

Article

Translocation of Endosulfan from Soil to Ginseng (*Panax ginseng* C. A. Meyer)

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Abstract: This study was conducted to examine the translocation of highly residual agrochemical in soil, the endosulfan (total), to ginseng (*Panax ginseng* C. A. Meyer). The soil with the level of the amount of 5.0 mg kg⁻¹ of endosulfan (total) was prepared in a Wagner pot into which the seedling of ginseng was transplanted and then the specimens of ginseng (root, leaf, and stem) were collected quarterly and analyzed through GC-MS. The level of residual of endosulfan (total) in the soil has decreased from 4.28 mg kg⁻¹ (April 2013) to 1.94 mg kg⁻¹ (December 2014) while the level in the specimens of leaf and stem of ginseng respectively sampled according to its growth phase in June and September from 2013 and 2014 showed an increase from 0.56 mg kg⁻¹ (June 2013) to 2.46 mg kg⁻¹ (September 2013) and decrease from 0.29 mg kg⁻¹ (June 2014) to 0.18 mg kg⁻¹ (September 2014). For the case of the root of ginseng, the level of the amount of 10.77 mg kg⁻¹ of endosulfan (total) was detected in June 2013 and then, the level has decreased to the level of 4.88 mg kg⁻¹ in December 2014. The translocation of residual endosulfan (total) in soil to ginseng with time was identified. The amount of residuals of α -endosulfan and β -endosulfan was also decreased with time however, the ratio of endosulfan-sulfate, the main metabolite, was gradually increasing. The retention of metabolite (endosulfan-sulfate) in soil identified thereby thus suggests the potential of its translocation to plants in the case of the soils containing the residual of endosulfan (total).

Keywords: agrochemical; endosulfan (total); ginseng; translocation

1. Introduction

The ginseng (*Panax ginseng* C. A. Meyer; hereinafter, ginseng) which is usually growing in semi-shady places frequently exhibits 38 kinds of disease and insect damage such as pythium rot or black shank etc. owing to moist environment and continuous cropping [1,2]. Thus, application of agrochemicals to the cultivation of ginseng would be unavoidable, however, the agrochemicals routinely used for the cultivation of plants are mostly introduced into soils irrespective of plants or targeted objects [3–6] and part of the agrochemicals that have fallen down onto soils and remain therein could be translocated into roots of plants [2]. Studies describing the transfer of pesticides into plants through their roots are important for the development and validation of plant uptake models allowing the prediction of contaminant accumulation, translocation, and transformation to edible parts of plants [7].

The number of cases of the survey on residual agrochemicals in soils for ginseng cultivation has been insufficient so far but, according to results of the survey conducted by National Agricultural

Products Quality Management Service, the incompatible residual agrochemicals of levels of 4.06% (2010), 4.07% (2011), and 5.87% (2012) were observed. Among the detected components of agrochemicals, the cypermethrin and tolclofos-methyl exceeded the limit of residual tolerance; and the components of agrochemicals like endosulfan and procymidone, of which production or sales was prohibited due to reasons of cancellation of registration etc., were also found [8]. Besides, the agrochemicals like tolclofos-methyl, endosulfan, and cadusafos were also detected from the monitoring of residual agrochemicals in soils of ginseng cultivation field conducted by National Institute of Agricultural Science and Technology; and according to results of the survey conducted by private institute, the main components such as endosulfan, fludioxonil, and cadusafos were also detected in which the occupancy of endosulfan (total) was prevalent.

Endosulfan, a broad spectrum cyclodiene subgroup of organochlorine pesticides, is widely used as a contact, stomach, and acaricide insecticide to control the pests of crops like cereal, oilseeds, coffee, vegetables, and food [9–11]. Many scientific reports attest that this compound is considered as a persistent organic pollutant throughout the world because it has been detected in various segments of the environment. Due to high persistence in the environment, it can easily bioaccumulate through the food chain and poses a risk of causing adverse effects to the environment and human beings [12]. Therefore, the application of endosulfan (total) to domestic edible plants has been prohibited since 2004. However, some agrochemicals containing it have been sold until December 2012 and since then the production and sales of all products containing endosulfan (total) have been completely cancelled [13,14]. Endosulfan (total) is a mixture of alpha and beta isomers and would create the principal metabolite, the endosulfan-sulfate, whose half-life ranges from 30 days to a maximum 6 years depending on the mixed ratio and environment [15]. Thus, the retention of endosulfan in soils of ginseng cultivation fields may induce the incompatibility of ginseng owing to the potential translocation of such component during the growing period of ginseng.

