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Monitoring and Risk Assessment of Pesticide Residues in Vegetables among the Resident of Seoul, Korea

서울 지역 유통 채소류의 잔류농약 모니터링과 위해도 평가

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ABSRACT

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This study was carried out to assess the exposure to pesticide residues from vegetable consumption of residents in Seoul using data on pesticide concentration and quantity of vegetables consumed. A total of 34,520 samples of 96 types of vegetable were collected from 2010 to 2014 by the Seoul Metropolitan Government Institute of Health and Environment (SIHE). Accredited multi-residue methods were used to analyze 283 types of pesticide. Among the vegetable samples, 86.1% did not contain any measurable levels of pesticide and 1.4% had residue exceeding the Maximum Residue Limit (MRL). A total of 105 types of pesticide residues were found and 45 residues exceeded the MRL. The most commonly found residues, which accounted for approximately 52% of all pesticide residues detected, were azoxystrobin, dietofencarb, procymidone, cypermethrin, tebufenpyrad. A total of 547 vegetable samples from 37 types of vegetable had residue exceeding the MRL. According to the Korea National Health and Nutrition Examination Survey 2012, the number of the kinds of vegetables consumed by the citizens of Seoul was 74 and the number of the kinds of vegetables analyzed by SIHE was 96. Among them, except 4 type vegetables matched to the vegetables subject to analysis. 99.9% of vegetables were analyzed in terms of the amount of vegetable consumption. From these results, 20 agrochemicals were chosen based on their high level of detection rate and violation of the MRL. The potential health risk associated with exposure to the pesticides through vegetable intake was estimated as a Risk Index (RI, %ADI), proportion of the estimated daily intake (EDI) of pesticide to the acceptable daily intake (ADI). In the citizen of Seoul, the RIs of the mean value and 97.5th percentile were shown to be 0.0~7.4% and 0.4~73.9% respectively. In the citizens of Seoul by age (consumers only), the highest RIs for children (under 6 years) and the elderly (over 65 years) were with chlorotharonil, and the EDIs were 56.0%, 112.5% repectively of its ADI. For adults (19~64 years old) and female, the highest RI was with chlorfenapyr and their EDI reached 118.6%, 119.1% of its ADI. These results show that, despite the high levels of some pesticides, the presence of pesticide residues may not be considered as a serious public health problem.

Key words: exposure, pesticide, MRL, food consumption, EDI, ADI, risk assessment

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Ⅰ. Introduction

Coverage in the media about the health benefits of vegetables and concerns about various adult diseases and cancers that are believed to be caused by the increased consumption of meat have since the 2000s generated greater interest in a vegetarian diet. Also the way that vegetables are eaten has changed markedly. Vegetable wraps, fresh vegetable juice, and uncooked vegetables such as salads have become very popular, while Namul, traditional steamed vegetables in Korea are less preferred than before (Cho, 2003). However, the consumption of fresh vegetables tends to increase exposure to hazardous chemicals because they are consumed without undergoing any cooking process and produced by intensive cultivation systems to maximize production per unit area. As overall health levels improve and national income levels rise, there is a greater demand for environment-friendly agricultural products, yet various pesticides are still being sprayed in order to improve the effectiveness and variety of pest controls (Ahn et al., 2013).

To prevent environmental pollution and the abuse and misuse of pesticides, strict controls have been established on the usage of individual pesticides through guidelines on the safe use of pesticides. Nevertheless a national management scheme survey in 2010 regarding the safety of pesticide residues revealed that 84% of consumers harbored a vague anxiety about pesticides (Woo et al., 2010). The Korea National Health & Nutrition Examination survey (KNHNEs) performed in 2012 showed that the intake of plant based foods by Koreans was 1,082 g/day with vegetable intake 327 g/day, which accounted for the largest proportion along with cereals. Although the acute toxicity of pesticides is very low and only very small amounts are present considering total daily food intake, pesticides are chemical substances that may kill living organisms and chronic toxicity could become a problem as the detection frequency and concentration of pesticides increases (Kim et al., 2009). Production and use changes of pesticides may have an influence on the health of the population, and this requires continuous public awareness about the health issues surrounding the use of agrochemicals (Lee and Woo, 2010). In an effort to establish scientific and systematic criteria, Korea had established MRLs for 440 active substances in accordance with the standards of the Codex Alimentarius and adopted good agricultural practices by 2014.

An exposure assessment of pesticides is important for evaluating any association between pesticides and health effects, and an essential part of pesticide management is the securing of specific information about individual pesticides to prepare an assessment of the health impact on the population for each pesticide (Lee, 2013).

To assess exposure to pesticides, it is useful to have monitoring data collected about pesticide residues at the closest point to food consumption. The Seoul Metropolitan Government Institute of Health and Environment (SIHE) under the Seoul City Government, has monitored pesticide residues in agricultural products since 1992. To ensure the safety of the food supply, Seoul City Government set up two regional offices in the northern and southern areas of the city respectively (Cho et al., 2009). In 2010, Chang presented a paper about the risk assessment of residual pesticides from vegetable intake in Seoul during 2007~2009 (Chang, 2010), but since then there have been many changes in pesticides detected, a tightening or loosening of the MRLs, and an increase in the number of pesticide analyses. This study sought to analyze the pesticide residues in vegetables at markets in Seoul between 2010~2014 and to assess the risk of pesticide residues from the vegetable intake of Seoul citizens by calculating the estimated daily intake (EDI) and acceptable daily intake (ADI) (Jeong et al., 2012). This report is based on data from the office in the southern area of the city, including Garak Market, which has the world's largest annual transaction of agricultural products at 7,500 tons per day.

Ⅱ. Materials and Methods

1. Pesticides Analysis

1.1. Sampling

Sampling was performed by authorized personnel in accordance with the Korean Food Code Guideline. Generally, samples were selected from representative vegetables that form a high proportion of the Korean diet and in which pesticides have been detected commonly, and with frequently found at Garak Market for auction. They were collected from agro-fishery product wholesale markets, big retailers, and department stores in Seoul. The total number of vegetables in 96 species was 34 520 and they were classified a leafy vegetables, stalk and stem vegetables, root and tuber vegetables, and fruiting vegetables (Table.1). Collected samples were preprocessed and used for analysis. The samples were composed of 99.5% domestic and 0.5% imported products.

Table 1.Vegetables group analyzed

Group	Commodity		
Leafy vegetables	amaranth	angelica gigas nakai	angelica decursiva
	bangpungnamul	beet leaves	brassica napus
	butterbur	broccoli	cabbage
	cauliflower	chamnamul	chard
	chicory(leaf)	chwinamul	cirsium setidens
	crown daisy	dacheongchae	day lily
	godlbaggi	gomchwi	hyangnamul
	kale	Kalameris	Korean cabbage
	lettuce(head)	lettuce(leaf)	lollo rosa
	marsh mallow	minicos	mugwort
	mustard green leaf	mustard leaf	new green
	oak leaf	pak choi	palma christi
	parsley	pepper leaf	perilla leaves
	pumpkin young leaf	radicho	radish leaf
	red	rocket	romaine
	rose	saeng chae	shepherd's purse
	shinsuncho	sowthistle	spinach
	ssamchu	sugar loaf	vitamin
	solomon’s seal leaf	wintergrown cabbage	
Stalk and stem vegetables	bamboo shoot	bud of aralia	bracken
	celery	kohlrabi	leek
	sebalnamul	sedum	sweet potato stalk
	taro stem	water dropwort	welsh onion
	wild garlic	wild chive	
Root and tuber vegetables	balloon flower	beet	bonnet bellflower
	burdock	carrot	garlic
	ginger	lotus root	onion
	radish	radish red round	solomon’s seal
	yacon		
Fruiting vegetables	cucumber	eggplant	korean melon
	melon	okra	paprika
	pepper	squash	tomato
	watermelon	sweet pepper	

English names of vegetables were referred by Pesticide MRLs in Food of MFDS (2014, ver.)

Table.1-1 Vegetables group analyzed (Korean version)

분류	품	목	
엽채류	비름나물	당귀잎	전호나물
	방풍나물	비트잎	유채
	머위	브로콜리	양배추
	컬리플라워	참나물	근대
	치커리잎	취나물	곤드레나물
	쑥갓	다청채	원추리
	고들빼기	곰취	향나물
	케일	쑥부쟁이	배추
	양상추	상추	롤라로사
	아욱	미니코스	쑥
	겨자채	갓	뉴그린
	오크잎	청경채	피마자잎
	파슬리	고춧잎	들깻잎
	호박잎	라디치오	무잎(열무 포함)
	레드	로켓트	로메인
	로즈	생채	냉이
	신선초	씀바귀	시금치
	쌈추	슈가로프	비타민
	둥글레잎	엇갈이배추(봄동 포함)	
엽경채류	죽순	두릅	고사리
	셀러리	콜라비	부추
	세발나물	돌나물	고구마 줄기
	토란줄기	미나리	파
	풋마늘	달래	
근채류	고사리	비트(사탕무)	도라지
	우엉	당근	마늘
	생강	연근	양파
	무	순무	둥글레
	야콘		
과채류	오이	가지	참외
	멜론	오크라	파프리카
	고추	애호박	토마토
	수박	피망	

1.2. Reagents

Certified reference standards for all test pesticides were of >98% purity except etrimfos(64.2%), thiometon(44%), and purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), Chemservice (Luxembourg, USA), and Wako(Tokyo, Japan). Stock standard solution were made by dissolving each analytical standard in aceton or methanol for a final concentration of 100mg/L and stored in the dark at -20℃. Working standard solutions were prepared freshly by dilution in the same solvent. For Sample extraction, aceton, hexane, dichlormethane made by Kanto (Tokyo, Japan) and acetonitrile, methanol by J.T. Baker (Phillipsberg, NJ, USA) were used. SPE-Florisil and SPE-NH2 (Agilent, USA) were used for the purification of impurities.

1.3. Sample preparation and purification

The sample size of each vegetable ranged from 1 to 2 kg. A representative portion of the sample was blended by a food processor (Robot Coupe Blixer 5 Plus, USA). Most samples were prepared as unwashed, unpeeled and roughly eliminated soil. The sample extraction procedures were carried out according to the method described in the Korea Food Standards Codex

(2009). A 50g of grinded sample was added with 100ml of acetonitrile extracted with a high speed homogenizer (Omni Macro ES, USA) for 2 min, and filtered into bottle with 10g sodium chloride. The extracts was vigorously shaken and allowed phase separation. The 10ml of acetonitrile layer was transferred into a beaker and evaporated to dryness on a 40℃ bath with a gentle stream of air. The dried extracts was dissolved in 2mL of 20% acetone/hexane and loaded onto a Sep-pak florisil cartridge (1g, 6cc) which washed with 5mL of Hexane and pre-equilibrated 5mL of 20% acetone/hexane. The cartridge was eluted with 7mL of 20% acetone/hexane. The elution was evaporated and dissolved with 2mL of 20% acetone/hexane for GC-μ ECD, GC-NPD, MS (mass spectrometry). For LC, the extract was dissolved in 3.5mL of 1% methanol/dichloro methane loaded onto a Sep-pak NH_2 cartridge (1g, 6ml) peconditioned with 1%methanol/dichloro methane (5mL) and the elution collected twice. The elution was evaporated and dissolved in acetonitrile (2mL). The 2mL of acetonitrile was filtered a 0.2μm nylon micro-disc, each 1mL for LC-DAD and LC-FLD (Cho et al., 2009).A summary of the analysis shown in Figure. 1.

