Original Article

Pesticide Residues in Pre-shipment Agricultural Products Grown in Gunma Prefecture

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Summary

An inspection of pesticide residues in 615 samples of pre-shipment agricultural products (total number of samples tested for individual pesticides, hereinafter referred to as "total number of samples": 50,782) grown in Gunma Prefecture was performed from FY 2003 – 2006. Traces of residues were detected in 154 (25.0%) of the pre-shipment products and in 233 (0.46%) of the total number of samples. None of these products contained pesticide residues exceeding the specified limits set by the Food Sanitation Law, securing the safety of all those products at the pre-shipment stage. However, 10 pesticides that were not registered with the Japanese Ministry of Agriculture, Forestry and Fisheries (non-MAFFregistered pesticides) were detected in 8 types of products and in 16 samples. Records of pesticide purchase and use maintained by relevant farming families showed no history of use of these pesticides in 14 cases (drift: 7 cases; soil contamination: 5 cases; and inadequate machinery/tool washing: 2 cases). In the remaining 2 cases involving minitomatoes, incorrect use of pesticides was evident, as they were confused for tomatoes. A comparison of different categories of agricultural products showed that the pesticide detection rate was highest in fruits, followed by fruit-type, leaf-and-stem, and root vegetables (p < 0.05). (Med Biol 155: 249-260 2011)

Key words: pesticide residues, pre-shipment agricultural products, non-MAFF-registered pesticides, drift

Introduction

With the diversification of diet in recent years, the quantity of imported agricultural products has increased leading to problems such as detection of pesticide residues at levels exceeding the pesticide residue specifications stipulated under the Food Sanitation Law¹⁾ and nationwide use of non-MAFF-registered pesticides. Consumer interest regarding the presence of pesticide residues in foodstuffs has lately increased to a greater extent with the growing apprehension about food safety. Under these circumstances, a positive-list system has been introduced since May 29, 2006 pursuant to the amended Food Sanitation Law, and legal specifications and test methods have been established for approximately 700 types of pesticides.

The "Local Ordinance Concerning Proper Sale, Use and Management of Pesticides in Gunma Prefecture" (hereinafter referred to as the Local Ordinance) was enacted in Gunma Prefecture in the fiscal year (FY) 2002 to prevent the use of non-MAFF-registered pesticides and ensure the proper use of pesticides. Efforts have thus been by an administrative body.

taken to implement the proper use of pesticides with emphasis on the following three approaches: maintenance of records of pesticides used, voluntary inspection, and confirmatory inspection

Gunma Prefecture bilaterally represents the consumer and the producer. As provided for by the Local Ordinance, agricultural products are subject to pre-shipment confirmatory pesticide residue tests to ensure safe supply of agricultural products to consumers. The tests need to be completed within the limited time to allow maximum provision of fresh agricultural products. By using the supercritical fluid extraction (SFE) method, we made it possible to attain test results within 2 days²⁻¹³⁾.

The use of hazardous organic solvents is minimized with SFE compared to conventional extraction with organic solvents, and purification can be omitted because of the scanty amount of interfering substances that are extracted. Thus, SFE has an advantage of lesser analytical time.

Only pre-shipment agricultural products were subjected to inspection in this study. Those products containing pesticide residues prior to the circulation stage were excluded. Therefore, sample products found to contain residues were examined for contamination based on the records of pesticide purchase and use maintained by pesticide users. Actual data of pesticide residue detection obtained in the study were statistically evaluated with respect to categorization of agricultural products with high rates of pesticide detection.

Materials and Methods

1. Food materials

Pursuant to the Local Ordinance, this study aimed to survey locally grown pre-shipment agricultural products obtained at collection centers in Gunma Prefecture from April 2003 to March 2007. This study included 615 samples from 28 pre-shipment agricultural products, as shown in Table 1.

2. Pesticides included in the study

A total of 163 pesticides were investigated, as shown in Table 2. They included 35 organophosphorus compounds, 17 organochlorine compounds, 18 carbamate compounds, 15 pyrethroid compounds, 76 organonitrogen compounds, and 2 other compounds.

3. Pesticides and reagents

(1) Standard pesticide materials

Standard materials for residual pesticide testing, manufactured by Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Kanto Chemical Co., Inc., (Tokyo, Japan), were used.