In this case, many reports proved that the endosulfan can translocate from the soil in the form of its isomers and metabolite (endosulfan sulfate) in different parts of the plants. For instance, Singh and Singh (2014) [12] found that a considerable amount of endosulfan isomers and metabolite in the root, stem and leaf matrix in various plants. Many scientists reported that the GC-MS has become a highly recommended tool for detecting trace levels of various pesticides including endosulfan in water, soil, plant, vegetables and fruits, etc., since it is found to be fast, easy to conduct, and used only small amount of reagents. Further, GC-MS provides good identification and quantification for the detection of pesticide residues in various samples. In relation to endosulfan, it has been determined the levels of endosulfan and its residues from soil and plant parts (including fruits and vegetables) by GC-MS analysis [16–20]. Thus, this study was designed to identify the translocation of mixed endosulfan (total) remaining in soils of ginseng cultivation through the analysis of specimens of root, leaf, and stem of ginseng collected quarterly in accordance with the growth phase of the seedling of ginseng transplanted onto the Wagner pot.

2. Materials and Methods

2.1. The Agrochemical

The contents and formulation of the agrochemical employed for the field test was the dusts of endosulfan 3% (Brand Name: Dongbang Agro Corporation, Seoul, Korea) of which physicochemical properties are as represented in Figure 1 and Table 1. The amount of 1000 mg kg⁻¹ for each reference material of α -endosulfan (Lot NO: CJ-1862), β -endosulfan (Lot NO: CJ-1833), and endosulfan-sulfate (Lot NO: CJ-1861) from Ultra scientific (North Kingstown, RI, USA) was employed for the analysis. The purity of each pesticide was 100%.

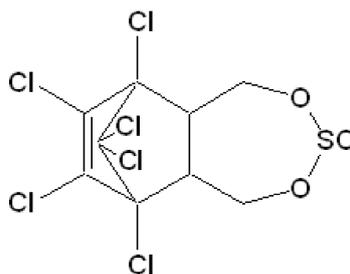


Figure 1. Chemical structure of endosulfan.

Table 1. Physicochemical properties of endosulfan.

Formular	Mol.wt.	M.P.	Kow logP	Activity
C ₉ H ₆ Cl ₆ O ₃ S	406.9	≥80 °C (tech); α- 109.2 °C; β- 213.3 °C	α- = 4.74; β- = 4.79 (both at pH 5, 22 °C)	Insecticide

2.2. Soil of Experimental Field

For the field test, the ginseng cultivation field of the Ginseng and Medicinal Herb Station of Gangwondo Agricultural Research and Extension Services located in the Cheolwon County was rented and the physicochemical properties of the soil (the level of detected endosulfan (total) was less than 0.001 mg kg⁻¹) are as summarized in Table 2.

Table 2. Physicochemical properties of experimental field.

pH (1:5)	OM1 (g kg ⁻¹)	Ca (cmol (+) kg ⁻¹)	K (cmol (+) kg ⁻¹)	Mg (cmol (+) kg ⁻¹)	Na (cmol (+) kg ⁻¹)	P ₂ O ₅ (mg kg ⁻¹)	NO ₃ (mg kg ⁻¹)	Sand (%)	Silt (%)	Clay (%)	Soil Texture
6.91	22.88	5.44	0.54	0.90	0.07	120.08	5.69	55.9	38.4	5.8	SL2

OM: organic matter; SL: sandy loam.

2.3. Preparation of the Mixture of Endosulfan (Total) and Transplantation of Seedling of Ginseng

The predetermined amount of product dusts of endosulfan 3% was mixed with soils to the extent of 5.0 mg kg⁻¹ in content and the mixture was put into Wagner pot and then the one-year-old seedling of ginseng (the species of Yeonpoong of which content of endosulfan (total) less than 0.001 mg kg⁻¹ was verified) was transplanted during 6~7 April 2013. The Wagner pot then buried into the soil of cultivation field to the predetermined depth.