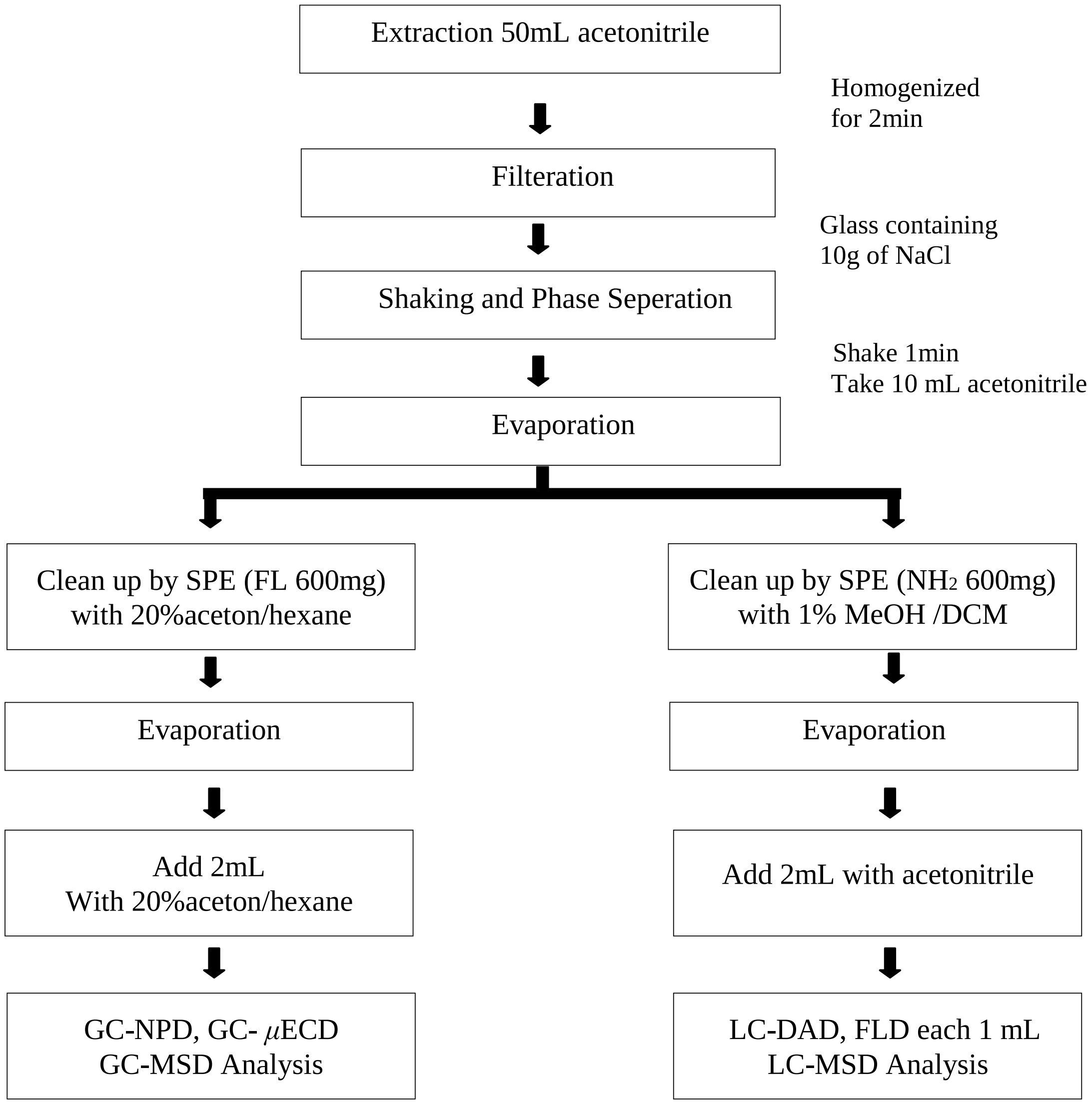

Figure 1. Schematic diagram of GC and LC analysis for multi-pesticide residues.

FL: Florisil catridge, DCM: dichloro methane

1.4. Instrumental analysis

Analysis of 283 pesticides was performed with the simultaneous analysis of multi residual pesticides according to the Korean Food Code. Pesticides detectable by method used in monitoring were classified according to pesticide types. The GC-NPD system for organophosphorus and nitrogen-containing compounds, the GC-μECD system for organochloride, dicarboximide, and pyrethroid compounds (Table 2), LC-FLD (fluorescence detector) system for carbamate pesticides, and the LC-DAD (Diode arrary detector) system for ultraviolet light detected compounds were employed(Table 3). The LC-MSD and GC-MSD system were analyzed to confirm positive findings. GC-MSD (5975C, Triple Axis Detector, Agilent, USA) was operated in electron impact ionization (70eV) scanning from *m/z* 50~550 at 2.91scan /sec. The ion source and quadrupole temperature were 230℃, 150℃ respectively. An Agilent 1200 series LC-MSD (6130, Quadrupole) equipped with MSD for Atmospheric Pressure Chemical Ionization (APCI) was employed. Operation conditions for APCI in positive mode were vaporizer temperature 325℃, nebulizer gas pressure 60psi, drying gas flow 7l/min, Capillary voltage 4000V scan range *m/z* 100~620.(Cho et al, 2009)

Table 2. Pesticides analyzed by GC

Classification	Dectected by GC/NPD			Dectected by GC/μECD		
Insecticide	azinphos-methyl	azinphos-ethyl	bromophos-methyl	acrinathrin	aldrin& dieldrin	BHC
	cadusafos	carbophenothion	chlorfenapyr	bifenthrin	chlordane	cycloprothrin
	chlorpyrifos	chlorpyrifos-methyl	cyanophos	cyfluthrin	cyhalothrin	cypermethrin
	diazinon	dichlorvos(DDVP)	dicrotophos	DDT	deltamethrin	dicofol
	dimethoate	dimethylvinphos	EPN	endosulfan	endrin	fenpropathrin
	ethion	ethoprophos	etrimfos	fenvalerate	fipronil	flonicamid
	fenitrothion	fenthion	fenobucarb	fluvalinate	heptachlor	indoxacarb
	fonofos	fosthiazate	furathiocarb	methoxychlor	nonachlor	permethrin
	isazofos	isofenphos	isofenphos-methyl	pyridalyl	pyrimidifen	quinalphos
	isoxathion	malathion	mecarbam	tefluthrin	tralomethrin	triflumuron
	methidathion	oxydemeton-methyl	parathion			
	parathion-methyl	phenthoate	phosalone			
	phosmet	phosphamidone	pirimicarb			
	pirimiphos-ethyl	pirimiphos-methyl	profenofos			
	prothiofos	pyraclofos	pyridaben			
	sulprofos	tebupirimfos	terbufos			
	tetrachlorvinphos	thiometon	tolfenpyrad			
	triazophos					
Fungicide	azaconazole	bupirimate	chinomethionat	binapacryl	captafol	captan
	cyproconazole	cyprodinil	diethofencarb	chlorothalonil	cyflufenamid	dichlofluanid
	diphenylamine	edifenphos	fenarimol	dicloran	diniconazole	fenamidone
	fluazinam	fludioxonil	flusilazole	fenarimol	fenbuconazole	fenoxanil
	iprobenfos(IBP)	kresoxim-methyl	mepanipyrim	flusulfamid	flutolanil	folpet
	mepronil	metconazole	myclobutanil	fthalide	hexachlorbenzene	imazalil
	oxadixyl	penconazole	pyrazophos	iprodione	isoprothiorane	iprovalicarb
	pyrifenox	simeconazole	triadimefon	metrafenone	nitrapyrin	nitrothal-isopropyl
	triticonazole			nuarimol	ofurace	picoxystrobin
				prochloraz	procymidone	pyrazophos
				quintozene	TCMTB	thifluzamide
				tolclofos-methyl	tolylfluanid	triflumizole
				vinclozolin	zoxamide	
Herbicide	ametryn	anilofos	atrazine	asulam	allidochlor(MS)	bromacil
	bromobutide	dimepiperate	dimethenamid	bromoxynil	butafenacil	chloridazone
	diphenamid	esprocarb	molinate	cinmethylin(MS)	chlorothal-methyl	clomeprop
	pendimethalin	piperophos	propazine	cyanazine	cycloate(MS)	diallate(MS)
	propisochlor	pyriminobac-methyl	terbuthylazine	diflufenican	dimethachlor	flumiclorac-pentyl
	thiazopyr	tribuphos		dithiopyr	fluthiacet-methyl	indanofan
				lactofen	mefenacet	mefenapyr-diethyl
				pebulate(MS)	picolinafen	propachlor(MS)
				propham(MS)	propyzamide	vernolate
Miticide	etoxazole	fenazaquin	fenothiocarb	bromopropylate	chlorobenzilate	tetradifon
	tebufenpyrad					
Growth regulator	paclobutrazole			uniconazole		
Plant activator				probenazole		

Table 3. Pesticides analyzed by HPLC

Classification	Dectected by HPLC/DAD		Dectected by HPLC/FLD	
Insecticide	acetamiprid	azamethiphos(MS)	aldicarb	bendiocarb
	chlorantraniliprole	chlorobenzuron	butocarboxim	carbaryl
	clothianidin	chromafenozide	carbofuran	ethiofencarb
	fenoxycarb	flubendiamide	fenobucarb(BPMC)	isoprocarb
	flufenoxuron	hexaflumuron	methiocarb	methomyl
	lufenuron	methoxyfenozide	metolcarb	oxamyl
	nitenpyram	novaluron	promecarb	propoxur
	pyriproxyfen	tebufenozide	thiodicarb	trimethacarb
	teflubenzuron	thiacloprid		
	thiamethoxam	XMC(MS)		
Fungicide	amisulbrom	azoxystrobin		
	boscalid	cyazofamid[b]		
	cymoxanil	dimethomorph		
	ethaboxam	fenhexamid		
	ferimzone	fluquinconazole		
	imibenconazole	pyraclostrobin		
	pyributicarb	pyrimethanil		
	pyroquilon	thiadinil		
	trifloxystrobin			
Herbicide	bensulide(MS)	cinosulfuron		
	chlorimuron-ethyl	chlorotoluron		
	cyhalofop-butyl	ethametsulfuron-methyl		
	flufenacet	flumioxazine		
	fluridone(MS)	imazamox		
	imazapic	imazethapyr		
	imazaquin	isoproturon		
	metamifop	methabenzthiazuron		
	oxaziclomefone	pentoxazone		
	phenmedipham	pyrazolate		
	pyribenzoxim	pyridate		
	quinoclamine	rimsulfuron		
	thenylchlor	tribenuron-methyl		
Miticide	benzoximate	fenpyroximate		
	fluacrypyrim	spiroclofen		
Growth regulator	forchlorfenuron			