(2) Organic solvents

Solvents for residual pesticide testing were used for extraction and purification, and solvents for liquid chromatography/mass spectrometry (LC/ MS) were used as mobile phases.

(3) Others

ENVI-Carb/NH₂ (500 mg/500 mg) cartridges

Table 1. The List of Investigated Samples	Samples	investigated	List of	The	Table 1.	Τ
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Domestic (615)
[Fruits(96)] Apple(28), Japanese apricot(27), Japanese pear(31), Plum(10)
[Leaf and stem vegetables(242)] Cabbage(30), Chinese cabbage(20), Garland chrysanthemum(20),
Komatsuna(20), Lettuce(19), Qing geng cai(19), Spinach(30), Udo(10), Brocoli(17), Nira(19),
Negi(38)
[Fruits vegetables(195)] Cucumber(30), Eggplant(30), Green soybeans(10), Strawberry(40), Tomato
(39), Sweetcoon(10), Kodamasuika(10), Suika(10), Minitomato(16)

[Root vegetables(82)] Edible burdock(20), Root of Japanese radish(22), Konnnyakuimo(20), Yamato imo(20) manufactured by Supelco GmbH (Sigma, St. Louis, MO, USA) were used for mini-column purification.

4. Instruments

(1) GC/MS: Model 5973N (Agilent Technologies,

Table 2. The List of Pesticides Tested

Organophosphorus pesticides (35)

[Insecticide] acephate, cadusafos, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, cyanophos(CYAP), diazinon, dichlorvos(DDVP), dimethoate, dimethylvinphos, disulfoton, EPN, ethoprophos, etrimfos, fenitrothion(MEP), fensulfothion, fosthiazate, isofenphos, isoxathion, malathion, methamidophos, methidathion, monocrotophos, phenthoate, phosalone, pirimiphos-methyl, prothiofos, pyraclofos, quinalphos, terbufos, thiometon, vamidothion

[Fungicide] edifenphos(EDDP), tolchlophos-methyl

[Herbicide] butamifos

Organochlorine pesticides (17)

[Insecticide] α -BHC, β -BHC, γ -BHC, δ -BHC, o,p'-DDT, p,p'-DDD, p,p' -DDE, aldrin, chlorobenzilate, dieldrin, dicofol, endrin

[Fungicide] captan, HCB, procymidone, quintozene(PCNB)

Carbamate pesticides (18)

[Insecticide] aldicarb, bendiocarb, benfuracarb, carbaryl(NAC), carbosulfan, ethiofencarb, fenobucarb(BPMC), isoprocarb(MIPC), methomyl, methiocarb, oxamyl, pirimicarb, propoxur(PHC), XMC

[Herbicide] chlorpropham(CIPC), esprocarb, pyributicarb, thiobencarb

Pyrethroid pesticides (15)

[Insecticide] acrinathrin, bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, etofenprox, fenpropathrin, fenvalerate, flucythrinate, fluvalinate, halfenprox, permethrin, silafluofen, tefluthrin

Organonitrogen pesticides (76)

- [Insecticide] acetamiprid, chlorfluazuron, chromafenozide, clofentezine, clothianidin, diflubenzuron, fenpyroximate, fipronil, flufenoxuron, imidacloprid, lufenuron, methoxyfenozide, pyridaben, pyrimidifen, pyriproxyfen, quinomethionat, tebufenozide, tebufenpyrad, teflubenzuron
- [Fungicide] azoxystrobin, bitertanol, carpropamid, cyazofamid, cymoxanil, cyproconazole, cyprodinil, dichlofluanid, diethofencarb, difenoconazole, dimethomorph, famoxadone, fenarimol, fenhexamid, ferimzone, fluazinam, flusilazole, flusulfamide, flutolanil, hexaconazole, imazalil, iprodione, mepronil, metalaxyl, myclobutanil, oxadixyl, penconazole, pencycuron, propiconazole, pyrifenox, tebuconazole, tetraconazole, thiabendazole(TBZ), thifluzamide, triadimefon, triadimenol, trifloxystrobin, triflumizole
- [Herbicide] alachlor, cafenstrole, diflufenican, dimethametryn, lenacil, linuron, mefenacet, metolachlor, naproanilide, napropamide, pendimethalin, prometryn, propanil, pyributicarb, simazine, simetryn, terbacil, trifluralin