2.4. Collection of Specimens of Soil and Ginseng (Leaf, Stem, and Root)

The specimens of soils were collected right after the preparatory mixing with the agrochemical dusts (7 April 2014) to check the concentration therein; and the specimens of ginseng (leaf, stem, and root) were collected quarterly in accordance with the growth phase of ginseng to check the translocation of endosulfan (total) contained in the soil (June 2013, September 2013, December 2013 (leaf and stem were excluded), March 2014 (leaf & stem were excluded), June 2014, and December 2014 (leaf and stem were excluded)).

2.5. Pretreatment of Specimens and Instrumental Analysis

2.5.1. Extraction and Refinement of Endosulfan (Total) from Soil Specimens

The amount of 0.2 N NH₄Cl 30 mL was applied to the 50 g of soil specimen and then settled for 30 min. Thereafter, 100 mL of acetonitrile was applied thereto and shook for 1 h to extract the

soil specimen. Then the applied acetonitrile was filtrated under reduced pressure and subsequently, the residual was concentrated under reduced pressure again. The 100 mL of distilled water and 50 mL of saturated brine were following applied to the concentrated residue and again, it was concentrated under reduced pressure after it was divided twice by applying 50 mL of *n*-hexane to each division. Finally, the concentration was resolved by applying 10 mL of *n*-hexane 10 mL. Thereafter, the solid phase extraction (SPE) Florisil Cartridge (Merck, Darmstadt, Germany) (1 g) was pre-washed with 5 mL of *n*-hexane and drained off by applying 10 mL of resolved specimen; and then the endosulfan (total) was eluted by using the 4 mL of mixed liquor (*n*-hexane:acetone = 70:30 (*v/v*)). The eluted solution was concentrated again under reduced pressure and then resolved again by applying 10 mL of acetone and thereafter, the resolved solution was analyzed through gas chromatography-mass spectrometry (GC-MS Agilent 7890, Agilent, Santa Clara, CA, USA). The conditions applied to the instrumental analysis are as summarized in Table 3.

Table 3. GC-MS operation conditions for endosulfan (total) in soil and ginseng (root, leaf-stem) samples.

Instrument		GC-MS 5975C (Agilent, Santa Clara, CA, USA)	
Column		DB-5MS (30 m × I.D. 0.25 mm, 0.25 μm)	
Temp.	Inlet	270 °C	
	Oven	100 °C (2 min hold) → increased at 20 °C min ⁻¹ to 280 °C (19 min hold)	
	Detector	300 °C	
Flow rate	1.0 mL min ⁻¹ (He)		
Injection volume	1 μL		
Split ratio	Splitless mode		
Mass range (<i>m/z</i>) (SIM1) mode)	α-Endosulfan	195, 237	
	β-Endosulfan	195, 237	
	Endosulfan-sulfate	272, 387, 422	

SIM: Selected ion monitoring.

2.5.2. Extraction and Refinement of Endosulfan (Total) from Specimens (Leaf, Stem, and Root) of Ginseng

The specimens of ginseng were divided into aerial and radix parts to examine the endosulfan (total) translocated and absorbed into ginseng from the soil. 100 mL of acetonitrile was commonly applied to each specimen of ginseng (20 g of root added with 20 g of NaCl and 10 g of leaf and stem) and the specimens were shaken for approx. 30 min at 200 rpm (Shaker: Lab. Companion IS-971R, Jeio Tech, Seoul, Korea). The shaken specimens were then ground in the fine cutter for 2 min at 1000 rpm and then, the acetonitrile contained in the resulted extract was filtrated under reduced pressure. Thereafter the remaining extract was concentrated again under reduced pressure. The 100 mL of distilled water and 50 mL of saturated brine were then applied to the concentrated residue and afterwards it was concentrated under reduced pressure after it was divided three times by applying 50 mL of dichloromethane to each division. Thereafter, the concentration was resolved by applying 10 mL of dichloromethane 10 mL. Subsequently, the SPE Cartridge (Phenomenex, Torrance, CA, USA) filled with 1 g of NH₂ was pre-washed with 5 mL of dichloromethane and drained off by applying 10 mL of resolved specimen; and then the endosulfan (total) was eluted by applying the 4 mL of mixed liquor (dichloromethane:methanol = 95:5 (*v/v*)). The eluted solution was concentrated again under reduced pressure and then resolved again by applying 4 mL of acetone. Thereafter, the resolved solution was analyzed through GC-MS. The conditions applied to the instrumental analysis are identical to those applied to the analysis of specimens of soils (Table 3). GC-MS total ion chromatogram of endosulfan in soil, ginseng leaf-stem and root samples are shown in Figure 2.