Instrumental analysis conditions are as Table 4~5 and the data analysis was used by Chemstation Software,

Table 4. Analytical conditions of GC/NPD and GC/ μ ECD

Instrument	Agilent 7890A	
Detector	Nitrogen-phosphorus detector	μ Electiomn capture detector
Column	Front: DB-1701 14% cyanopropyl phenyl methyl (30 m×320 ㎛ ID× 0.25 ㎛ film thickness) Back: HP-5 5% phenyl methyl siloxane (30 m×320 ㎛ ID× 0.25 ㎛ film thickness)	
Oven temp.	100℃ (2min)→10℃/min→200℃(1min) →10℃/min→260℃ (9 min)	150℃ (2min)→10℃/min→240℃ (2min) →15℃/min→280℃ (25min)
Injection temp.	210℃	230℃
Detector temp.	320℃	320℃
Gas flow	N_2 (1.5 mL/min) Air (120 mL/min): blos bead H_2 (3 mL/min)	N_2 (1.5mL/min)

Table 5. Analytical conditions of HPLC/FLD and HPLC/DAD

Instrument	Waters e2695			Agilent 1200 series		
Column	Carbamate analysis column (3.9×150 mm)			ZORBAX Eclipse XDB-C18 (5.0 µm, 4.6×150 mm)		
Detector	Fluorescence detector (Excitation λ:340 nm, Emission λ:445 nm)			Diode Array Detector (λ:254 nm, scan λ:190-400 nm)		
Flow rate	1.2mL/min			1.0mL/min		
Column oven	42℃			42℃		
Injection vol.	20 µL			10 µL		
Mobile Phase	A (Water), B (Methanol)			A (Water), B (Methanol)		
	Time(min)	A (%)	B (%)	Time(min)	A (%)	B (%)
	0.00	90	10	0.00	70	30
	1.00	60	40	5.00	50	50
	2.00	50	50	10.00	20	80
	7.00	40	60	15.00	5	95
	8.00	0	100	20.00	0	100
	9.00	0	100	23.00	50	50
	10.00	90	10	25.00	70	30

2. Food Consumption Data

Intake estimates were based on food consumption data from the Korea National Health & Nutrition Examination Survey (KNHNES) performed in 2012 by the Korea Centers for Disease Control and Prevention. The KNHNES examines about 10,000 individuals aged 1 year and over extracted a probability sample of 20 households throughout 192 regions each year. Subject was questioned twice about their consumption of food using a 24 h-recall method. In this study, the data from the survey were presented as the average daily food intake (g/ day) for three sub populations: young children (under 6 years old), adults (19–64 years old), and the elderly (more than 65 years old) and male-female of the citizen of Seoul. Intake estimates were analyzed using the third code of the Nutrition survey(Food intake survey Ⅱ), and the sum of raw material of a vegetable was calculated as a comprehensive amount, for example the intake estimates of Korea cabbage and radish included a sum of the weight of kimchi as well as the weight of the raw material. Also, to take into account the worst-case, the weight of the main raw material, for example Korea cabbage, in kimchi was assumed to be 100%.

3. Method of Risk Assessment

3.1. Estimation of dietary exposure to pesticide residues

The estimates of dietary exposure to pesticides were calculated from the amount of pesticide residues found in vegetables, the daily intake of vegetables by general population, by sex and by age group, and the mean body weight of the each group. According to the US EPA method, if the remaining amount of pesticide residue is not more than the detection limit of the pesticide, it is recommended that the average is applied to the sample by assuming a concentration of one-half the detection limit (EPA, 2007). To estimate pesticide exposure conservatively, samples that had no detectable levels of pesticide were computed as 0 (zero) for the estimation of dietary exposure. Intake of vegetables investigated by KNHNES in each region was assumed to be the average daily intake by group throughout the year. The average weight of the sub populations (by sex and by age) was based on data provided by the Korean Agency for Technology and Standards under the Ministry of Trade Industry and Energy. Using the above data were calculated for each estimated dietary intake(EDI) of pesticide that can be exposed to vegetable consumption based on the average intake of residual pesticides in vegetables.

3.2. Risk characterization

Risk assessments were performed using EDI and ADI. Pesticide exposures per one day were calculated by multiplying the daily vegetable intake and amount of pesticide residues. Then EDI, the daily dosage, was calculated by dividing this by the average weight of consumers. The average weight of an Asian, 55 kg was applied as the average weight in this study. ADI is the standard for risk assessment based on the chronic toxicity of pesticides for humans. The criteria for ADIs were in accordance with those of the Pesticides and Veterinary Drugs Information of KFDA, except that for uniconazole, was referred with those of the Ministry of Health, Labor and Welfare (MHLW) in Japan. Exposures were calculated deterministically and were assumed from the average consumption as well as 97.5th percentile of consumption in the general population and the citizens of Seoul and sub populations for the citizen of Seoul (Claeys et al., 2008).

If RI value was greater than 100, it was considered to be hazardous since it exceeds acceptable daily intakes of pesticides while RI value was less than 100, potential risk can be determined to be low.

4. Method Validation

The validation of the analytical methods was carried out in accordance with KFDA pesticides guidelines. Sample preparation and analytical methods were validated in terms of limits of detection, linearity and recovery. The linearity of the standard curves was injected at concentration 0.01, 0.025, 0.05, 0.1 and 0.2 mg/L, respectively (five replications). The limits of detection (LOD) were measured as analytic concentration based on a signal to noise ratio S/N 3, the limit of quantification (LOQ), S/N 10. Method accuracy and repeatability were evaluated by Recovery test., using pesticide free lettuce. Depending on LOD, blank, pesticides of low levels (0.01, 0.02, 0.2,) high levels (0.1, 0.2, 2,) were conducted by spiking homogenized samples. That was carried out with three replications and expressed as relative standard deviation (RSD %).

Ⅲ. Results

1. Validation of the Method

From 283 agrochemicals, 20 pesticides were chosen based on their detection rate and violation rate of their MRL. The limit of detection (LOD), limit of quantification (LOQ), recovery, coefficient correlation, and MRLs of 20 pesticides for the validation study are presented in Table 6 ~7. The correlation coefficient showed good linearity to 0.9976 ~ 0.9999. The detection limit of the analysis of pesticides was from 0.0006 to 0.024 mg/kg and LOQs ranged between 0.001 and 0.072 mg/kg, which are below the permitted MRLs. The recovery rate was 82.5% to 103.1%, which is within the acceptable recovery range of 70%~120% and the relative standard deviation (RSD) of less than 10% also met requirements. These results confirm that the analytical method used in this study is adequate for monitoring pesticide residues (Cho et al., 2009).

Table 6. Validation parameters**.**

Instrument	Pestcide	LOD(mg/L)	LOQ(mg/L)	recovery	r^2	MRL(mg/L)
GC/ECD	Bifenthrin	0.0006	0.002	82.19±0.5	0.9999	0.05～2.0
	Chlorthalonil	0.0014	0.004	114.8±7.5	0.9996	0.01~7.0
	Cypermethrin	0.0027	0.003	94.1±2.1	0.9990	0.05~20
	Diniconazole	0.0011	0.003	104.1±6.1	0.9984	0.05~1.0
	Endosulfan	0.0026	0.009	92.35±0.1	0.9998	0.05~0.2
	Procymidone	0.0012	0.004	112.32±1.4	0.9987	0.01~10
	Uniconazole*	0.0009	0.003	101.5±4.8	0.9984	ND
GC/NPD	Chlorpyrifos	0.0006	0.002	88.51±2.4	0.9997	0.01~3.0
	Chlorfenapyr	0.0008	0.023	87.92±1.9	0.9999	0.05~20
	Diazinon	0.0004	0.001	90.5±5.7	0.9999	0.01~0.7
	Diethofencarb	0.025	0.074	86.6±1.4	0.9996	0.05~10
	Ethoprophos	0.005	0.014	100.67±5.53	0.9996	0.005~0.02
	Fludioxonil	0.012	0.036	85.22±5.58	0.9996	0.02~20
	Paclobutrazol	0.002	0.061	107.8±2.1	0.9989	0.05~5.0
	Tebufenpyrad	0.011	0.034	98.22±7.99	0.9999	0.05~3.0
HPLC/DAD	Azoxystrobin	0.0008	0.025	106.48±8.87	0.9999	0.05~20
	Boscalid	0.0004	0.013	91.6±0.24	0.9999	0.05~30
	Dimethomorph	0.007	0.022	86.3±1.2	0.9999	0.1~20
	Flubendiamide	0.026	0.072	88.37±2.27	0.9999	0.05~35
	Flufenoxuron	0.024	0.072	76.5±3.62	0.9998	0.05~20

＊MRL is Not Detected but LOD is no less than 0.05mg/kg recommended (by KFDA)

2. Levels of Pesticide Residues on Vegetables

2.1. Detection of pesticide residues on vegetables

Pesticides detected in vegetables exceeded the standards were determined in accordance with the criteria announced by the KFDA for agricultural pesticides. The determination of not MRLs established on its agricultural pesticides detected were applied to Codex standards and this was followed by applying the lowest of the residue limits of the pesticide for a similar agricultural products among Korean MRLs and then by the lowest of the residue limits of the pesticide among Korean MLRs (KFDA).

The number of monitoring samples decreased slightly from 7340 samples in 2010 to 6500 samples in 2014. The largest commodity group was leafy vegetables, which accounted for 78.6% of total vegetables; and the proportions for stalk and stem vegetables, root and tuber vegetables, and fruiting vegetables were 7.6%, 6.0%, and 7.8% respectively. There is a tendency for detection rates to increase because of improvement in analytical instruments such as micro ECD and blos bead NPD. A summary of the frequency of occurrence of 283 pesticides residues and the range of levels in 2010~2014 (Table 7) shows that 105 types of residues were found with 45 pesticide residues exceeding their MRLs. The most commonly found pesticides, which accounted for approximately 51% of the total detected, as seen in Figure 2. The violation rates of MRLs for carbofuran, EPN, etoxazole, fosthiazate, methidathion, and uniconazole were more than 70% while the detection rates were low. The pesticides that exceeded their MRLs most frequently were paclobutrazol, diazinon, chlorpyrifos, endosulfan, and procymidone with violation rates of 13.2%, 10.9%, 8.9%, 7.6%, and 7.1% respectively

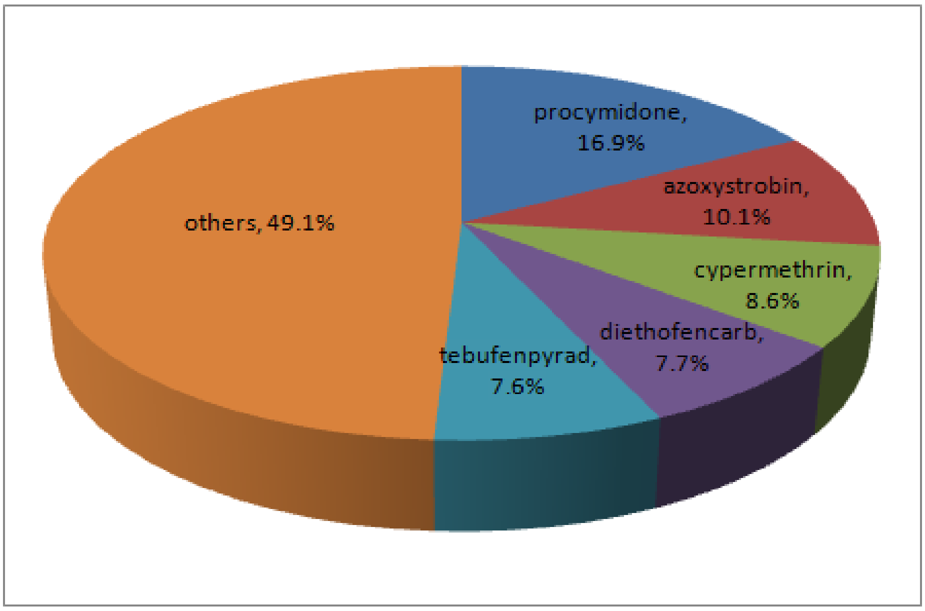

Figure 2. Pesticides with high frequencies of detection for 5 years.