[Plant growth regulator] paclobutrazol

Other	pesticides	(2)
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(Herbicide) benfuresate

[Plant growth regulator] dimethipin

- (2) GC/FPD: Model GC2010 (Shimadzu Corp., Kyoto, Japan)
- (3) LC/MS/MS: Model AP12000 (Applied Biosystems, Inc., Foster City CA, USA)

(4) Extractor: SFE apparatus Model SFX 220(ISCO Inc., Lincoln, NE, USA)

5. Measurement conditions

- (1) GC/MS conditions
 - (i) GC section: Model 6890 (Agilent Technologies, Inc.)
 - (ii) MS section: Model 5973N (Agilent Technologies, Inc.)
 - (iii) Column: DB-XLB
 - (iv) Column temperature: 80-300°C; initial time, 1 min at 80°C; rise, 20°C/min to 140°C -0 min; rise, 4°C/min to 200°C -0 min; and rise, 8°C/min to 300°C -5 min
- (2) GC/FPD conditions
 - (i) Column: DB-210 (Internal diameter: 0.53 mm, length: 15 m, membrane thickness: 1 μ m)
 - (ii) Column temperature: 100 -240°C; initial time, 1 min at 100°C; rise, 10°C/min to 240°C -10 min
 - (iii) Injection port temperature: 220°C
 - (iv) Injection volume: 1.0 μ 1
 - (v) Detector temperature: $250^{\circ}C$
 - (vi) Carrier gas: Helium
- (3) LC/MS/MS conditions
 - (i) HPLC pump: Model 1100 (Agilent Technologies, Inc.)
 - (ii) MS section: Model AP12000 (Applied Biosystems, Inc.)
 - (iii) Column: Ascentis C18 or Zorbax Eclipse XDB -C18
- (4) SFE extraction conditions
 - (i) Extraction vessel: Polymer cartridge 10 ml
 - (ii) Extraction vessel oven temperature: 50°C
 - (iii) Pressure: 2500 psi
 - (iv) CO₂ density: 0.749 g/ml
 - (v) CO_2 flow rate: 3 -4 ml/min

6. Methods

Pesticide components were extracted from the samples by SFE²⁻¹³⁾, followed by dissolution in acetone and subsequent concentration. These components were then quantified, according to the procedures described previously¹⁴), by gas chromatography (GC) with a flame photometric detector (GC/FPD), GC with mass spectrometry (GC/MS), and liquid chromatography with tandem mass spectrometry (LC/MS/MS). When the results of the analysis suggested a possible violation of Food Sanitation Law specifications or when non-MAFF-registered pesticide components were detected, confirmatory tests were conducted using the test methods described in a previous report¹⁴).

The analytical values were considered acceptable when the recovery rates were between 70% and 120% and the relative standard deviations were within 20%. The lower limit of quantification was set at 0.005 μ g/g.

7. Statistical analysis

Statistical comparisons among groups of agricultural products were performed using Fisher's χ^2 test. The SPSS software package (version 10.0, SPSS Inc., Chicago, IL) was used for the statistical analysis. A p value of <0.05 was considered statistically significant.

Results and Discussion

1. Pre-shipment inspection of agricultural products for residual pesticides

Table 3 shows the pesticide detection status of pre-shipment agricultural products tested during the period FY 2003 -2006. Of the 615 samples tested, 154 (25.0%) contained pesticide residues exceeding the lower limits of quantification, and 233 (0.45%) of the 50,782 samples tested for individual pesticides contained detectable pesticides. However, the levels of the pesticides detected were extremely low and none of the tested products contained pesticide residues exceeding

