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^{14}C-Dimethoate Residues in Tomatoes and Tomato Products

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Dimethoate *(o,o,*-dimethyl *S*-methylcarbamoylmethyl, phosphorodithioate) is a systemic organophosphorus insecticide recommended for the control of a wide variety of pests on crops as well as for housefly control. It is effective at 300-700 g a.i./ha by contact, and systemic action against a broad range of Acari, Aphididae, Aleyrodidae, Coccoidea, Coleoptera, Collembola, Diptera, Lepidoptera, Pseudococcoidae and Thysanoptera in cereals, citrus, coffee, cotton, fruits grapes, pastures, tea, tobacco and vegetables. This insecticide is a cholinesterase inhibitor with toxicity of acute oral (rat) LD_{50} 291-325 mg a.i./kg. Acceptable daily intake (ADI) for dimethoate is 0.01 mg/kg body weight in human (Worthing and Hance 1991; Steller et al. 1972).

Frank et al. (1991) have worked on residues of some pesticides in raw and processed tomatoes. They have explained results of residue analyses for parent compound and their metabolites in raw and tomato juice, between day 0 and day 8 following field application. At the spraying rate of 335 a.i. g ha^{-1}, 0.002 mg kg^{-1} of dimethoate residue was found in both raw fruit and juice at the harvesting time of 1 day and 6 day after spraying. Whereas after the 3 days application, raw fruit and juice included 0.002 mg kg^{-1} and 0.005 mg kg^{-1} dimethoate, respectively. As to omethoate residues, fruit and juice included 0.002 mg kg^{-1} at the all harvesting time.

Tomato is important vegetable in Turkey. According to 2001 statistics, it has an annual production of 8 425 000 ton (Anonymous 2001). The maximum residue level (MRL) for dimethoate is established in tomato as a 0.02 mg/kg, and 1 mg/kg, by the European Union Directive (02/71/C), and Codex Alimentarius, respectively (Anonymous 2003; Anonymous 1999).

The purpose of this study reported here was to determine the level and nature of ^{14}C-dimethoate residues in tomatoes and tomato products and to investigate the effect of food processing on dimethoate residue by radiotracer technique.

MATERIALS AND METHODS

^{14}C-Dimethoate *(o, o,* -dimethyl *S*-methylcarbomylmethyl, phosphorodithioate) was supplied by IZINTA Isotope Trading Enterprise, Budapest. The chemical had a specific activity of 185 MBq $mmol^{-1}$ and radiochemical purity was over 99%.

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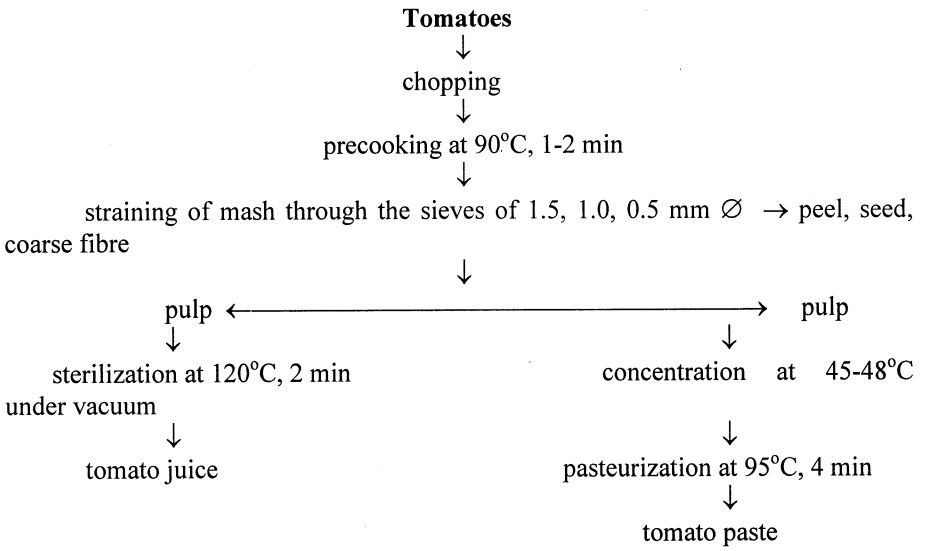

Figure 1. Schematic diagram of tomato processing.