2.2. Distribution of pesticide Residues on vegetables

The 61 types of vegetables contain pesticide residues, and the 547 vegetables of the 37 types exceeded MRLs (Table 8). For vegetables that violated the MRLs for pesticide residues, among leafy vegetables there were 87 cases for mustard green, 74 for perilla leaves, and 47 for chamnamul; among stalk and stem vegetables there were 14 cases for leek, 5 cases for celery, and 5 cases for Welsh onion; among fruiting vegetables there were 7 cases for squash and 1 for pepper; and among root and tuber vegetables there was one case for carrot. The vegetables that recorded the highest proportion of cases of pesticide residues were pepper leaves with 33 of 49 (67.3%), perilla leaves with 2575 out of 6827 (37.7%), chamnamul with 480 out of 1234 (38.9%), parsley with 33 out of 87 (37.9%), and mustard green with 175 out of 636 (27.5%). Leafy vegetables comprised the largest group with pesticide residues because pesticides may easily attach to their broad leafy surface and are less likely to decompose owing to rain, photolysis, or wind from cultivation activities(Hong et al., 2003)

Table 7. Pesticide levels detected in vegetables from 2010 to 2014

Pesticides	Number of detected Residue						Number of detected over MRL						Range(mg/kg)			Frequency Rate of over MRL (%)
	2010	2011	2012	2013	2014	Total	2010	2011	2012	2013	2014	Total				
Acetamiprid	4	2	1	6	6	19	1			2		3	0.35	~	1.183	15.8
Amisulbrom				1	5	6						0	0.27	~	2.461	0.0
Azoxystrobin	120	65	64	112	233	594	4	2	1	2	3	12	0.033	~	40.54	2.0
Bifenthrin	19	19	24	14	31	107		1	2	1	6	10	0.011	~	2.542	9.3
Boscalid	10	17	15	29	39	110	1	4		1	2	8	0.02	~	17.12	7.3
Cabofuran	5	5	2	1		13	4	4	2	1		11	0.038	~	2.94	84.6
Cadusafos	1	1	3	1	5	11	1	1				2	0.006	~	2.801	18.2
Carbendazim[a]	30	43	26			99	5	2				7	0.348	~	11.52	7.1
Chlorantraniliprole		2	4	6	25	37			1			1	0.157	~	2.644	2.7
Chlorfenapyr	42	28	31	20	21	142	1		3		2	6	0.002	~	68.5	4.2
Chlorpyrifos	15	19	9	7	28	78	10	15	4	4	15	48	0.004	~	7.634	61.5
Chlorpyrifosmethyl	1	5	4	1	2	13		2	3	1		6	0.015	~	4.928	46.2
Chlorthalonil	16	12	13	13	26	80	1	1	1	5	1	9	0.009	~	19.77	11.3
Cyazofamid	1			1	2	4						0	0.361	~	1.206	0.0
Cyflufenamid				4	3	7					1	1	0.041	~	0.242	14.3
Cyhalothrin	4	2	15	2	5	28						0	0.014	~	1.24	0.0
Cypermethrin	37	30	63	106	271	507				1	2	3	0.024	~	9.157	0.6
Cyprodinil				3	1	4						0	0.096	~	0.896	0.0
Diazinon	81	36	41	45	42	245	20	7	9	9	14	59	0.004	~	11.26	24.1
Diclufluanid	3	1	1			5						0	0.024	~	2.523	0.0
Diethofencarb	75	92	84	94	108	453	1	3	4	2	4	14	0.013	~	23.39	3.1
Dimetomorph	33	19	17	37	72	178	1	1		2	2	6	0.123	~	17.66	3.4
Diniconazole	22	21	10	20	48	121	6	14	4	5	4	33	0.011	~	10.26	27.3
Endosulfan	73	52	26	5	22	178	19	11	6	1	4	41	0.002	~	7.002	23.0
Ethoprophos	14	5	5	5	13	42		1	2	1	2	6	0.004	~	0.854	14.3

Table 7. Continued

Pesticides	Number of detected Residue						Number of detected over MRL						Range(mg/kg)	Frequency Rate of over MRL (%)
	2010	2011	2012	2013	2014	Total	2010	2011	2012	2013	2014	Total		
Etoxazole	1			1	4	6	1			1	2	4	0.076 ~ 4.165	66.7
Fenarimol	1	7	1	3		12						0	0.075 ~ 0.83	0.0
Fenazaquin	4	1	2	5	6	18	1					1	0.082 ~ 2.09	5.6
Fenitrothion	3		3		3	9			1		1	2	0.021 ~ 5.2	22.2
Boscalid	10	17	15	29	39	110	1	4		1	2	8	0.02 ~ 17.12	7.3
Fenobucarb	1			1	1	3						0	0.124 ~ 0.161	0.0
Fenpropathrin	2		2	4	5	13	1			1		2	0.05 ~ 2.675	15.4
Fenproxymate	3	9	7	13	107	139						0	0.134 ~ 6.196	0.0
Fenvalerate	1	2	3		6	12						0	0.076 ~ 0.441	0.0
Flubendiamide	1	2	5	33	78	119						0	0.135 ~ 12.90	0.0
Fludioxonil	10	20	9	23	17	79		1	1		2	4	0.075 ~ 11.13	5.1
Flufenoxuron	1	4	6	5	31	47			1		7	8	0.112 ~ 1.922	17.0
Flunicamid	1	1		2	7	11					1	1	0.017 ~ 0.119	9.1
Flutolanil	1	4		5	8	18	1	3		2		6	0.066 ~ 3.422	33.3
Hexaconazol[a]	1	1	3			5	1		1			2	0.658 ~ 2.730	40.0
Indoxacarb	2	8	6	21	22	59		1				1	0.088 ~ 9.243	1.7
Imidacloprid[a]	13	7	6			26		1				1	0.138 ~ 1.523	3.8
Iprobenfos	3	2	2	1	1	9	1					1	0.016 ~ 0.087	11.1
Iprodione	3	3	1	3	10	20	1	1			4	6	0.047 ~ 28.88	30.0
Isoprothiolane	4	1	3	1	5	14			1			1	0.007 ~ 9.08	7.1
Kresoximmethyl	10	4	7	4	7	32	6		3	1	2	12	0.04 ~ 27.32	37.5
Lufenuron	1	4	10	6	22	43					1	1	0.153 ~ 2.755	2.3
Metalaxyl[a]	25	6	6			37	1	1				2	0.028 ~ 1.702	5.4
Metaflumizone[a]	1	11	11			23						0	0.028 ~ 3.631	0.0
Methidathion	6	1	1	1	2	11	6	1			1	8	0.007 ~ 3.311	72.7

Table 7. Continued

	Number of detected Residue						Number of detected over MRL						Range(mg/kg)			Frequency Rate of over MRL (%)
Pesticides	2010	2011	2012	2013	2014	Total	2010	2011	2012	2013	2014	Total				
Paclobutrazol	29	16	4	16	22	87	25	13	3	12	18	71	0.016	~	5.977	81.6
Pencycuron	8	5	1			14	3	5				8	0.054	~	4.89	57.1
Pendimethalin	3		2	1	3	9						0	0.059	~	0.306	0.0
Phenthoate	4	1	2	6	4	17	1			3	4	8	0.01	~	4.038	47.1
Primicarb	6	1				7						0	0.033	~	0.192	0.0
Procymidone	148	139	221	233	247	988	10	4	4	13	7	38	0.008	~	56.04	3.8
Propamocarb[a]	4	1	1			6						0	0.015		0.553	0.0
Pyraclostrobin	2	2	5	11	24	44				2		2	0.121	~	3.964	4.5
Pyridaben	4	3	5	6	2	20			1	1		2	0.035	~	8.01	10.0
Pyridalyl	3	3	3	3	6	18		1			1	2	0.035	~	7.13	11.1
Pyrimethanil	23	8	4	11	14	60						0	0.065	~	3.817	0.0
tebuconazole[a]	2	14	7		26	49						0	0.101	~	3.9	0.0
Tebufenozide				2	5	7					1	1	0.426	~	3.074	14.3
Tebufenpyrad	46	48	54	93	203	444	2	1				3	0.023	~	2.8	0.7
Tefluthrin				1	4	5						0	0.017	~	0.155	0.0
Tetraconazole[a]	7	2	6			15	2					2	0.016	~	6.6	13.3
Thiacloprid	1		1	4	4	10					1	1	0.211	~	1.687	10.0
Tolclofosmethyl	7	2	1	1		11	6	1				7	0.02	~	13.31	63.6
Trifloxystrobin		2		6	7	15		1		3	4	8	0.1	~	5.78	53.3
Triflumizole	2		2	5	3	12						0	0.039	~	2.17	0.0
Unoconazole			15	9	5	29			15	9	5	29	0.098	~	2.2	100.0
Vinclozolin	11	11	6	2	1	31		1				1	0.014	~	6.691	3.2

*This table does not include pesticides that is found for less than four times for years