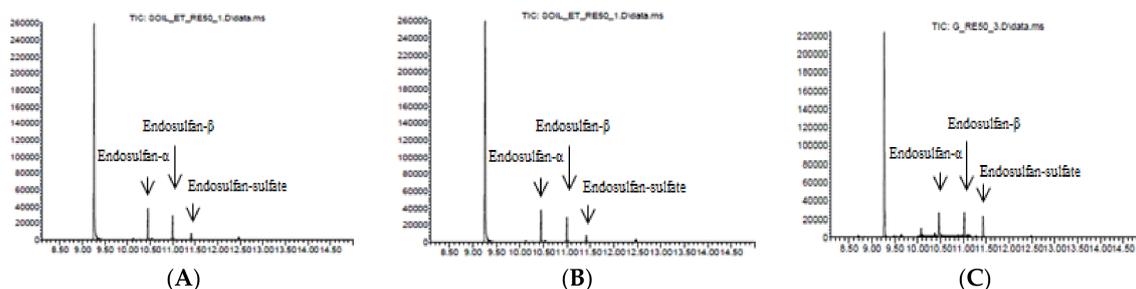


Figure 2. GC-MS total ion chromatogram of endosulfan in soil, ginseng leaf-stem, root samples (fortification level: $LOQ \times 50$). ((A) Soil samples; (B) ginseng leaf-stem samples; (C) ginseng root samples).

2.6. Recovery of Endosulfan (Total) from Specimens of Soil and Ginseng (Leaf, Stem, and Root)

The level of 10 times (0.2 mg kg^{-1}) and 50 times (1.0 mg kg^{-1}) of the limit of quantitation (LOQ) of reference material were prepared and mixed uniformly with specimens of non-treated soil and ginseng (root, leaf, and stem) to obtain each recovery through above analysis conducted for three times at each treatment level.

3. Result and Discussions

3.1. Standard Calibration Curve of Endosulfan (Total)

The reference materials (α -endosulfan, β -endosulfan, and endosulfan-sulfate) of each amount of 1000 mg kg^{-1} of targeted agrochemical were taken and diluted stepwise to draw the standard calibration curve for the quantitation of endosulfan (total) contained in specimens of the soil and ginseng (root, leaf, and stem). The reference materials diluted stepwise and non-treated specimens extracted through identical methods of analysis used in this study were mixed in the ratio of 1:1 to take the matrix effect into account and thereby the matrix matched standard calibration curves were drawn. The resulted all correlation coefficients (R^2) between the amount of reference materials and peak area showed the linearity of over 0.99 and thus the analysis employed in this study for the quantitation of pesticide was validated.

3.2. Limit of Quantitation and Recovery of the Analysis

The resulted LOQ of endosulfan (total) was 0.02 mg kg^{-1} ; and recoveries of specimens of the soil (83.3~95.6%), leaf and stem of ginseng (74.5~103.1%), and root of ginseng (79.3~112.5%) were all fell into the range of effective recovery (70.0~120.0%) with analytical error less than 10% thus the analysis employed in this study was also validated (Table 4).

3.3. Translocation Characteristics of Endosulfan (Total) in Soil to Leaf, Stem, and Root of Ginseng

3.3.1. Retention of Endosulfan (Total) in Soil

The residual amounts of endosulfan (total) in soil are presented in Figure 3. In this study, initial level of retention of endosulfan (total) in soil in April was 4.28 mg kg^{-1} which was an approximation to the level of artificial treatment (5.0 mg kg^{-1}), and the retention measured by each quarter were 4.17 mg kg^{-1} (June 2013) and 1.94 mg kg^{-1} (December 2014) showing a decreasing tendency (but insignificant) after a certain duration of time. The level of retention of α -endosulfan and β -endosulfan has decreased but the level of retention of endosulfan-sulfate which is the main metabolite showed temporary increase followed by subsequent decrease. Endosulfan is stable in light and its solubility in water is low (α -endosulfan 0.32 mg L^{-1} , β -endosulfan 0.33 mg L^{-1}) [1]. The level of its coefficient of adhesion to soil is approx. 11,000 and thus it tends to be remaining in soil strongly and would generate