Table3. Detected pesticides of domestic agricultural products

	-	samples		pestici	de		No. of	Detected	Casmatui	
Groups	Commodity	Total number	detected a)	Total of tested number	detected b)	Detected pesticide	No. of positive	Detected value(mg/kg)	Geometri mean	
							Iprodione	3	0.006~0.04	0.017
						Chlorpyrifos	13	0.009~0.08	0.017	
						Silafluofen	4	0.017~0.14	0.041	
	Apple	28	20	2,664	31	Tebufenpyrad	1	0.01	0.01	
	rippie	20	20	2,004	51	Trifloxystrobin	7	0.01~0.18	0.042	
						Bifenthrin	1	0.01	0.01	
						Flufenoxuron	1	0.03	0.03	
						Prothiofos	1	0.06	0.06	
						Carbaryl	6	0.017~0.23	0.045	
						Acetamiprid	2	0.011,0.011	0.011	
						Iprodione	4	0.02~0.111	0.041	
						Chlorpyrifos	3	0.01	0.01	
						Clothianidin	1	0.017	0.017	
						Difenoconazole	3	0.007~0.02	0.015	
Fruits	Japanese pear	31	19	2,678	28	Cypermethrin	3	0.04~0.099	0.058	
i i uito	sapanese pear	51	17	2,070	20	Diflubenzuron	1	0.04 0.099	0.007	
						Methomyl	1	0.007	0.016	
						Fenvalerate			0.018	
							1	0.09	-	
						Fenitrothion	1	0.029	0.029	
						Flufenoxuron	1	0.027	0.027	
						Fluvalinate	1	0.01	0.01	
						Iprodione	4	0.08~0.45	0.139	
	Plum	10	4	990	6	Chlorpyrifos	1	0.02	0.02	
						Difenoconazole *	1	0.01	0.01	
	Japanese apricot		9	2,307	11	Iprodione	2	0.019,0.031	0.024	
		27				Difenoconazole	7	0.009~0.17	0.041	
						Bitertanol	1	0.03	0.03	
						Fenitrothion	1	0.03	0.03	
	Subtotal	96	52	8,639	76					
	Udo	10	0	1,270	0					
	040	10	0	1,270	0	Acephate	5	0.009~0.09	0.037	
	Cabbage					Oxadixyl	2	0.00 0.00	0.014	
						Tefluthrin	1		0.014	
			11	2 700	10			0.015		
		30	11	2,700	19	Tolchlophos-methyl	1	0.006	0.006	
						Procymidone	6	0.011~0.027	0.017	
						Metalaxyl	1	0.015	0.015	
						Methamidophos	3	0.03	0.03	
		20	5	1,500		Cyazofamid	1	0.03	0.03	
						Cypermethrin	3	0.096~0.15	0.113	
					,500 9	Tefluthrin	1	0.01	0.01	
	Komatsuna					Procymidone *	2	0.007,0.008	0.007	
						Fosthiazate *	1	0.008	0.008	
						Metalaxyl	1	0.00	0.000	
						Oxadixyl	2	0.007, 0.071	0.01	
T C 1										
Leaf and stem	Garland		-			Trifluralin *	2	0.02,0.04	0.028	
vegetables	chrysanthemum	20	6	2,020	8	Fenitrothion	1	0.01	0.01	
						Fenpyroximate *	1	0.007	0.007	
						Fosthiazate *	2	0.005,0.021	0.01	
						Acetamiprid	2	0.018,0.094	0.041	
	Qing geng cai	19	4	1,368	5	Flufenoxuron	1	0.08	0.08	
	Quing geing cai	19	4	1,308	3	Procymidone *	1	0.007	0.007	
						Fosthiazate *	1	0.01	0.01	
	Nira	19	0	1,180	0		İ			
				,		EPN	2	0.02,0.04	0.028	
	Negi	38	4	2,496	4	Cypermethrin	1	0.02(0.04	0.028	
	1,051	50	- T	2,770		Permethrin	1	0.010	0.010	
						Acephate	1	0.01	0.01	
						Iprodione	3	0.006~0.011	0.009	
	Chinese cabbage	20	6	1,830	9	T C	1 1	0.005	0.005	
	Chinese cabbage	20	6	1,830	9	Etofenprox	1	0.005	0.005	
	Chinese cabbage	20	6	1,830	9	Fenvalerate	3	0.005	0.003	