[a]pesticides analyzed until 2012

Table 8. Distribution of Pesticide residues in vegetables from 2010 to 2014

Group	Commodity	Number of samples					Number of samples detected (%)					Number of samples over MRLs (%)				
		2010	2011	2012	2013	2014	2010	2011	2012	2013	2014	2010	2011	2012	2013	2014
	perilla leaf	1516	1291	1362	1305	1353	422(27.8)	304(23.5)	338(24.8)	458(35.1)	1053(77.8)	19(1.3)	16(1.2)	10(0.7)	9(0.7)	20(1.5)
	korean cabbage	162	99	72	62	143	10(6.2)	4(4.0)	2(2.8)	2(3.2)	15(10.5)	2(1.2)				1(0.7)
	lettuce(leaf)	736	690	1060	976	866	57(7.7)	33(4.8)	42(4.0)	45(4.6)	103(11.9)	12(1.6)	5(0.7)		5(0.5)	4(0.5)
	spinach	340	359	239	200	258	31(9.1)	37(10.3)	24(10.0)	38(19.0)	60(23.3)	3(0.9)	13(3.6)	4(1.7%)	1(0.5)	7(2.7)
Leafy	radish leaf	200	179	191	197	137	11(5.5)	7(3.9)	7(3.7)	17(8.6%)	25(18.2)	1(0.5%)			1(0.5)	3(2.2)
Vegetables	chard	323	360	239	231	170	55(17.0)	40(11.1)	31(13.0)	46(19.9)	68(40.0)	15(4.6)	8(2.2)	1(0.4)	8(3.5)	10(5.9)
	crown daisy	253	274	147	117	99	41(16.2)	22(8.0)	28(19.0)	19(16.2)	24(24.2)	12(4.7)	7(2.6)	8(5.4)	9(7.7)	6(6.1)
	chicory(leaf)	245	214	253	289	234	18(7.3)	16(7.5)	19(7.5)	18(6.2)	17(7.3)		1(0.5)		3(1.0)	6(2.6)
	marsh mallow	212	208	150	202	179	9(4.2)	10(4.8)	12(8.0)	10(5.0)	21(11.7)	2(0.9)		1(0.7)	1(0.5)	2(1.1)
	chamnamul	300	358	214	230	132	71(23.7)	87(24.3)	93(43.5)	112(48.7)	117(88.6)	13(4.3)	9(2.5)	5(2.3)	2(0.9)	18(13.6)
	pak choi	105	72	65	55	48	4(3.8)	5(6.9)	4(6.2)	3(5.5)	12(25.0)	2(1.9)		1(1.5)	1(1.8)	
	romaine	123	114	131	110	114	8(6.5)	8(7.0)	11(8.4)	12(10.9)	28(24.6)	1(0.8)	3(2.6%)		3(2.7)	5(4.4)
	vitamin	47	57	79	52	53	3(6.4)	2(3.5)	2(2.5)	4(7.7)	3(5.7)				1(1.9)	1(1.9)
	mustard green	310	186	82	33	25	54(17.4)	45(24.2)	29(35.4)	26(78.8)	21(84.0)	32(10.3)	16(8.6)	17(20.7)	12(36.4	10(40.0)
	angelica gigas nakai	101	81	66	49	47	21(20.8)	21(25.9)	8(12.1)	13(26.5)	20(42.6)	5(5.0)	2(2.5)	2(3.0)		4(8.5)
	kale	93	75	95	46	37	6(6.5)	5(6.7)	12(12.6)	14(30.4)	7(18.9)			5(5.3)	7(15.2)	2(5.4)
	lettuce(head)	86	77	99	80	118	2(2.3)	2(2.6)	6(6.1)	5(6.3)	11(9.3)					
	amaranth	43	55	26	20	11	9(20.9)	9(16.4)	3(11.5)	6(30.0)	1(9.1)	1(2.3)	3(5.5)	1(3.8)	1(5.0)	
	cabbage	78	129	121	88	152										
	rose	27	24		34	49		1(4.2)		1(2.9)	6(12.2)					1(2.0)
	shinsuncho	43	46	80	46	38	8(18.6)	5(10.9)	12(15.0)	13(28.3)	2(5.3)		1(2.2)	1(1.3)	1(2.2)	1(2.6)
	mustard leaf	21	15	14	14	10	1(4.8)	2(13.3)	2(14.3)	2(14.3)	1(10.0)	1(4.8%)		1(7.1)		
	new green	11	8	16	11	8	3(27.3)	2(25.0)	2(12.5)	3(27.3)	3(37.5)				1(9.1)	
	lollo rosa	6	16	22	19	15		5(31.3)	1(4.5)	1(5.3)	3(20.0)		2(12.5)			

Table 8. Continued

Group	Commodity	Number of samples					Number of samples detected (%)					Number of samples over MRLs (%)				
		2010	**2011**	**2012**	**2013**	**2014**	**2010**	**2011**	**2012**	**2013**	**2014**	2010	2011	2012	2013	2014
Leafy vegitables	**oak leaf**	**9**	**13**	**36**	**33**	**31**	**1(11.1)**	**2(15.4)**	**2(5.6)**	**1(3.0)**	**1(3.2)**					**1(3.2)**
	chicon	**12**	**31**	**31**	**8**	**16**	**2(16.7)**	**1(3.2)**								
	parsley	**29**	**23**	**13**	**11**	**11**	**4(13.8)**	**11(47.8)**	**10(76.9)**	**5(45.5)**	**3(27.3)**	**2(6.9)**	**5(21.7)**	**6(46.2)**	**2(18.2)**	**3(27.3)**
	chwinamul	**44**	**29**	**27**	**25**	**33**	**9(20.5)**	**4(13.8)**	**7(25.9)**	**3(12.0)**	**17(51.5)**	**3(6.8)**				**5(15.2)**
	beet	**20**	**17**	**37**	**17**	**21**	**2(10.0)**		**2(5.4)**	**1(5.9)**	**5(23.8)**					**2(9.5)**
	Leaf parsley	**6**	**10**	**37**	**31**	**26**	**4(66.7)**	**2(20.0%)**	**6(16.2)**	**5(16.1)**	**10(38.5)**	**2(33.3)**				**2(7.7)**
	pepper leaf	**14**	**12**	**14**	**9**		**7(50.0)**	**7(58.3)**	**11(78.6)**	**8(88.9)**		**4(28.6)**	**2(16.7)**	**3(21.4)**	**7(77.8)**	
	bangpungnamul	**9**	**3**	**2**	**11**	**13**					**2(15.4)**					**2(15.4)**
	dacheongchae	**9**	**5**	**8**	**6**	**1**	**2(22.2)**	**1(20.0)**					**1(20.0)**			
	betterbur	**19**	**9**	**12**	**14**	**10**	**2(10.5)**	**3(33.3)**	**3(25.0)**	**3(21.4)**	**6(60.0)**		**1(11.1)**		**1(7.1)**	**1(10.0)**
	wintergrown cabbage	**199**	**272**	**240**	**175**	**148**	**13(6.5)**	**27(9.9)**	**28(11.7)**	**35(20.0)**	**41(27.7)**	**1(0.5)**	**6(2.2)**	**5(2.1)**	**1(0.6)**	**3(2.0)**
	godlbaggi	**3**		**8**	**13**	**12**	**2(66.7)**					**2(66.7)**				
	shepherd's purse	**21**	**5**	**11**	**9**	**17**	**2(9.5)**									
	radicho	**4**	**5**	**8**	**12**	**26**			**1(12.5)**	**2(16.7)**						
	Rapeseed	**7**	**2**	**2**	**2**	**4**			**1(50)**					**1(50)**		
	mugwort	**11**	**7**		**10**	**6**	**1(9.1)**				**1(16.7)**	**1(9.1)**				
	Rocket	**6**	**3**	**24**	**22**	**23**			**3(12.5)**		**1(4.3)**			**1(4.2)**		
	wild chive	**9**	**3**	**4**	**10**	**12**	**1(11.1)**				**1(8.3)**					
	Kohlrabi	**4**	**8**	**8**	**4**	**14**			**1(12.5)**							
Stalk and stem vegetables	**welsh onion**	**236**	**163**	**173**	**140**	**141**	**30(12.7)**	**14(8.6)**	**22(12.7)**	**24(17.1)**	**25(17.7)**	**3(1.3)**				**2(1.4)**
	sedum	**90**	**72**	**51**	**71**	**45**	**22(24.4)**	**15(20.8)**	**11(21.6)**	**37(52.1)**	**28(62.2)**	**1(1.1)**	**1(1.4)**			**2(4.4)**
	leek	**127**	**98**	**89**	**78**	**76**	**28(22)**	**23(23.5)**	**39(43.8)**	**28(35.9)**	**33(43.4)**	**4(3.1)**	**3(3.1)**	**3(3.4)**	**2(2.6)**	**2(2.6)**
	water dropwort	**48**	**52**	**53**	**52**	**89**	**1(2.1)**		**2(3.8)**		**1(1.1)**					**1(1.1)**
	celery	**87**	**64**	**69**	**39**	**62**	**13(14.9)**	**11(17.2)**	**8(11.6)**	**9(23.1)**	**17(27.4)**	**2(2.3)**	**1(1.6)**			**2(3.2)**

Table 8. Continued

Group	Commodity	Number of samples					Number of samples detected (%)					Number of samples over MRLs (%)				
		2010	**2011**	**2012**	**2013**	**2014**	**2010**	**2011**	**2012**	**2013**	**2014**	2010	2011	2012	2013	2014
Stalk and stem vegetables	**green galic**	**18**	**23**	**35**	**24**	**41**	**7(38.9)**	**2(8.7)**	**2(5.7)**		**4(9.8)**					**1(2.4)**
	day lily	**3**	**1**	**2**	**2**	**3**			**1(50)**							
	radish	**89**	**97**	**123**	**97**	**88**	**2(2.2)**	**3(3.1)**	**4(3.3)**							
	radish red round	**7**	**5**	**22**	**17**	**28**										
Root and tuberVegetables	**carrot**	**30**	**57**	**90**	**56**	**59**		**1(1.8)**	**4(4.4)**	**1(1.8)**	**3(5.1)**					**1(1.7)**
	pepper	**108**	**112**	**63**	**98**	**219**	**20(18.5)**	**37(33)**	**18(28.6)**	**13(13.3)**	**87(39.7)**		**1(0.9)**			
	cucumber	**97**	**154**	**124**	**108**	**155**	**2(2.1)**	**8(5.2)**	**11(8.9)**	**5(4.6)**	**19(12.3)**					
	squash	**56**	**72**	**123**	**94**	**169**	**1(1.8)**		**4(3.3)**	**3(3.2)**	**7(4.1)**					**7(4.1)**
Fruiting vegetables	**tomato**	**39**	**35**	**33**	**14**	**38**				**2(14.3)**	**1(2.6)**					**1(2.6)**
	paprika(sweet pepper)	**39**	**25**	**22**	**59**	**71**	**6(15.4)**		**3(13.6)**	**9(15.3)**	**11(15.5)**					
	korea melon	**55**	**14**	**21**	**31**	**10**	**2(3.6)**			**1(3.2)**	**1(10)**					
	eggplant	**38**	**56**	**94**	**96**	**57**	**1(2.6)**	**3(5.4%)**	**2(2.1)**		**3(5.3%)**					

3. Assessment of Vegetable Intakes

According to the Korea National Health and Nutrition Examination Survey 2012, the number of the kinds of vegetables consumed by the citizens of Seoul was 74 and the number of the kinds of vegetables with pesticide residues was 45. The number of the kinds of vegetables analyzed by Seoul City was 96. Among them, ligularia stenocephala, asparagus, scallion and single leaf green were not included in the vegetables, which were analyzed to contain pesticide residues, but matched to the vegetables subject to analysis. Since 94.6% of vegetables were analyzed in terms of the kinds of vegetables consumed by the citizens of Seoul and 99.9% of vegetables were analyzed in terms of the amount of vegetable consumption, this research may seem suitable for risk assessment of vegetable consumption of the citizens of Seoul.