its metabolite, the endosulfan-sulfate, through the oxidation of sulfur contained therein induced by microbes [15,21]. The decomposition half-life of endosulfan (total) varies according to ratio of isomers and environment and, depending on the process of metabolism, the length of half-life spans from 30 days to maximum 6 years [22,23]. Further, environmental factors such as concentration, ionic strength, pH, surface loading, type of sorbent, and time also all affect the type of sorption complex [24]. Thus, the level of retention of endosulfan (total) in soil may decrease continuously due to its physicochemical properties, however, the resulting consequence of decrease in level of retention is expected to be insignificant.

Table 4. Typical recoveries and limit of quantitation for endosulfan (total) in soil and ginseng (root, leaf-stem) samples.

Matrixes	Agrochemicals	Fortification Level (mg kg ⁻¹)	Mean ± CV (%)	LOQ (mg kg ⁻¹)
Soil	alpha	0.2	95.6 ± 1.7	0.02
		1.0	90.7 ± 2.3	
	beta	0.2	91.9 ± 2.3	
		1.0	83.3 ± 2.2	
	sulfate	0.2	85.3 ± 4.8	
		1.0	93.4 ± 4.1	
Ginseng root	alpha	0.2	85.2 ± 3.8	
		1.0	79.3 ± 0.5	
	beta	0.2	93.5 ± 0.9	
		1.0	83.4 ± 0.6	
	sulfate	0.2	112.5 ± 0.6	
		1.0	97.1 ± 0.3	
Ginseng leaf-stem	alpha	0.2	103.1 ± 7.6	
		1.0	81.8 ± 2.5	
	beta	0.2	79.3 ± 5.0	
		1.0	75.1 ± 2.7	
	sulfate	0.2	80.4 ± 4.5	
		1.0	74.5 ± 3.8	

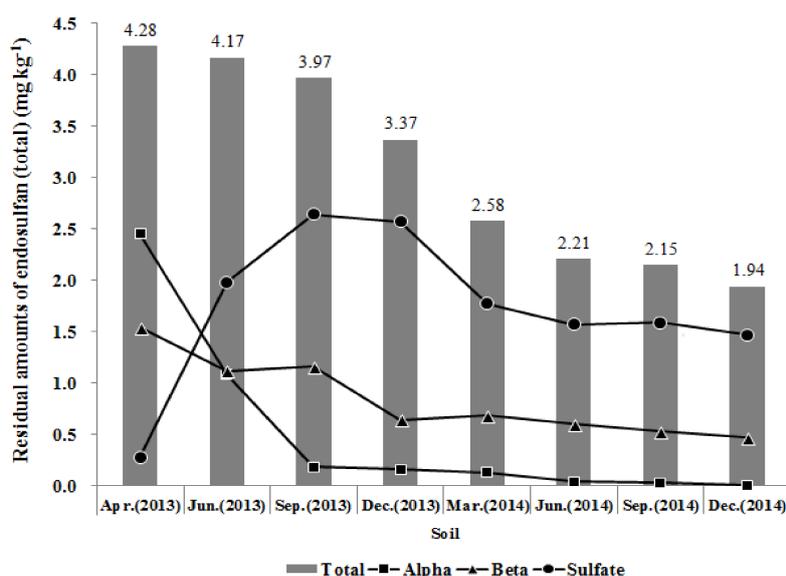


Figure 3. Residual amounts of endosulfan in soil samples.