Commercial cold dimethoate was IZGOR. Scintillation cocktails were *Insta Gel* (Packard, 6013004) and *Rotiszint eco plus* (Carl Roth GmbH+Co., Karlsruhe). Merck Kieselgel 60 F-254 (Art. 5715) plates were used for thin layer chromatography.

Tomato plants of Super California variety were grown under the outdoor conditions in galvanized steel boxes which have been described by Kohli et al.(1973). Soil texture was sandy clay.

^{14}C-dimethoate was diluted with nonlabelled dimethoate and then applied to the leaves until run off point with a sprayer two month after transplanting of seedlings to the boxes. Application rate and specific activity were 7.24 μCi dimethoate/plant and 1607 dpm/μg, respectively.

The total rainfall and mean air temperature during the growing season were 69.3 mm and 18.8°C, respectively. Necessary cultural works such as irrigation, fertilization, hoeing were done as in described earlier publications (Aysal et al. 1999). Tomatoes were harvested September and October and stored in a deep-freeze until being analyzed.

Harvested tomatoes belonging to the same harvesting season were combined as in industrial process and sub-samples in a certain amount (~500 g) were processed into juice, and paste as shown in Figure 1.

To determine total dimethoate residues in the tomato and its processing product, samples were combusted in a Harvey Biological Oxidizer, OX-600. Combustion products were trapped in external traps which contain trapping solution. $^{14}CO_2$

released by combustion were analyzed in 1550 Tri-Carb Liquid Scintillation Analyzer (Anonymous 1991).

In order to determine the effect of food processing on the residue, food processing factor and concentration constants of the residue in tomato products were calculated to evaluate of the results in respect to acceptable daily intake (Anonymous 1994 ; Tiryaki et al. 1995 and Aysal et al. 1999).

Dimethoate and related residues were extracted from tomatoes, tomato juices, and pastes with cold methanol. Extracts were concentrated and then chromatographed on silica gel F_{254} (Merck) chromatoplates by using benzene+acetone (2:1 v/v) developing solvent system to characterize the radioactive residues. Spots were visualized by exposure to UV lamp (λ=254 nm). Rf values of dimethoate and its metabolite omethoate were 0.46 ± 0,06 and 0,13 ± 0,02 respectively. For radio scanning, the material in these zones was scrapped off the plate to scintillation vial and added *Rotiszint* scintillation cocktail for liquid scintillation counting (L'Annunziata 1979).

The samples were also subjected to supercritical fluid extraction (SFE). Schematic diagram of the SFE is explained by Tiryaki and Aysal (2000). The solvent (methanol) was compressed by the HPLC pump (Waters 600 E) up to 2200 psi, passed through preheated capillary in to the extraction vessel which includes samples to be extracted. Preheating of the capillary and tomato sample was carried out in a gas chromatograph oven maintained at 250°C and purged continuously nitrogen to avoid formation of an explosive mixture of air-organic solvent (methanol). The extracts were passed through the cooler and then through the regulating valve, finally collected in a 100 ml measuring cylinder with a flow rate of 1 ml/min. Small amount of extract was subjected to LSC for determining radioactivity. The remainder of extract was concentrated for thin layer chromatographic (TLC) analysis.

RESULTS AND DISCUSSION

The amount of total ^{14}C-residues in tomato and tomato products harvested at mid and late seasons were shown in Table 1. Total dimethoate related residues in tomatoes harvested at mid and late season were determined 0.49 and 0.45 ppm, respectively. These residue levels in tomatoes were above European Union maximum residue limits (0.02 ppm), but below the Codex Alimentarius Commission limits (1 ppm).

The distribution of dimethoate related residues in the tomato juice and tomato paste is also shown in Table 1. Tomato paste contained relatively higher residues, since tomato pulp is intended to concentrate 3-4 times during paste production. At the mid season harvesting time, it was observed that 2.12 ppm and 0.49 ppm residue in the paste and juice, respectively. Extractable residues in tomatoes ranged between 83.9-90.6 %, of the total residue, 83.0-89.8 % in tomato juices, and 50.0-49.3 % in tomato pastes (Table 1).

Table 1. Total and extractable residues in tomatoes and tomato products.