There were no relevant differences between vegetable consumption of Seoul citizens at 315.9g and people in other areas of the country at 309.4g (data not shown). Table 9 demonstrates the consumption of 45 vegetables with pesticide residues among the vegetables analyzed from 2010 to 2014 after calculating with the food codes of Korea National Health and Nutrition Examination Survey data.

The vegetables with 10g of average daily per capita intake of vegetables of Seoul citizens include Korea cabbage, tomato, pepper, cucumber and welsh onion. Vegetable consumption of 45 kinds of vegetables with pesticide residues by sex and by age of Seoul citizens is shown in Table 10. This table contains the data from consumers only. The intake of tomato was the highest in all age groups. Those between 19 and 64 years old consumed 1572.4g /day of vegetables and those over 65 years old consumed the highest amount of vegetables at 1628.3g/day. In particular, those over 65 consumed twice more beet, marsh mallow, and Pak choi than other age groups.

Table 9. Daily intakes of vegetables detected with pesticides in general population and in the citizen of Seoul

Vegetables	General population(g/day)		citizen of Seoul (g/day)	
	mean	97.5th	mean	97.5th
angelica gigas nakai	0.00	0.00	0.00	0.00
amaranth	0.19	0.00	0.17	0.00
beet	0.01	0.00	0.02	0.00
betterbur	0.32	0.00	0.11	0.00
Brassica napus	0.57	0.00	0.57	0.00
broccoli	1.02	0.00	0.73	0.00
carrot	6.19	41.75	6.98	43.31
celery	0.26	0.00	0.10	0.00
chamnamul	0.58	0.00	0.93	0.00
chard	0.26	0.00	0.32	0.00
chicory(leaf)	0.14	0.00	0.27	0.00
chwinamul	2.75	24.47	3.56	40.00
crown daisy	0.59	6.37	0.71	6.72
cucumber	15.98	152.28	18.58	145.26
day lily	0.01	0.00	0.05	0.00
eggplant	2.67	27.12	2.39	24.41
kale	0.06	0.00	0.05	0.00
kohlrabi	0.27	0.00	0.27	0.00
Korean cabbage	70.91	303.74	69.02	303.71
Korean lettuce	0.00	0.00	0.00	0.00
leek	3.14	37.50	3.16	35.79
lettuce	7.19	76.83	7.19	76.83
lettuce(head)	1.39	14.95	2.46	33.53
mugwort	0.15	0.00	0.16	0.00
marsh mallow	2.75	0.00	3.48	0.00
mustard green	0.07	0.00	0.07	0.00
mustard leaf	0.00	0.00	0.00	0.00
paprika	0.82	1.48	0.82	1.48
parsley	0.05	0.00	0.05	0.00
pak choi	0.10	0.00	0.08	0.00
pepper	24.480	126.207	22.41	115.81
pepper leaf	0.20	0.00	0.09	0.00
perilla leaf	4.32	47.03	3.97	39.43
radish	7.30	51.73	7.41	48.57
radish leaf	0.71	0.00	0.32	0.00

Table 9. Continued

sedum	0.20	0.00	0.04	0.00
shepherd's purse	0.22	0.00	0.23	0.00
shinsuncho	0.43	0.00	0.37	0.00
spinach	6.05	69.69	5.29	59.35
squash	9.08	72.76	9.71	81.94
sweet pepper	0.74	7.90	1.23	13.17
tomato	21.82	260.40	24.58	259.88
water dropwort	1.42	12.5	1.14	6.67
welsh onion	11.65	55.28	10.85	45.65
wild chive	0.08	0.00	0.19	0.00
sum	207.14	1389.99	210.11	1381.51

Table 10. Daily intakes of vegetables detected with pesticides in the citizen of Seoul by sex and by age

Vegetables	By sex (g/day)		By age (g/day)		
	male	female	Under 6*	19~64*	Over 65*
angelica gigas nakai	0.00	0.94	0.00	0.94	0.00
amaranth	34.46	16.14	0.00	19.48	35.57
beet	22.56	6.00	0.00	22.56	0.00
betterbur	23.57	32.44	0.00	26.31	33.49
Brassica napus	0.00	63.13	0.00	63.13	0.00
broccoli	25.19	39.76	5.19	32.43	70.69
carrot	15.56	12.46	5.27	15.00	14.25
celery	12.49	5.24	1.35	13.00	21.70
chamnamul	74.84	67.96	0.00	49.66	78.68
chard	33.81	64.16	16.11	42.33	98.37
chicory(leaf)	14.46	13.11	0.00	13.78	11.67
chwinamul	64.10	51.90	24.19	59.64	62.02
crown daisy	11.02	10.64	0.84	11.76	20.12
cucumber	53.98	55.36	19.17	59.19	63.34
day lily	78.41	79.36	0.00	0.00	78.95
eggplant	63.45	92.03	86.59	64.74	0.00
kale	3.90	14.69	0.00	13.17	3.93
kohlrabi	15.01	287.51	0.00	88.39	94.50
Korean cabbage	66.03	71.13	11.38	74.03	77.67
Korean lettuce	40.11	42.50	0.00	43.83	32.48
leek	22.83	31.26	4.60	33.22	24.16
lettuce	39.28	39.91	1.13	41.71	29.54
lettuce(head)	48.22	37.85	11.65	48.05	25.36
mugwort	11.02	10.64	0.84	11.76	20.12
marsh mallow	38.46	68.69	16.16	30.78	163.89
mustard green	0.00	21.56	0.00	27.90	3.07
mustard leaf	42.50	27.74	0.00	0.00	0.00
paprika	20.44	34.55	11.58	28.01	50.17
parsley	0.09	1.27	0.12	2.15	0.00
pak choi	52.92	24.48	0.00	12.50	52.92
pepper	32.83	25.40	5.21	32.26	27.35
pepper leaves	21.36	5.82	0.00	11.26	9.60
perilla leaves	22.11	24.28	7.80	23.96	35.23
radish	59.47	36.49	5.08	20.32	24.76
radish leaf	63.98	61.80	0.00	65.00	0.00

*years old

Table 10. Continued

sedum	15.18	0.00	0.00	17.00	0.00
shepherd's purse	17.03	20.69	17.64	22.25	6.14
shinsuncho	0.00	101.37	100.00	135.41	7.19
spinach	36.37	27.29	12.67	31.82	34.15
squash	36.92	33.53	10.88	36.81	52.46
sweet pepper	6.56	5.87	2.10	6.79	9.33
tomato	155.34	138.52	43.20	159.74	218.63
water dropwort	30.81	15.26	1.58	27.16	22.59
welsh onion	16.77	11.36	3.85	14.21	10.20
wild chive	16.02	14.12	12.45	18.96	4.01
sum	1459.46	1846.22	438.62	1572.37	1628.28

4. Risk Assessment of Pesticide Residues

4.1. Risk assessment of the citizen of Seoul

In case of the RI of the general population (Table 11), although the EDI of mean consumption was high for azoxystrobin, dimethomorph, and paclobutrazol, the RIs for flubediamide, chlorthalonil, and ethoprophos at 7.9%, 4.8%, and 4.0% respectively were higher than for other pesticides. The EDI for high consumers (97.5 percentile) was similar to that of the general population, although flubediamide replaced paclobutrazol, and the RIs were slightly higher at 84.5%, 36.8%, and 42.4% respectively. Although their EDIs were not as high as those of other pesticides, their RIs were high because of lower ADIs (Lozowicka et al., 2013). The EDIs and RIs of the citizens of Seoul flubediamide, chlorthalonil, and ethoprophos should be considered more closely because the RIs for high consumers (97.5 percentile) were 73.9%, 35.7%, and 33.1% respectively,

4.2. Risk assessment of the citizen of Seoul by sex group

RI of the citizens of Seoul for sex groups includes only consumers (Table 12). For the sex group of male and female, the lowest RI was for Fludioxonil with 0.6%, 1.2% respectively. The EDI of male was high for azoxystrobin, chlorothalonil, and paclobutrazol while the RIs for chlorothalonil, diazinon, flubediamide at 50.0%, 40.3%, 30.3% respectively was higher than other pesticides. The EDI of female was high for chlorfenapyr, dimethomorph, paclobutrazol but the RI of chlorothalonil, diazinon was relatively high with 67.3%, 38.4%. For chlorfenapyr the value of EDI reached 119.1 % of the ADIs

4.3. Risk assessment of the citizen of Seoul by age group

RI of the citizens of Seoul for different age groups includes only consumers (Table 13). For the age group of under 6 years, the lowest RI was for procymidone with 0.8%; while the lowest RI for both the group of 19~64 years and over 65 years was for fludioxonil. Chlorothalonil showed the high RI from all age group and particularly for over 65years old, chlorfenapyr was the highest RI for 19~64 age group. Their dietary exposure slightly exceeded with threshold with 113%and 119% respectively of the ADIs (EPSA, 2013). Except them, the value of RI was within 100%.

Table 11. Risk assessment of pesticides detected in vegetables for general population and the citizen of Seoul

Pestcide	ADI[1)] (mg/person /day)	General Population				Citizen of Seoul			
		mean		P 97.5		mean		P 97.5	
		EDI[2)]	RI[3)]	EDI	RI	EDI	RI	EDI	RI
Azoxystrobin	0.200	0.002	1.0	0.016	8.2	0.002	1.0	0.016	7.9
Bifenthrin	0.010	0.000	1.1	0.001	9.5	0.000	0.9	0.001	8.4
Boscaslid	0.040	0.001	3.0	0.010	25.1	0.001	2.8	0.009	22.9
Chlorfenapyr	0.026	0.000	1.0	0.001	4.1	0.000	0.9	0.001	3.8
Chlorothalonil	0.020	0.001	4.7	0.007	36.8	0.001	5.6	0.007	33.2
Chlorpyrifos	0.010	0.000	1.8	0.001	12.5	0.000	1.6	0.001	10.7
Cypermethrin	0.020	0.000	2.0	0.003	15.2	0.000	1.8	0.003	13.3
Diazinon	0.005	0.000	2.5	0.001	21.5	0.000	2.5	0.001	20.4
Diethofencarb	0.430	0.001	0.1	0.005	1.3	0.000	0.1	0.005	1.2
Dimethomorph	0.200	0.001	0.7	0.012	5.9	0.001	0.6	0.010	5.2
Diniconazole	0.020	0.000	1.1	0.002	11.3	0.000	0.6	0.001	6.1
Endosulfan	0.006	0.000	3.3	0.002	30.3	0.000	3.0	0.002	27.0
Ethoprophos	0.0004	0.000	4.5	0.000	40.9	0.000	4.5	0.000	36.4
Flubendiamide	0.017	0.001	7.9	0.014	84.5	0.001	7.4	0.013	73.9
Fludioxonil	0.400	0.000	0.0	0.002	0.5	0.000	0.0	0.002	0.4
Flufenoxuron	0.010	0.000	2.2	0.002	19.6	0.000	2.0	0.002	16.7
Procymidone	0.100	0.000	0.1	0.001	0.5	0.000	0.1	0.000	0.5
Paclobutrazol	0.100	0.001	1.4	0.012	11.5	0.001	1.4	0.011	10.8
Tebufenpyrad	0.010	0.000	0.4	0.000	3.5	0.000	0.4	0.000	3.6
Uniconazole	0.016	0.000	0.3	0.001	3.6	0.000	0.3	0.001	3.4

