

Research Article



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국내 논토양 및 밭토양 중 농약유래 잔류성유기오염물질의 노출량 평가

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Exposure Assessment of Pesticide-Originated Persistent Organic Pollutants in Paddy and Upland Soils in Korea

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Abstract

BACKGROUND: This study was conducted to investigate residual organochlorine pesticides (ROCPs) in agricultural soils and crops. Agricultural soil samples and crop samples were collected from 93 cities and counties.

METHODS AND RESULTS: Extraction and clean-up for the quantitative analysis of ROCPs were conducted by the modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) method. Recovery and limit of detection (LOD) of ROCPs in agricultural soils and crops were 76.5-103.0 and 75.2-93.2%, 0.01-0.08 and 0.10-0.15 µg/kg, respectively. Detected ROCPs in agricultural soils were α-endosulfan, β-endosulfan, and endosulfan sulfate, the residue were 2.0-12.0, 1.2-53.1, and 2.2-329.8 µg/kg, respectively. But these pesticides in all green perilla leaf and green pepper samples were not detected.

CONCLUSION: These results showed that ROCPs residues in agricultural soils were not as high as crop safety threatening.

Key words: Agricultural soils, Monitoring, Organochlorine pesticides, Persistent organic pollutants

서론

가 (Boards *et al.*, 2011, Kim *et al.*, 2014; Park *et al.*, 2011; Lee *et al.*, 2015; Lim *et al.*, 2016). (persistent organic pollutants, POPs)

(Lim *et al.*, 2016). aldrin, dieldrin, endrin, dichlorodiphenyltrichloroethane (DDT), endosulfan, heptachlor, hexachlorobenzene (HCB), α-hexachlorocyclohexane (HCH), β-HCH, pentachlorobenzene (PCB) toxaphene 11

(Ministry of Food and Drug Safety, MFDS) aldrin dieldrin 0.01-0.1, endrin 0.01-0.05, endosulfan 0.05-0.2, DDT 0.05-0.2, heptachlor 0.01-0.02 mg/kg (Korea

Food Code, 2016; Lim *et al.*, 2016).

Lim *et al.* (2016)

dieldrin, β-endosulfan endosulfan sulfate (63,815 ha, Ministry of Agriculture, Food and Rural Affairs,

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MAFRA, 2015)

(1,643,599 ha(895,739 ha, 747,860 ha),

Korean Statistical Information Service, KOSIS, 2016)

8 93

재료 및 방법

시약 및 표준품

aldrin (99.0% purity), 2,4-dichlorodiphenyldichloroethane (DDD, 99.5% purity), 4,4-DDD (99% purity), 2,4-dichlorodiphenyldichloroethylene (DDE, 97.0% purity), 4,4-DDE (98.5% purity), 2,4-dichlorodiphenyltrichloroethane (DDT, 98.0% purity), 4,4-DDT (98.0% purity), dieldrin (98.3% purity), endrin (99.0% purity), α -endosulfan (97.0% purity), β -endosulfan (99.5% purity), endosulfan sulfate (98.5% purity), heptachlor (98.5% purity), heptachlor epoxide (98.5% purity), hexachlorobenzene (HCB, 99.5% purity), α -hexachlorocyclohexane (α -HCH, 98% purity), β -HCH (97.7% purity), γ -HCH (99.0% purity) δ -HCH (98.5% purity) Dr. Ehrenstorfer GmbH (Ausburg, Germany)

acetonitrile dichloromethane Tedia (Ohio, USA), activated carbon, magnesium sulfate, sodium chloride sodium citrate Sigma-Aldrich (Saint Louis, USA), Q-sep® quick, easy, cheap, effective, rugged, and safe (QuEChERS) dispersive solid phase extraction (dSPE) tube (150 mg magnesium sulfate, 50 mg primary secondary amine, 50 mg C₁₈, 2 mL) Restek (Pennsylvania, USA)

시료채취 및 시료조제

Table 1. Sampling sites and numbers for monitoring of residual organochlorine pesticides

Region	Paddy soil	Upland soil	Crop
Jeonnam	35	35	2
Jeonbuk	17	17	4
Gyeongnam	26	25	3
Gyeongbuk	28	28	-
Chungnam	20	20	3
Chungbuk	18	18	-
Gyeonggi	16	14	1
Kangwon	22	28	4
Total	182	185	17

8 93

182 185
50 μ g/kg

17

(Table 1).

2016 4 9 6

10 10 cm 100-200 g
500 g 2 mm

(Lim *et al.*,

2016a, 2016b, and 2016c).