		samples		pesticide				Detected	Gaamatria
Groups	Commodity	Total number	detected ^{a)}	Total of tested number	detected b)	Detected pesticide	No. of positive	Detected value(mg/kg)	Geometric mean
	Brocoli	17	1	939	1	Chromafenozide	1	0.01	0.01
						Imidacloprid	3	0.005~0.59	0.042
	Spinach	30	6	2,590	7	Clothianidin *	1	0.01	0.01
TCL	Spinach	50	0	2,390	/	Cyazofamid	1	0.17	0.17
Leaf and stem vegetables						Cypermethrin	2	0.03,0.13	0.062
vegetables						Iprodione	2	0.01,0.016	0.013
	Lettuce	19	4	1,346	4	Fenvalerate	1	0.01	0.01
						Procymidone	1	0.03	0.03
	Subtotal	242	47	19,239	66				
						Acetamiprid	6	0.01~0.81	0.076
						Azoxystrobin	4	0.006~0.097	0.028
						Acrinathrin	2	0.012,0.088	0.032
						Dicofol	1	0.06	0.06
						Tetraconazole	2	0.014,0.019	0.016
						Tebufenpyrad	4	0.011~0.146	0.044
						Triflumizole	3	0.02~0.48	0.122
	Strawberry	40	18	3,140	37	Bitertanol	3	0.018~0.154	0.038
	Suawberry	40	10	5,140	51	Pyridaben	1	0.018-0.134	0.038
						Fenarimol	1		
						Procymidone	1	0.11	0.11
						Fosthiazate	1	0.012	0.012
						Myclobutanil	6	0.012~0.211	0.049
						Metalaxyl	1	0.02	0.02
						Lufenuron	1	0.02	0.02
	Green soybeans	10	1	420	1	Tebufenpyrad *	1	0.043	0.043
						Acrinathrin	1	0.03	0.03
				2,510		Acetamiprid	2	0.006,0.028	0.013
					15	Clothianidin	1	0.01	0.01
	Cucumber					Cymoxanil	1	0.008	0.008
Emite		30	10			Methomyl *	1	0.013	0.013
Fruits vegetables		50	10			Triflumizole	1	0.023	0.023
regenieres						Flufenoxuron	1	0.006	0.006
						Procymidone	1	0.12	0.12
						Fosthiazate	3	0.006~0.007	0.006
						Metalaxyl	3	0.005~0.017	0.009
	Kodamasuika	10	0	500	0				
	Sweetcorn	10	0	1,450	0				
	Suika	10		1,510	6	Acetamiprid	3	0.009~0.018	0.012
			5			Iprodione	2	0.008,0.014	0.011
						Oxadixyl	1	0.008	0.008
		1				Acetamiprid	2	0.015,0.026	0.02
						Azoxystrobin	1	0.049	0.049
						Iprodione	2	0.016, 0.38	0.078
	Tomato	39	9	3,276	17	Diethofencarb	7	0.015~0.21	0.041
					- '	Pyridaben	2	0.006,0.006	0.006
						Procymidone	1	0.12	0.12
						Metalaxyl	2	0.01,0.04	0.02
		1				Cyazofamid	1	0.01(0.04	0.02
	Eggplant	30	3	2,750	3	Triflumizole	2	0.015,0.019	0.007
		1				Captan *	1	0.013\0.019	0.017
	Minitomato	16	6 2	1,000	2	Quinomethionat *	1	0.2	0.2
	Subtotal	195	48	16,556	81	Zumomennonai	1	0.1	0.1
	Edible burdock	20	40	1,850	1	Fosthiazate	1	0.006	0.006
		20	1	1	1	Metalaxyl	1	0.008	0.008
	Konnnyakuimo	20	1	1,310	1		2		
Root	Root of		-	2 100		Oxamyl		0.011,0.018	0.014
vegetables	Japanese radish	22	5	2,108	8	Disulfoton	4	0.006~0.026	0.01
	37 .			1.005		Fosthiazate	2	0.05,0.051	0.05
	Yamanoimo	20	0	1,080	0				
	Subtotal	82	7	6,348	10				
	Fotal	615	154	50,782	233		233		

a) Number of Samples in which pesticide was detectedb) Total number of pesticide detected in commodity※ non-MAFF-registered pesticide

the pesticide residue specifications stipulated under the Food Sanitation Law.

(1) Pesticide detection rates according to agricultural product category

The pesticide detection rate according to agricultural product category was highest in fruits, followed by fruit-type vegetables, leaf-and-stem vegetables, and root vegetables (4 types) in order, with significant inter-category differences (p < 0.05).

When compared with previously reported data concerning domestic agricultural products¹⁴, the pesticide detection rate for fruits among the preshipment agricultural products was significantly higher that that previously reported for fruits among domestic agricultural products (p < 0.01).

The detection rate for products in pre-shipment stage was higher than that for those in the distribution stage due to their shorter periods after exposure to pesticides.

