 4.9 mg/kg and RSD 20% (Table 3). These values are lower than the expected concentration at the time of application calculated on the basis of the application rate (10 mg/kg), suggesting that a great part of the product applied is not retained by the tubers. The concentrations calculated in composite samples taken 28 postapplication ranged between 3.1 and 4.2 mg/kg (average 3.8 mg/kg, RSD 15%), while the concentrations determined by analysis of whole tubers was of the order of 3.2 mg/kg. The concentrations determined in composite samples of whole tubers taken 65 days postapplication ranged between 2.6 and 3.2 (mean 2.9 mg/kg, RSD 11%).

From the data set of Table 2, a variability factor v of up to 2 is estimated as the ratio of the highest residue levels found in individual tubers to the corresponding residue levels seen in the composite samples (*2*). This value is considerably lower than the variability coefficients recommended by WHO to be used as default values for the estimation of consumer exposure (5 for crops with large-sized units weighting >250 g and 10 for crops with medium-sized units weighting 25−250 g (*2*). It is also lower than the factor of 7, considered by JMPR as a more realistic value for medium-sized units (*9*). Comparison of the concentration levels in the individual tubers with the average concentrations in the composite samples, shows that some individual tubers contained higher residues than the average value (7.6 and 5.6 mg/kg, first sampling; 3.4, 3.6, 3.3, 3.3, 4.0, and 4.1 mg/kg, second sampling; 3.1, 3.8, 3.8, and 3.6 mg/kg, third sampling (Table 2). Regression analysis of the data of Table 2 shows that there is no correlation between the weight of tubers and residue concentration ($p < 0.05$). This may be attributed to the formulation type (DP) and the application mode. Washing, in the way it was performed, reduced residue concentrations by 33% on average (first sampling) or 47% (second sampling) (Table 3). Tsumura-Hasegawa et al. (*10*) found that a more rigorous washing (shaking 3 times for 1 min at 120 shakes/min in beakers containing 5 times the weight of sample of distilled water) removed 88% of chlorpropham from potatoes (cultivar not known) treated with an emulsified solution of chlorpropham 0.1% applied at the rate of 50 mL of spraying solution per 87 kg of potatoes. The highest quantity of chemical was associated with the peels that contained, on average, 33.9 and 26.0 mg/kg (first and second sampling, respectively) (Table 2). Thus, the amounts of chlorpropham removed by peeling were 98% and 91% from the first and second sampling, respectively. These results are consistent with earlier findings: Coxon and Filmer (*5*) using ^{14}C or ^{36}Cl radiolabeled chlorpropham found that little penetration of chlorpropham beyond the peel layer occurred even after 6 months of storage and that the compound remains mainly in the outer layers of treated tubers. Camire et al. (*11*) also found that peels of Russet Burbank potatoes, gassed with chlorpropham in storage using a proprietary-commercial scale technique, contained 33 mg/kg of chlorpropham on average. Lewis et al. (*12*) also concluded that chlorpropham residues remain on the tuber surface because of its nonsystemic nature and are affected directly by the removal of the surface layers during processing.

Table 2. Residues of Chlorpropham in Individual Potato Tubers

	interval between application and sampling (days)					
	10		28		65	
tuber no	weight (kg)	conc (mg/kg)	weight (kg)	conc (mg/kg)	weight (kg)	conc (mg/kg)
1	0.29	4.0	0.35	2.4	0.18	0.8
2	0.35	3.0	0.26	0.7	0.19	1.7
3	0.25	1.9	0.30	2.5	0.26	1.7
4	0.35	1.8	0.21	2.7	0.16	0.8
5	0.24	2.7	0.50	3.1	0.19	1.2
6	0.19	4.1	0.26	2.9	0.21	1.2
7	0.27	7.6	0.27	3.4	0.15	2.5
8	0.30	2.2	0.21	3.6	0.23	2.3
9	0.22	4.1	0.17	3.3	0.23	3.1
10	0.19	4.7	0.21	3.3	0.17	3.8
11	0.15	3.7	0.20	3.1	0.21	3.8
12	0.16	3.5	0.24	2.7	0.19	2.5
13	0.14	4.1	0.16	3.2	0.12	3.6
14	0.17	4.4	0.13	4.0	0.18	1.4
15	0.16	3.1	0.12	2.1	0.14	2.8
16	0.10	5.6	0.14	4.1	-	-
mean	0.22	3.8	0.23	2.9	0.19	2.2
RSD%	34	39	41	28	20	48
median	0.22	3.8	0.21	3.1	0.19	2.25