[1)] (Detected concentration (mg/kg) X Daily food intake (g) / 1000) / 55kg (Average body weight of Korean)

[2)] ADI (mg/person/day)

[3)] EDI/ADI X 100 (%)

Table 12. Risk assessment of pesticides detected in vegetables for sex group (Consumers only)

Pestcide	Average conc (mg/kg)	Male			Female		
		EDI[1)]	ADI	RI (%)	EDI[2)]	ADI	RI (%)
Azoxystrobin	2.213	0.680	11.588	5.9	0.609	9.758	6.2
Bifenthrin	0.229	0.049	0.579	8.5	0.068	0.488	14
Boscaslid	2.717	0.400	2.318	17.3	0.545	1.952	27.9
Chlorfenapyr	0.816	0.148	1.506	9.8	1.51	1.269	119.1
Chlorothalonil	2.654	0.580	1.159	50	0.657	0.976	67.3
Chlorpyrifos	0.362	0.166	0.579	28.6	0.155	0.488	31.7
Cypermethrin	0.593	0.137	1.159	11.9	0.137	0.976	14.1
Diazinon	0.408	0.117	0.29	40.3	0.094	0.244	38.4
Diethofencarb	1.256	0.318	24.914	1.3	0.308	20.98	1.5
Dimethomorph	1.962	0.572	11.588	4.9	0.755	9.758	7.7
Diniconazole	0.708	0.147	1.159	12.7	0.114	0.976	11.6
Endosulfan	0.321	0.082	0.348	23.5	0.082	0.293	28
Ethoprophos	0.1	0.007	0.023	29.6	0.006	0.02	31.3
Flubendiamide	3.585	0.298	0.985	30.3	0.303	0.829	36.6
Fludioxonil	1.438	0.128	23.176	0.6	0.236	19.516	1.2
Flufenoxuron	0.631	0.074	0.579	12.8	0.084	0.488	17.2
Procymidone	1.096	0.104	5.794	1.8	0.122	4.879	2.5
Paclobutrazol	1.444	0.745	5.794	12.9	0.755	4.879	15.5
Tebufenpyrad	0.328	0.046	0.579	7.9	0.086	0.488	17.7
Uniconazole	0.485	0.021	0.927	2.3	0.039	0.781	5

[1)] (Detected concentration (mg/kg) X Daily food intake (g) /1000) / 57.9kg (Average body weight of male)

[2)] (Detected concentration (mg/kg) X Daily food intake (g) /1000) / 47.9kg (Average body weight of female)

Table 13. Risk assessment of pesticides detected in vegetables for age group (Consumers only)

Pestcide	The citizen of Seoul (Consumer only)						
	under 6 years old			19~64 years old		over 65years old	
	ADI	EDI[1)]	RI (%)	EDI[2)]	RI (%)	EDI[3)]	RI (%)
Azoxystrobin	0.200	0.007	3.6	0.010	5.1	0.012	6.0
Bifenthrin	0.010	0.001	10.6	0.001	12.4	0.002	16.9
Boscaslid	0.040	0.005	13.4	0.008	20.7	0.009	23.2
Chlorfenapyr	0.026	0.010	40.3	0.031	118.6	0.004	15.9
Chlorothalonil	0.020	0.011	56.1	0.010	51.6	0.023	112.5
Chlorpyrifos	0.010	0.001	9.3	0.002	20.4	0.003	33.0
Cypermethrin	0.020	0.002	8.4	0.002	11.5	0.003	14.5
Diazinon	0.005	0.001	17.4	0.002	35.4	0.002	47.4
Diethofencarb	0.430	0.004	0.9	0.005	1.1	0.007	1.5
Dimethomorph	0.200	0.011	5.5	0.011	5.4	0.019	9.4
Diniconazole	0.020	0.002	9.3	0.002	11.9	0.002	11.8
Endosulfan	0.006	0.001	15.6	0.001	20.7	0.002	26.8
Ethoprophos	0.0004	0.000	31.2	0.000	27.5	0.000	42.3
Flubendiamide	0.017	0.005	31.9	0.006	37.4	0.008	49.0
Fludioxonil	0.400	0.005	1.2	0.003	0.8	0.004	0.9
Flufenoxuron	0.010	0.002	17.4	0.002	16.3	0.002	24.9
Procymidone	0.100	0.001	0.7	0.002	2.3	0.002	1.9
Paclobutrazol	0.100	0.014	14.1	0.012	12.1	0.017	16.6
Tebufenpyrad	0.010	0.004	36.1	0.002	15.5	0.001	7.8
Uniconazole	0.016	0.001	4.7	0.001	5.6	0.001	6.1

[1)] (Detected concentration (mg/kg) X Daily food intake (g) /1000) / 16.1kg (Average body weight of under 6)
[2)] (Detected concentration (mg/kg) X Daily food intake (g) /1000) / 63.7kg (Average body weight of 19~64)
[3)] (Detected concentration (mg/kg) X Daily food intake (g) /1000) / 59.1kg (Average body weight of over 65)

Ⅳ. Discussion

1. Detection Characteristics of Pesticides

A total of 34,520 samples of 96 types of vegetable were collected under a regulatory pesticide monitoring program organized by the SIHE. All samples were analyzed for 283 pesticides.

Of the total tested samples, 98.6% were within the legal limits and 86.6% contained no quantifiable residue at all. The rate of vegetables in which pesticide was detected by year from 2010 to 2014 was 12.4%, 10.5%, 11.6%, 13.8%, and 21.3% respectively. The rates of violation of MRLs were 1.7%, 1.3%, 0.8%, 1.1%, and 1.6 % respectively for 5 years (Figure.3).

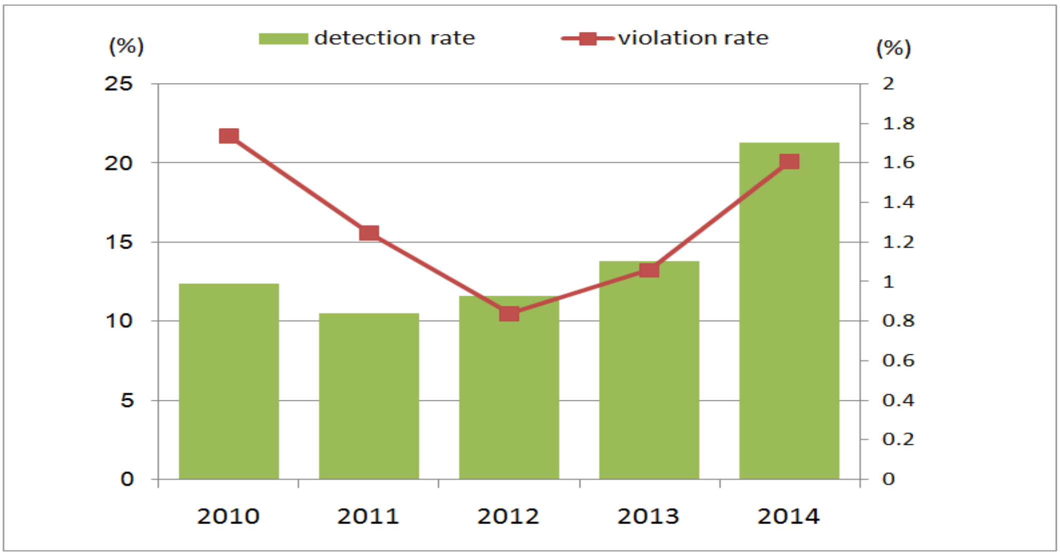

Figure 3. Detection frequency and exceeded MRL rate of pesticides from 2010 to 2014.

The violation rate decreased gradually until 2012 and began to increase again. Such changes refer mainly to the commodity group collected from market and enforcement of MRLs and differences in the pesticides analyzed

According to KFDA' report (Chang et al., 2014), chlorpyrofos, procymidone and flubendiamide were identified as frequently detected pesticides in the data on the analysis of 232 products of the total produce, and the detection rate of azoxystrobin and tebufenpyrad was also high in this research. Leaf vegetables accounted for 78.6% in this paper, which analyzed vegetables only, and the detected amount of the above-mentioned two pesticides was high, indicating a different tendency.

The usage of tebufenpyrad and cypermethrin in 2014 surged 4~7 times compared with that in 2010. In particular, the detection of tebufenpyrad, which is commonly used in commercial greenhouses, increased to 224 cases (10.4%) in 2014 compared with 12 cases (1.6%) in 2007 reported in another study (Chang, 2010).

For 3 years between 2010 and 2012, a research on the conditions of pesticide residues in Incheon (Kim et al., 2013) discovered the pesticides with a high violation rate including endosulfan, chlorpyrifos and diazinon and in the report by Gyenggido Institute of Health and Environmen (GIHE, 2012), procymidone, diazinon, chlorpyrifos were shown to have the highest percentage of residues exceeding their MRLs. This study showed a similar result, except for the highest violation rate of paclobutrazol.

Paclobutrazol, a plant growth retardant and triazole fungicide, is absorbed by the roots of leaf showing excellent growth inhibition, makes leaf strong and increases the commercial value (KCPA, 2014). That has no MRL for vegetables and applied an MRL of 0.05 mg/kg, the lowest MRL of a similar commodity group among Korea MRLs. Another growth regulator Uniconazole, no MRL has been set in Korea and the violation rate (5.4%) is considered high. Also, chlorpyrifos is "one of the most widely used organophosphate insecticides", according to the United States Environmental Protection Agency (EPA). Also the National Agricultural Produce Quality Management Service reported in 2014 that chlorpyrifos was the pesticide that exceeded its MRL most frequently with 53 cases (NQMS, 2014). Endosulfan was prohibited from 2012, and the decline in its use is indicated by the decrease in cases from 76 in 2010 to 22 in 2014.

Among 547 vegetables of exceeding MRL, leafy vegetables including mustard green, perilla leaves and chamnamul (Pimpinella brachycarpa) accounted for 76%, which was similar to the proportion of violative vegetables in Incheon of 75%. The violation rate was high in chinamul (Aster scaber), followed by perilla leaves and crown daisy. Other researches (Kwon et al,) identified that leaf vegetables including crown daisy, chard and spinach have commonly high violation rates. Often, the maximum residue limits on such vegetables have not been set due to the lack of registered agrochemicals, since most of them are minor crops. Therefore, it is considered that the high violation rate increased as the minimum residue limits applied to the vegetables among similar commodity (Ji, 2010).

In terms of pesticide residues some samples contained more than one pesticide (multiple residues). They were found in 21.9% of the samples. The product with the highest percentage of samples with multiple residues was perilla leaves (48.6%).