(2) Detection of pesticides according to agricultural product category

Nineteen types of pesticides were detected in fruits, the most frequent being chlorpyrifos, followed by iprodione, difenoconazole, trifloxystrobin, and silafluofen in order. Twentythree pesticides were detected in leaf-and-stem vegetables, the most frequent being procymidone, followed by acephate and cypermethrin, iprodione, oxadixyl, fosthiazate, and fenvalerate in order. Twenty-six pesticides were detected in fruit-type vegetables, the most frequent being acetamiprid, followed by diethofencarb, triflumizole, metalaxyl, myclobutanil, and azoxystrobin in order. Four pesticides were detected in root vegetables, and the most frequent being disulfoton followed by fosthiazate and others.

Overall, the fungicide iprodione was most frequently detected in pre-shipment agricultural products, followed by chlorpyrifos and acetamiprid (insecticides), procymidone (fungicide), and difenoconazole (fungicide).

When compared with previously reported data concerning domestic agricultural products¹⁴. fungicides tended to be relatively more frequent among the pesticide categories detected in pre-shipment agricultural products, whereas insecticides were considerably more frequently detected in previously reported domestic fungicides agricultural products. Generally, applied to kill microorganisms pathogenic to plants are used when vegetables are prone to contract a plant disease due to elevated humidity in plastic hothouses or due to long spells of rainy weather. The relatively frequent detection of fungicides in pre-shipment agricultural products during this study might be attributed to the fact that a considerable proportion of agricultural products tested were those grown in vinyl plastic hothouses. (3) Detection of non-MAFF-registered pesticides

The present results showed that none of the tested samples violated the Food Sanitation Law, but 10 non-MAFF-registered pesticides were detected in 16 samples among 8 agricultural product categories (Table 4).

Among the agricultural products tested positive for pesticide detection, garland chrysanthemum reported positive for pesticide detection the maximum number of times (detected in 5 samples) followed by komatsuna (detected in 3 samples), and qing geng cai and minitomato (detected in 2 samples each). Of the non-MAFF-registered pesticides, the most frequently detected was the insecticide fosthiazate in 4 samples, followed by the fungicide procymidone in 3 samples, and the herbicide trifluralin in 2 samples. Akiyama et al.¹⁵⁾ also documented a case of methomyl, a non-MAFF-registered insecticide, detected in unripe kidney beans as a case indicative of improper use of pesticides.

2. Sources of non-MAFF-registered pesticides

Table 5 shows the results of an investigation, based on pesticide category, exploring the causes

that led to the detection of non-MAFF-registered pesticide components in this study, on the basis of records of pesticide purchase and usage maintained by the users.

The most frequently detected non-MAFFregistered pesticide was fosthiazate (insecticide), followed by procymidone (fungicide), trifluralin (herbicide), and others. The most frequently estimated cause for detecting pesticides in preshipment products was drift (7 samples, 44%), followed by possible soil residues (5 samples, 31.3%), inadequate washing of farm machinery/ tools (2 samples, 12.5%), and misuse (2 samples, 12.5%).

Groups	Commodity	non-MAFF- registered pesticides Detected		Sources
Fruits	Plum	Difenoconazole	1	Drift
	V	Procymidone	2	Drift
	Komatsuna	Fosthiazate	1	soil contamination
		Trifluralin	2	Drift
Leaf and stem	Garland chrysanthemum	Fenpyroximate	1	inadequate machinery/tool washing
vegetables		Fosthiazate	2	soil contamination
	Qing geng cai	Procymidone	1	soil contamination
		Fosthiazate	1	soil contamination
	Spinach	Clothianidin	1	Drift
	Green soybeans	Tebufenpyrad	1	Drift
Fruits vegetables	Cucumber	Methomyl	1	inadequate machinery/tool washing
	Minida marta	Captan	1	incorrect use
	Minitomato	Quinomethionat	1	incorrect use
	Total		16	

Table 4. Detection of non-MAFF-registered pesticides

Table 5.	Sources	of non-MA	FF-registered	pesticides
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					Sources	
No	non-MAFF- registrred pesticide	Detected	Drift	soil contamination	inadequate machinery /tool washing	incorrect use
1	Captan	1				1
2	Clothianidin	1	1			
3	Difenoconazole	1	1			
4	Fenpyroximate	1			1	
5	Fosthiazate	4		4		
6	Methomyl	1			1	
7	Procymidone	3	2	1		
8	Quinomethionat	1				1
9	Tebufenpyrad	1	1			
10	Trifluralin	2	2			
	Total	16	7	5	2	2