The residues in the fried potatoes ranged from 0.06 to 0.34 mg/kg (mean 0.2 mg/kg) (first sampling) and

Table 3. Results[a] of Chlorpropham in Potatoes (Composite Samples), Processed Products, and Liquid Media

	interval between application and samplings (days)					
	10		28		65	
product	mg/kg	%RSD	mg/kg	%RSD	mg/kg	%RSD
unwashed whole potatoes	4.9[b]	20	3.8[b]	15	2.9[c]	11
			3.2[c]	80		
unwashed flesh	0.3	30	0.1	22		
unwashed skin	33.9	21	26.0	14		
washed whole potatoes	3.3	46	2.9	16		
french fries from washed, peeled potatoes	0.2	88	0.05	10		
boiled whole potatoes (washed, unpeeled)	0.3	35	0.2	7		
frying oil	0.2	38	0.1	22		
boiling water	0.2	22	0.2	36		

[a] Mean of three samples of 6 or 5 tubers each, analyzed in duplicate. [b] Values calculated from the concentrations determined in flesh and peel and the weight of samples. [c] Determined by analysis of three samples of whole potatoes of 5 tubers each.

Table 4. Monitoring Data of Chlorpropham in Frozen Prefried Fries

		concentration detected (mg/kg)	
year	origin	ECD	TSD
1998	Turkey	0.94	NA[a]
		0.57	NA[a]
		2.60	NA[a]
		0.80	NA[a]
	unknown	0.13	NA[a]
		1	NA[a]
1999	France	0.45	NA[a]
		0.54	NA[a]
		0.84	NA[a]
		ND[b]	NA[a]
		0.76	1.05
		ND[b]	NA[a]
		0.43	0.52
	Holland	0.62	NA[a]
		0.34	0.41
		0.01	0.05
	Belgium	0.09	NA[a]
		0.50	NA[a]
	Poland	ND[b]	NA[a]
		ND[b]	NA[a]
		ND[b]	NA[a]
	unknown	2	2.7
		ND[b]	NA[a]
		0.94	1.2
		1.1	1.4
		0.05	NA[a]
		ND[b]	NA[a]
		1.6	NA[a]
		0.1	NA[a]
		ND[b]	NA[a]
		0.83	1.25
		ND[b]	NA[a]
		ND[b]	NA[a]
		ND[b]	NA[a]
		ND[b]	NA[a]
		0.36	
		0.65	1.1

[a] Not analyzed. [b] Not detectable.

were of the order of 0.05 mg/kg in the second sampling (Table 3). The weight of the sample after drying was reduced by 54−65%. The residues found in the oil ranged from 0.1 to 0.3 mg/kg (mean 0.2 mg/kg) (first sampling) and were of the order of 0.1 mg/kg (second sampling). However, a balance of the amount of chemical present before and after processing cannot be established, since the exact concentration in the raw material (washed, peeled, and cut potatoes) was not exactly known, and extrapolation from the concentration in washed flesh in other samples may be misleading. Boiling of potatoes did not reduce the weight of samples significantly. The residues in the whole, washed, and boiled tubers ranged between 0.2 and 0.4 mg/kg (first sampling) and between 0.2 and 0.3 mg/kg (mean 0.3 mg/kg) (second sampling). The residues recovered in the boiling water were on the order of 0.1−0.2 mg/L (first sampling) or 0.1−0.2 mg/L (second sampling). Again, the balance cannot be determined for the same above reasons.

The fact that detectable residues remain in the processed potato products is confirmed by the results of monitoring carried out in other countries (*13*) and by our laboratory, as shown in Table 4. Chlorpropham was also detected at concentrations of the order of 2−3 mg/kg in fresh (raw) potatoes of cultivar Rosetta imported from Egypt and destined for industrial processing.

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