Sample		Total residue		Extractable residue		
		dpm/g	µg/g*	dpm/g	µg/g	%
Tomatoes	mid season	782.61	0.49	656.57	0.41	83.9
	late season	723.11	0.45	655.34	0.41	90.6
	average	**752.86**	**0.47**	**655.955**	**0.41**	**87.25**
Tomato juice	mid season	793.86	0.49	658.87	0.41	83.0
	late season	766.54	0.48	688.21	0.43	89.8
	average	**780.2**	**0.485**	**673.54**	**0.42**	**86.4**
Tomato paste	mid season	3402.02	2.12	1704.00	1.06	50.0
	late season	2604.95	1.62	1283.00	0.80	49.3
	average	**3003.48**	**1.87**	**1493.5**	**0.93**	**49.65**

*: Residue in sample (µg/g) = radioactivity amount in sample (dpm/g) / specific activity of the application (dpm/µg).

The effect of processing on residue will depend on the residue levels and the method of processing (Table 2). During the processing of harvested tomatoes to juice and paste, total residue losses were in the range of 10.86-15.46 %.

Table 2. Residue losses during processing of tomatoes harvested at mid and late season.

Processing steps	Residue losses, %	
	Mid season	Late season
Tomatoes	0.00	0,00
Precooking	0.68	1.44
Peel, seed,coarse fibre	10.18	12.94
Tomato juice	**10.86***	**14.38***
Pasteurization of paste	0.89	1.08
Tomato paste	**13.75***	**15.46***

*: Total loss in final products.

The data in Table 3 indicate that the effect of food processing on residue distribution were variable. In the processed paste the residues of ^{14}C-dimethoate in juice is higher by 3.96 times than in the raw tomatoes. The food processing retention factor F_r of 0.87 in tomato paste indicates that 87 % of the ^{14}C-dimethoate present in tomato paste is retained after the processing. F_r values have to be divided by the relevant P_e values to obtain overall effect. For example an F_r value of 0.87 for tomato paste indicates 87 % of residue in present paste, but owing to 22 % yield of paste, the concentration of ^{14}C-dimethoate residue in tomato paste is 0.87/0.22 =3.96 times the concentration of ^{14}C-dimethoate in the unprocessed tomato.

The published value for ADI is 0.01 mg/kg body weight day. Maximum permissible intake (MPI) for dimethoate is then calculated as follows:

MPI = ADI x body weight
= 0.01 mg/kg.day x 70 kg
= 0.7 mg/day

In considering them, a 70 kg weight-adult can consume 1.489 kg (0.7/0.47) of tomatoes (MPI/residue amount in raw material) containing 0.47 mg/kg dimethoate residue (average of two season). If the same person uses tomato products instead of that tomatoes, maximum permissible amount (MPA) of products are shown in the last column of Table 3.

Table 3. Food processing retention factor (F_r) and processing efficiency (P_e) for tomato products.

Product		dpm/g	Total activity dpm	Sample amount g	Ret. factor[a] F_r	Proces. efficiency[b] P_e	Conc. constant[c]	MPA[d] kg
Tomato	mid season	782.61	571089	729.72				
	late season	723.11	250150	345.94				
	average							
Tomato juice	mid season	793.86	499465	629.16	0.87	0.86	1.01	
	late season	766.54	232185	302.90	0.93	0.87	1.06	
	average				**0.90**	**0,86**	**1.04**	**1.43**
Tomato paste	mid season	3402.02	485020	142.57	0.85	0.19	4.35	
	late season	2604.95	229669	88.17	0.91	0.25	3.60	
	average				**0.87**	**0.22**	**3.96**	**0.37**

[a] Retention factor, F_r = Total residue amont in product/Total residue amount in raw material.

[b] Processing efficiency, P_e = Total processed amount (g)/Total amount in raw material (g).

[c] Concentration constant = F_r/ P_e

[d] Maximum permissible amount of product =MPI of raw material/Concentration constant; 1.489/3.96 = 0.37

The methanol extracts were chromatographed on thin layers of silica to characterize radioactive residues (Table 4). Most of the radioactivity remained at the spotting line (conjugated residue) with range of 84.42-88.0 in tomato and processed products. Extracts of tomato contained conjugated, omethoate and dimethoate in the percent of 85.47, 6.64 and 7.89 of total residues, respectively. These percentage were 86.80, 9.26 and 3.93 in tomato juice , and 86.81, 8.40 and 4.99 in tomato paste. In order to verify the performance of the entire analytical procedure, spiked tomato were also extracted and then analyzed by TLC. The distribution of the residue was 9.7%, 16.7% and 73.6% as a conjugated, omethoate and dimethoate, respectively.