Procymidone and trifluralin were detected in 2 samples each, and the cause was speculated to be drift. Soil residues were suspected to be the cause for detecting fosthiazate in 4 samples, accounting for 80% of those suspected to be due to soil residues. Carron et al.¹⁶⁾ discussed the aspect of drift, voicing concern about environmental pollution based on near-field air concentration of pesticides as a function of distance from the measurement site and time elapse after pesticide spraying. White et al.¹⁷⁾ also discussed drift with concerns about the influence of pesticides on environmental pollution based on farm and nonfarm ambient air pesticide concentrations. These studies do not necessarily consider the detection of non-MAFF-registered pesticide components in agricultural products as major, which is currently an issue in Japan, but raise a question about their effects on the environment, particularly about the influence on wild animals. Schampheleire et al.¹⁸⁾ have reported major factors contributing to drift based on the evaporation of active pesticide ingredients. Procymidone, among others detected in the present study, can be used on cucumbers, tomatoes, and eggplants even until the day before shipping. Therefore, adjustments with neighboring farming families enabling mutually concerted cooperation are essential.

Regarding pesticide residues in soil, Giannakou et al.¹⁹⁾ and Tsiropoulos et al.²⁰⁾ discussed the efficacy of fosthiazate and other agents as soil nematocides based on their characteristic of remaining in the soil, whereas Bedos et al.²¹⁾ demonstrated that incorporating pesticides into the soil resulted in a reduction in the ambient pesticide concentration based on its volatilizing effect by measuring the pesticide half-life in soil. Sakai et al.²²⁾ proposed that dieldrin pollution in soil can be estimated by measuring the organic carbon quantity.

Captan and quinomethionat became unusable for minitomatoes because of legally required separate registration of agricultural products and the definition that tomatoes no more than 3 cm in diameter are not included in the tomato category pursuant to the 2002 amendment to the Agricultural Chemicals Regulation Law. Thorough guidance of farming families needs to be recognized.

Good Agricultural Practice (GAP) is already an effective means to secure safety of agricultural products and conserve the environment by improving the quality of agricultural products and ensuring labor safety. A report has documented the effectiveness of GAP implementation which requires an explanation to be provided to consumers and food workers regarding field activities to be practiced to ensure agricultural product safety and quality, planning of farming operations from the viewpoint of quality assurance as well, and keeping records of operations and confirmed outcome thereof²³). Pre-marketing tests/ inspections of pre-shipment agricultural products are considered to yield effective and efficient results for GAP implementation.

Furthermore, the mutually concerted cooperation among farming families is of importance to ensure smooth negotiations, which are inevitable, between neighboring farming families.

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References

- Kondo T.: Countermeasure of the pesticide residue of frozen spinach from China. Food Sanit Res 53(1): 23-26, 2003 (in Japanese)
- 2) Valverde A., Aguilera A., et al.: Evaluation

of a multiresidue method for pesticides in cereals using supercritical fluid extraction and gas chromatographic detection. J Environ Sci Health, Part B. **44:** 204-213, 2009

- Lang Q., Wai C.M.: Supercritical fluid extraction in herbal and natural studies - A practical review. Talanta 53: 771-782, 2001
- Aguilera A., Rodriguez M., et al.: Evaluation of supercritical fluid extraction/aminopropyl solid-phase "in-line" cleanup for analysis of pesticides residues in rice. J Agric Food Chem, 53: 9374-9382, 2005
- Motohashi N., Nagashima H., et al.: Supercritical fluid extraction for the analysis of pesticides residues in miscellaneous samples. J Biochem Biophys Methods 43: 313-28, 2000
- Anastassiades M., Schwack W.: Analysis of carbendazim, benomyl, thiophanate methyl and 2,4-dichlorophenoxyacetic acid in fruits and vegetables after supercritical fluid extraction. J Chromatogr A. 825: 45-54, 1998
- Lehotay S.J.: Supercritical fluid extraction of pesticides in food. J Chromatogr A 785: 289-312, 1997
- Eller K.L., Lehotay S.J.: Evaluation of hydromatrix and magnesium sulfate drying agents for supercritical fluid extraction of multiple pesticides in produce. Analyst 122: 429-35, 1997
- 9) Lehotay S.J., Valverde-Garcia A.: Evaluation of different solid-phase traps for automated collection and clean-up in the analysis of multiple pesticides in fruits and vegetables after supercritical fluid extraction. J Chromatogr A 765: 69-84, 1997
- Lehotay S.J., Eller K.I.: Development of a method of analysis for 46 pesticides in fruits and vegetables by supercritical fluid extraction and gas chromatography/ion trap mass spectrometry. J AOAC Int 78: 821-830, 1995