Lim *et al.* (2016)

10 100-200 g

1 kg

분석법의 유효성 검증

Lim *et al.* (2016)

(limits of detection, LOD) (relative standard deviation, RSD)

Lim *et al.* (2016) 2 group (Group I (10)):

α -HCH, β -HCH, γ -HCH, δ -HCH, α -endosulfan, β

Table 2. Analytical conditions for residual organochlorine pesticides

Items	Analytical conditions			
Column	RTX-5MS (30 m×250 μ m, 0.25 μ m, Restek, Pennsylvania, USA)			
Carrier gas	N ₂ (1.5 mL/min)			
Injection volume	1 mL			
Injection mode	Splitless			
Inlet temperature	250°C			
Detector temperature	300°C			
	Stage	Rate (°C/min)	Temperature (°C)	Hold time (min)
	Initial	-	60	2
Oven temperature	Ramp 1	20	130	3
	Ramp 2	1.5	210	4
	Ramp 3	10	240	3

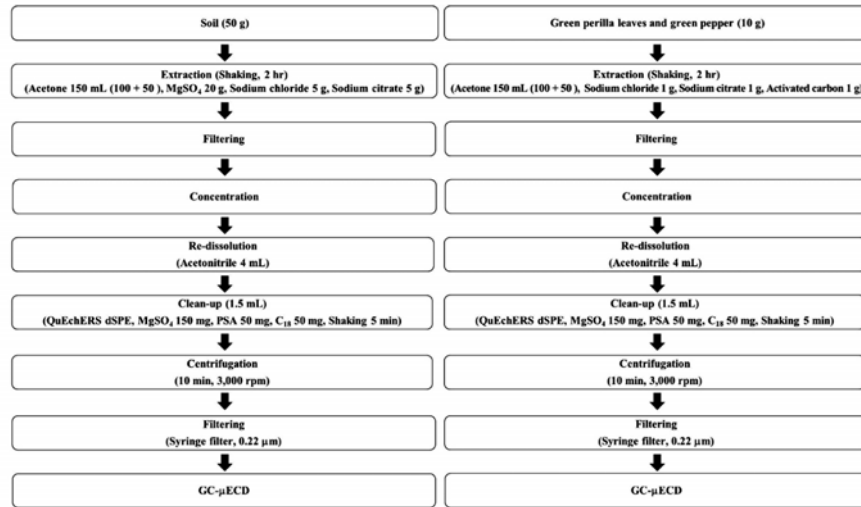


Fig. 1. Flow chart for analysis of residual organochlorine pesticides in soil (left) and crops (right).

-endosulfan, endosulfan sulfate, endrin, 4,4-DDE, 2,4-DDT, Group II (9): aldrin, dieldrin, HCB, heptachlor, heptachlorepoide, 2,4-DDD, 2,4-DDE, 4,4-DDD, 4,4-DDT) 1-5,000 μg/L (Table 2). LOD S/N (signal to noise ratio) 가 3.3

DAIHAN, Daejeon, Korea) 5 10 (3,000 rpm) (Combi 514R, Hanil, Incheon, Korea), syringe filter (0.22 μm) gas chromatography (GC, Agilent Technologies, Santa Clara, USA)-micro electron capture detector (μECD) (Fig. 1, Table 2). POPs

$$LOD (mg/kg) = \frac{(ng) \times (mL)}{(\mu L) \times (g)}$$

Group I Group II
4 20 μg/kg, 10 50 μg/L
Fig. 1 3

가
RSD

시료 중 잔류성유기염소계 농약 분석

Lim et al. (2016) QuEChERS (50 g) magnesium sulfate 20 g, sodium chloride 5 g sodium citrate 5 g 가 acetone 150 (100+50) mL 가 2 (2 hr) Acetone 40°C (IKA RV 10 Digital, Staufen, Germany), acetonitrile 4 mL 가 1.5 mL magnesium sulfate 150 mg, primary secondary amine (PSA) 50 mg C₁₈ 50 mg 2 mL QuEChERS dSPE tube Vortex mixer (VM-10,

QuEChERS 10 g sodium chloride 1 g, sodium citrate 1 g (activated carbon) 1 g 가 , acetone 150 (100+50) mL 가 2 (2 hr) 40°C (IKA RV 10 Digital, Staufen, Germany), acetonitrile 4 mL 가 1.5 mL magnesium sulfate 150 mg, PSA 50 mg C₁₈ 50 mg 2 mL QuEChERS dSPE tube Vortex mixer 5 (10 min, 3,000 rpm) syringe filter (0.22 μm) , GC-μECD (Fig. 1, Table 2). GC-μECD

GC-mass spectrometry (MS) (Agilent Technologies, Santa Clara, USA)

결과 및 고찰

검량선, 회수율 및 정량한계

19 Table 2 Group I α -HCH 25.49, β-HCH 28.46, γ-HCH 28.85, δ-HCH

31.64, α -endosulfan 48.80, 4,4-DDE 52.60, endrin 54.09, β -endosulfan 55.26, 2,4-DDT 57.47 endosulfan sulfate 60.26 , Group II HCB 26.13, heptachlor 36.49, aldrin 40.17, heptachlorepoxide 45.38, 2,4-DDE 48.81, dieldrin 51.80, 2,4-DDD 53.38, 4,4-DDD 57.29 4,4-DDT 61.47 , 1-5,000 $\mu\text{g/L}$ (R^2)가 ≥ 0.9989 (Fig. 2).