The tomatoes subjected to SFE, contained residues of conjugated, omethoate and dimethoate in the percent of 23.49, 18.02 and 58.49, respectively (Table 5). The spiked tomato were also SFE extracted and then analyzed by TLC. The distribution of the residue was 13.9 %, 27.7 % and 58.4 % as a conjugated, omethoate and dimethoate, respectively.

Table 4. Thin layer chromatographic analysis of tomato and tomato products after cold extraction.*

Sample		Conjugated residue, %	Omethoate, %	Dimethoate, %
Tomatoes	mid season	85.23	9.49	5.29
	late season	85.72	3.79	10.49
	average	**85.47**	**6.64**	**7.89**
Tomato juice	mid season	85.18	8.99	5.83
	late season	88.43	9.54	2.03
	average	**86.80**	**8.40**	**4.99**
Tomato paste	mid season	84.42	10.26	5.32
	late season	88.80	6.53	4.66
	average	**86.61**	**8.40**	**4.99**
Spiked tomatoes		9.7	16.7	73.6

*Percentage of total residue of the sample.

Table 5. Thin layer chromatographic analysis of tomato samples after supercritical fluid extraction (SFE).*

Sample		Conjugated residue, %	Omethoate,%	Dimethoate,%
Tomatoes	mid season	23.10	28.73	48.18
	late season	23.88	7.32	68.81
	average	**23.49**	**18.02**	**58.49**
Spiked tomatoes		13.9	27.7	58.40

*Percentage of total residue of the sample.

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REFERENCES

Anonymous (1991) Laboratory training manual on the use of nuclear and associated techniques in pesticide research. Technical Report Series No.329, International Atomic Energy Agency, Vienna.

Anonymous (1994) Guidelines for agricultural countermeasures following an accidental release of radionuclides. Technical Report Series No.363, International Atomic Energy Agency, Vienna.

Anonymous (1999) Codex Alimentarius: Pesticide Residues in Food. Maximum Residue Limits. Extraneous Maximum Residue Limits Last updated 2 September 1999. http://apps.fao.org/CodexSystem/pestdes/pest_q-e.htm

Anonymous (2001) T.C. Tarım ve Köyişleri Bakanlığı .Üretim İstatistikleri.Bitkisel Üretim. Sebze Üretimi. Yıllar itibariyle sebze üretimleri (ton). http://www.tarim.gov.tr/arayuz/5/icerik.asp?efl=uretim/istatistikler/istatistikler.htm&curdir=\uretim\istatistikler&fl=uretim_istatistikleri/Bitkisel_uretim/turkiye/tr_sebze_uretimi.htm

Anonymous (2003) European Union MRL's sorted by pesticide directives (02/71/EC), updated 28 October 2003. http://europa.eu.int/comm/food/fs/ph_ps/pest/mrl_pesticides_11-03.xls

Frank R, Braun HE, Ripley BD, Pitblado R (1991) Residues of nine insecticides and two fungicides in raw and processed tomatoes. J Food Prot 54: 41-46

Kohli J, Zarif S, Weisberger I, Klein W, Korte FJ (1973) Fate of aldrin-^{14}C in sugar beets and soil under outdoor conditions. J Agr Food Chem 21:855-857.

Aysal P, Gözek K, Artık N, Tuncbilek AŞ (1999) ^{14}C-Chlorpyrifos residues in tomates and tomato products. Bull Environ Contam Toxicol 62:377-382.

L'Annunziata MF (1979) Radiotracers in agricultural chemistry. Academic Press, London, New York, San Fransisco.

Steller WA, Pasarela NR (1972) Gas-liquid chromatographic method for the determination of Dimethoate and dimethoxon residues in plant and animal tissues. Journal of the AOAC 55: 1281-1287.

Tiryaki O, Gözek K, Yucel U, Ilim M (1995) The effect of food processing on ^{14}C-Trifluralin residues in carrots. Toxicol Environ Chem 53:227-233.

Tiryaki O, Aysal P (2000) Bound pesticides residues in soils and plants, and their determination. Turkish J Nuc Sci 26: 43-62.

Worthing CR, Hance JR (1991) Dimethoate. The pesticide manual, 9 th Edition, British Crop Protection Council, Farnham, Surrey GU9 7PH, UK., p: 294-295.