- Lehotay S.J., Ibrahim M.A.: Supercritical fluid extraction and gas chromatography/ion trap mass spectrometry of pentachloronitrobenzene pesticides in vegetables. J AOAC Int 78: 445-452, 1995
- Ono Y., Yamagami T.: Pesticide multiresidue analysis of 303 compounds using supercritical fluid extraction. Analytical Sciences 22: 1473-1476, 2006
- Camel V.: Recent extraction techniques for solid matrices-supercritical fluid extraction, pressurized fluid extraction and microwaveassisted extraction: their potential and pitfalls. Analyst 126: 1182-1193, 2001
- 14) Funada K., Takei F., et al.: Pesticide residues in commercially distributed agricultural products in Gunma Prefecture. Medicine and Biology 154(9): 402-413, 2010
- Akiyama Y., Yoshioka N., et al.: Study of pesticide residues in agricultural products towards the "Positive List" system. J Food Hyg Soc Jpn 46(6): 305-318, 2005 (in Japanese)
- 16) Garron C. A., Davis K. C., et al.: Near-field air concentration of pesticides in potato agriculture in Prince Edward Island. Pest Manag Sci 65: 688-695, 2009
- White L. M., Ernst W. R., et al.: Ambient air concentration of pesticides used in potato cultivation in Prince Edward Island, Canada. Pest Manag Sci 62: 126-136, 2009
- Schampheleire M. D.E., Nuyttens D., et al.: Evaporation drift of pesticides active ingredients. Comm Appl Biol Sci Ghent University 73: 739-742, 2008
- Giannakou I. O., Karpouzas D.G., et al.: Factors affecting the efficacy of nonfumigant nematicides for controlling rootknot nematodes. Pest Manag Sci 61: 961-972, 2005
- 20) Tsiropoulos N. G., Likas D. T., et al.: Liquid chromatographic determination of fosthiazate

residues in environmental samples and application of the method to a fosthiazate field dissipation study. J AOAC Int **88:** 1827-1833, 2005

- 21) Bedos C., Rousseau-Djabri M. F., et al.: Measurement of trifluralin volatilization in the field: relation to soil residue and effect of soil incorporation. Environmental Pollution 144: 958-966, 2006
- 22) Sakai M., Seike N., et al.: Relationship between dieldrin uptake in cucumber and solvent-extractable residue in soil. J Agric

Food Chem 57: 11261-11266, 2009

23) Morita K.: Production process control measure for food safety in the field-GAP-.
Food Sanit Res 59(5): 35-40, 2009 (in Japanese)

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群馬県内で生産された出荷前農産物の残留農薬実態

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要旨

2003 年度から 2006 年度に、出荷前農産物 615 検体(農薬別延べ検体:以下延べ検体: 50,782)の残留農薬検査を実施した。その結果、出荷前農産物の 154 検体(25.0%)、延 べ検体の 233 検体(0.46%)から極めて微量の農薬が検出された。すべての農産物にお いて、食品衛生法に定められた残留基準を超えるものはなく、出荷前の段階での安全 性が確保された。しかし、8 種類の農産物から農薬取締法での登録が適用されていない 農薬(以下、登録適用外農薬)の 10 種類が、延べ 16 検体から検出された。この検出 された 16 事例について、適用外農薬の検出原因について、生産農家の農薬購入履歴や 農薬使用記録等を全国に先駆け調査したところ、このうち 14 事例(ドリフト:7 事例、 土壌汚染:5 事例、器具の洗浄不足:2 事例)で農薬使用履歴がなった。一方、誤使用 の 2 事例のミニトマトについては、トマトとして使用したものであった。また、農産 物の分類別農薬検出状況について、果実類>果菜類>葉茎菜類>根菜類の順で高く、そ れぞれの分類間で有意差が認められた(p<0.05)。

キーワード:残留農薬、出荷前農産物、登録適用外農薬、ドリフト

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