4 20 $\mu\text{g/kg}$ RSD 76.5-103.0% 1.5-4.4% LOD 0.01-0.08 $\mu\text{g/kg}$ (Fig 2, Table 3). 19 α -endosulfan, β -endosulfan endosulfan sulfate RSD 75.2-93.2% 2.4-5.2% , LOD 0.15, 0.10 0.15 $\mu\text{g/kg}$ (Fig. 2, Table 4).

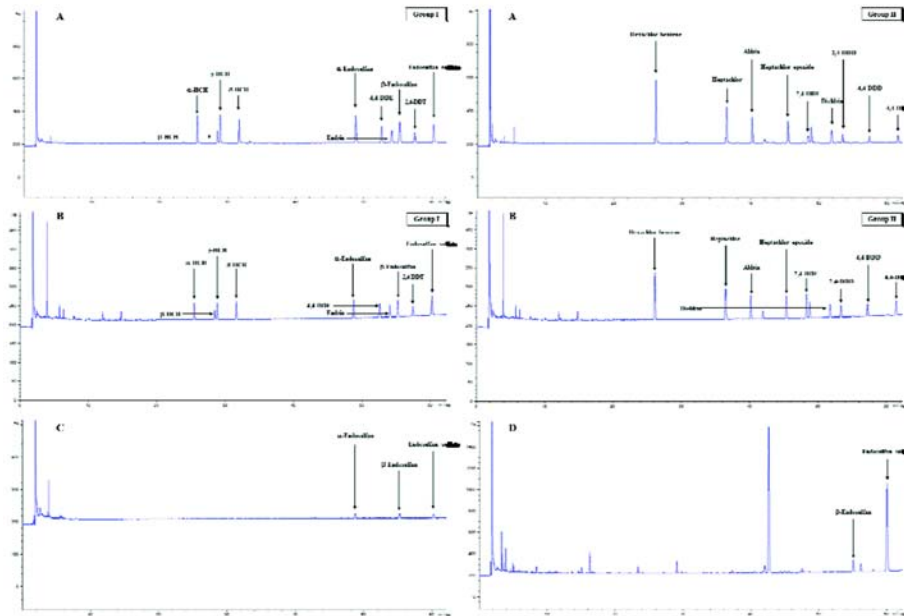


Fig. 2. Representative standard (A), soil recovery (B), crop recovery (C), and soil sample chromatogram (D) of residual organochlorine pesticides.

Table 3. Recovery, LOD, and RSD of residual organochlorine pesticides in soil

Pesticides	Recovery (%)		LOD ($\mu\text{g/kg}$)	RSD (%)	
	4 $\mu\text{g/kg}$	20 $\mu\text{g/kg}$		4 $\mu\text{g/kg}$	20 $\mu\text{g/kg}$
Group I					
α -HCH	88.6 \pm 2.4	90.4 \pm 2.8	0.05	2.7	3.1
β -HCH	98.4 \pm 3.0	102.4 \pm 2.4	0.07	3.0	2.3
γ -HCH	90.2 \pm 3.2	95.4 \pm 1.8	0.04	3.5	1.9
δ -HCH	88.2 \pm 2.2	84.3 \pm 2.6	0.04	2.5	3.1
α -Endosulfan	90.4 \pm 2.8	103.0 \pm 1.6	0.03	3.1	1.6
β -Endosulfan	100.3 \pm 2.2	102.3 \pm 3.2	0.02	2.2	3.1
Endosulfan sulfate	98.2 \pm 2.4	95.4 \pm 2.8	0.03	2.4	2.9
Endrin	90.4 \pm 1.4	94.4 \pm 2.6	0.03	1.5	2.8
4,4-DDE	96.4 \pm 2.6	94.6 \pm 3.0	0.03	2.7	3.2
2,4-DDT	88.4 \pm 2.2	92.4 \pm 2.4	0.04	2.5	2.6
Group II					
Aldrin	96.4 \pm 3.4	90.5 \pm 1.8	0.03	3.5	2.0
Dieldrin	86.4 \pm 2.4	88.6 \pm 2.2	0.03	2.8	2.5
HCB	76.5 \pm 3.4	82.6 \pm 1.8	0.02	4.4	2.2
Heptachlor	80.4 \pm 2.8	84.8 \pm 2.4	0.01	3.5	2.8
Heptachlorepoxide	88.2 \pm 2.2	83.6 \pm 3.4	0.03	2.5	4.1
2,4-DDD	92.7 \pm 3.0	83.7 \pm 2.8	0.03	3.2	3.3
2,4-DDE	84.8 \pm 2.2	79.6 \pm 1.6	0.03	2.6	2.0
4,4-DDD	82.4 \pm 2.5	86.4 \pm 3.2	0.08	3.0	3.7
4,4-DDT	90.4 \pm 2.4	80.4 \pm 2.0	0.03	2.7	2.5

α -endosulfan, β -endosulfan endosulfan sulfate가
 12.0, 53.1 329.8 $\mu\text{g}/\text{kg}$
 1/333
 (0.15, 0.10 0.15 $\mu\text{g}/\text{kg}$)
 α -endosulfan, β -endosulfan endosulfan
 sulfate 3

Notes

The author declare no conflict of interest.

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