2. Risk Assessment

The RI value of Seoul general population and their consumers only were whithin100%. The safety of the general population and the citizens of Seoul may be under control in terms of pesticide through vegetable consumption (Lozowicka et al., 2013). Flubendiamide showed both group the high RI. That belongs to chemical family of benzenedicarboxy with insecticidal activity, leading to the cessation of feeding immediately after ingestion of the compound (FAO). That was attributed to its high pesticide average value of 3.585 mg/kg with an MRL for leafy vegetables higher than that for other commodities and a relatively low ADI.

The RI value of male was all under 50%, while that of female were mostly higher than male. Women consumed more at 1848.2g/day compared to men at 1459.5g/day. Women consumed all vegetables except for sedum and men did not consume angelica gigas nakai, shinsuncho (angelica keiskei), brassica napus (canola) and mustard green.

In 2012, pesticide value of chlorofenapyr was detected with 68.5mg/kg in shinsuncho. Women's intake of shinsuncho was 101.4g/day with the highest EDI value and relatively low ADI value, making the RI value over 100%. While there was no consumption of shinsuncho by men, their RI showed different tendency.

Chronic exposure was negligible or within the toxicological acceptable dose (below the ADI). For young children under 6 years and people over 65years old , the highest RI was for chlorothalonil, which appeared to have the second highest amount of pesticide residues in this age group and a relatively low ADI. In case of people in the over 65 years group, eat more vegetables than those in other age groups with a high intake, in particular, of both marsh mallow and chard at 163.9 g/day and 98.4 g/day respectively, and chlorothalonil levels also exceeded the MRLs (5.0 mg/L) by 2~3 times. The highest EDI for chlorfenapyr in the adult group in 2012 was attributed to the high pesticide residues of shinsuncho as female' case. For all age groups, the RIs of chlorthalonil, flubendiamide, and ethoprophos were higher than those of other pesticides. Chlorthalonil and ethoprophos also were two of the 24 pesticides that were selected and recommended for intensive regulation in Korea based on the amounts and toxicity of individual active ingredients (Cha at al., 2014). According to previous research (Chang, 2010), it was analyzed pesticides and risk assessment by vegetable intakes in Seoul between 2007~2009, revealed the highest RIs for diniconazole, endosulfan, and diazinon of the citizen of Seoul for 3 years, the exceeding rate of the maximum residue limits of azoxystrobin, paclobutrazol, endosulfan, diniconazole, procymidone was high but the RI value of diazinon was high because it had the lowest ADI value, except for ethoprophos of 0.005 mg/kg body weight

Endosulfan, which can pose unacceptable neurological and reproductive risks to farmworkers and wildlife, usage and produce of endosulfan has been banned in USA from 2010(EPA) and also in Korea since 2012.

Endosulfan of the detection rate and violation rate has fallen substantially. However, the pesticide seems to be used on a continuous basis with 22 cases of detection in 2014 and it is required to train and promote the safe use of pesticides.

As mentioned above, Excessive pesticide use can affects the EDI value, higher MRLs of some vegetables may leads to higher average pesticide residues. They can cause health problems in future for humans by exposure through vegetable consumption, and there is a need for continuous monitoring of the health impact of pesticides.

On the other hand, vegetables are practically consumed freshly. Since the pesticide residues are cleaned by 8-68% with flowing water at home depending on the type of pesticides and characteristics of vegetables(Kwon et al., 2013)., the risk of the pesticide residues can be lowered, which makes the risk of pesticides for Seoul citizens' intake of vegetables not serious.

3. Limitation

It should be noted that this study focused on vegetables only (excluding fruit, cereals), exposure of the general population to pesticides occurs primarily through food and drinking water contaminated with pesticide residues, whereas substantial exposure can also occur in environment including in or around home(Christos and Ilias, 2011). Since there are few researches on exposure to pesticides through water quality and living environment after their application except for food, the risk evaluation on comprehensive test has not been conducted. These are likely to have led to an underestimation of the total exposure to pesticides. (Lee, 2012)

Data that was collected for the detected pesticides was confirmed by GC-MSD and LC-MSD, and in case there were half of the lowest MRL among Korean MRLs was considered to be no quantifiable residues. In addition, no detected levels of pesticides were computed as 0 (zero), and the treatment of non–detects as zero may underestimate the dietary exposure because the true value may fall between zero and the LOD (Wong et al., 2014).

There is still controversy over how a reliable and pertinent investigation can be conducted for dietary intake. It is not possible to characterize the true intake of consumers because only per capita dietary consumption data is available; therefore, population variation cannot be considered (Ferrier et al., 2010). For food consumption data, for example, in case of tomato, it is also distributed in the form of processed foods such as tomato juice, tomato ketchup, and spaghetti sauce; Since the pesticide residues of vegetables are highly likely to be reduced during the cooking and processing process including peeling and washing, it is required to correct the actual amount of intake of pesticides using the processing factor in calculating the value (GIHE, 2012). For food intake in this study, no consideration was given to any calculation ratio for raw materials and processing factors. Therefore, these can lead to an overestimation.

Ⅴ. Conclusion

A total of 34,520 vegetables obtained from markets in Seoul from 2010 to 2014 were analyzed for pesticides in order to assess exposure to pesticides. Pesticide residues were found in 17.0% of the samples and exceeded the permitted residue levels in 1.4% of the total vegetable samples. The 20 pesticides that were both detected frequently and exceeded the permitted residue levels were assessed to determine human exposure through intake of vegetables.

The pesticides detected most frequently were azoxystrobin, diethofencarb, procymidone, cypermerhrin, and tebufenpyrad, and they accounted for 52% of detected samples. Since 2010, the rate of violations of MRLs by the plant growth regulators paclobutrazol and uniconazole has increased substantially, while the highest rate of violations has been maintained for several years by chlorpyrifos, diazinon, and procymidone.

With respect to risk assessment of the 20 pesticides, the RIs for the general population and consumers only by the citizens of Seoul were both less than

100% even for the 97.5 percentile, which suggests that they pose an acceptable health risk. Although some RIs for the citizens of Seoul (consumers only) showed excessively high RIs between 56.0~119.1%, this was attributed to extreme amounts of pesticides and lack of food consumption data. Considering that the above findings correspond to a worst-case scenario, pesticide exposure from vegetable intake is not at the level to be of any concern (Lozowicka et al., 2013).

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ABSTRACT IN KOREAN

서울 지역 유통 채소류의 잔류농약 모니터링과 위해도 평가

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서울지역에서 2010년부터 2014년까지 유통된 채소류 96종 34520건에 대해 잔류농약을 분석하여 오염도를 파악하고, 2012년 국민건강영양조사 자료에서 서울시민의 채소류 섭취량을 산정하여 채소류 섭취에 따른 농약성분의 위해성을 평가하였다. 식품공전의 동시 다성분 잔류농약 분석법 중 제2법으로 283종의 잔류농약을 분석하였다. 분석 된 채소류 중 86.1%가 잔류 농약이 검출되지 않았으며 1.4%는 최대 잔류허용량 (Maximum Level Limit)을 초과하였다. 105종의 농약에서 검출되었고 그 중 45종의 농약은 MRL을 초과하였다.

잔류 농약 중에서 가장 일반적으로 검출이 많았던 농약 azoxystrobin,

diethfencarb, procymidone (이상 살균제), cypermethrin (살충제), tebufenpyrad (살비제)로 검출된 잔류 농약의 52%를 차지했다. 5년간 부적합이 많았던 농약은 paclobutrazol, diazinon, chlorpyrifos, endo-sulfan 과 procymidone로 각각 13.2%, 10.9%, 8.9%, 7.6%와 7.1%였다. 총 검출된 5864건의 잔류 농약 중에서 살균제는 54.3%, 살충제는 32.6%, 살비제 (응애제거제)는 10.1%, 유니코나졸을 비롯한 생장조절제도 2.0%로 115건이 검출되었다.

채소류의 37종 547건에서 농약의 최대잔류허용량을 초과해서 검출되었다. 부적합 비율이 높은 채소류는 겨자채 87건, 들깻잎 74, 참나물 47건으로 모두 엽채류였다. 잔류농약 검출 비율이 가장 높은 채소류는 고춧잎 49건 중 33건(37.3%), 들깻잎은 6827건 중 2575건(37.7%), 참나물은 1234건 중 480건(38.9%)에서 농약이 검출되었다. 2종이상의 농약이 동시에 검출된 경우도 채소류는 21.9%였고 그 중에서 들깻잎이 48.6%로 가장 많았다.

2012년 국민건강영양조사에 따르면 서울시민이 섭취한 채소류의 종류는 74종이며 잔류농약이 검출된 채소류는 45종이었다. 서울시가 분석한 채소류는 96종이며 4종을 제외한 그 외 채소류는 분석대상 채소류와 일치하였다. 서울시민이 섭취한 채소류의 종류로는 94.6%를 섭취량 기준으로는 99.9%를 분석하였으므로 이 연구는 서울시민의 채소류 섭취에 따른 위해도 평가에 적절하다고 할 수 있다.

서울시민의 채소 섭취량은 먼저 전국민의 평균섭취량과 서울시 전체섭취량을 비교하였고 서울시민 섭취자(consumer only)의 평균값과 97.5th 분위의 값을 구했다. 또 서울시민을 연령별로 6세 이하, 19~64세, 65세 이상 세 그룹과 남, 여로 구분하여 채소류 섭취량을 구하여

노출평가에 이용하였다. 농약이 검출된 채소류의 섭취량에서는 65세 이상에서 1628.28g/day으로 연령별 섭취량에서 가장 높았고 남자보다 여자가 1846.22g/day으로 더 많이 섭취하였다.

위의 결과로부터 5년간 검출빈도와 부적합율이 높은 농약 20종을 선별하여 위해도 평가를 하였다. 20종의 농약에 대해서는 상추를 이용하여 회수율과 LOD와 LOQ 실험을 하였으며 회수율은 76.5~112.3%였다.

채소류 섭취를 통해 농약 노출과 관련된 잠재적인 건강 위험 요소를 위해지수 (RI, % ADI)로 추정하였으며 일일 허용 섭취량 (ADI)에 대한 농약의 추정 섭취량 (EDI)의 비율로 구해진다. 서울 시민의 평균값과 97.5th 백분위의 RI값들은 각각 0.0 ~ 7.4 % 및 0.4 ~ 73.9 %였다. 서울시민의 남녀별 RI 값은 Chlorfenapyr를 제외하고는 100%이하였으며 서울 시민의 연령별 (소비자 만 해당) RI를 보면 6세 이하 어린이와 노인(65 세)는 chlorotharonil이 가장 높았고 그들의 EDIs은 각각 ADI의 56.0 %, 112.5 %였다. 성인(19세~64세)과 여자의 가장 높은 RI는 Chlorfenapyr 였고, EDI는 각각 ADI의 118.6 %, 119.1%에 달했다. 그러나 일부 농약의 높은 잔류량에도 불구하고 실제 섭취 시에는 세척 및 조리과정을 통해 농약성분이 분해되므로 채소류 섭취에 의한 잔류 농약의 위해 정도는 심각한 수준이 아님을 보여준다.

주요 단어: 노출, 농약, MRL, 식품 소비, EDI, ADI, 위해도 평가