3.3.2. Retention of Endosulfan (Total) in Leaf and Stem of Ginseng

The specimens of ginseng were divided into aerial and radix parts to examine the translocation of endosulfan (total) from soil to ginseng. The average weight leaf and stem of ginseng and residual amounts of endosulfan (total) in soil are shown in Figure 4A,B. Specimens of the leaf and stem of ginseng were collected in June and September by taking the growth phase of ginseng into account, and the analyzed level of retention of endosulfan (total) were initially 0.56 mg kg⁻¹ (June 2013) and 2.46 mg kg⁻¹ (September 2013) and then they became 0.29 mg kg⁻¹ (June 2014) and 0.18 mg kg⁻¹ (September 2014). The level of retention of endosulfan (total) in the specimens of leaf and stem of ginseng collected in 2013 tended to increase but, the level of retention of endosulfan (total) in the specimens of leaf and stem of ginseng collected in 2014 was lower than the specimens collected in 2013. Besides, the specimens collected in September in 2013 and in 2014 were concluded that they would be inappropriate to derive tendencies of the varied retention of endosulfan (total), therefrom, because the early defoliation owing to the growth phase of ginseng coincided with the season. However, the specimens collected in June 2013 and in 2014 revealed the varied level of retention of endosulfan (total) in specimens collected in 2014 decreased by approx. twice as much as the level of retention of endosulfan (total) in specimens collected in 2013. Consequently, it concluded that it would be attributable to the growth of the aerial part of ginseng from the second to the third year resulted in increased length and width (plant height, stem length, stem diameter, leaf area, etc.).

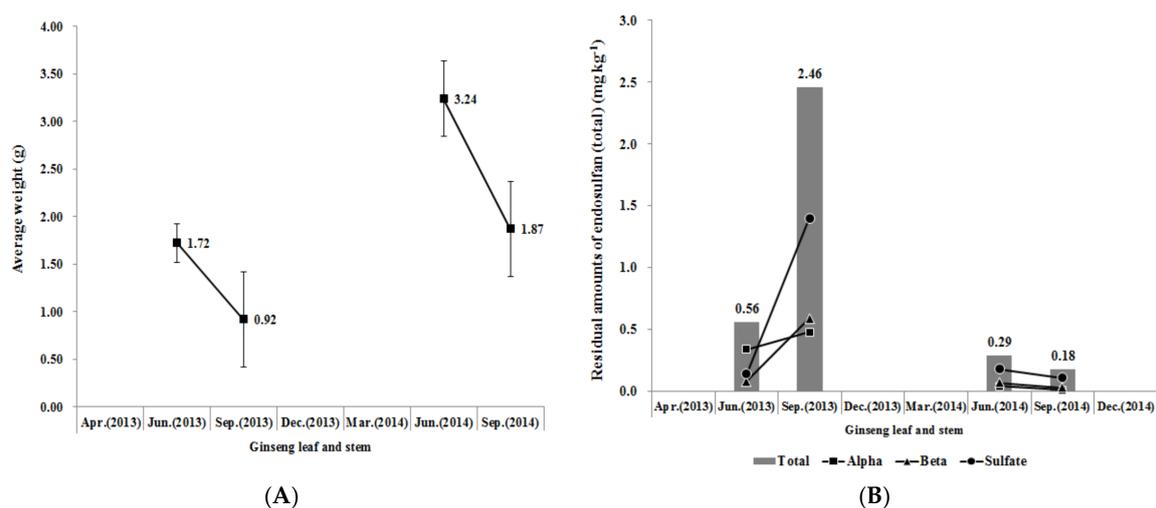


Figure 4. (A) Variation of ginseng leaf-stem samples weight during experimental periods and (B) residual amounts of endosulfan in ginseng leaf-stem samples. (Total: alpha (mg kg⁻¹) + beta (mg kg⁻¹) + sulfate (mg kg⁻¹)).

3.3.3. Retention of Endosulfan (Total) in Root of Ginseng

The level of retention of endosulfan (total) in specimens of the root of ginseng was as illustrated in Figure 5A,B. The specimen of the root of ginseng collected in 2013 tended to show the increase in level of retention of endosulfan (total). The level of retention of α -endosulfan and β -endosulfan have decreased with time, but the level of retention of endosulfan-sulfate, the main metabolite, showed an increase followed by subsequent decrease with time. The level of retention of endosulfan (total) in specimens of the root of ginseng collected in March 2013 showed the level similar to that of the specimen collected in December 2013 that was rapidly decreased in the specimen collected in June and kept decreasing thereafter. The initial level of retention of endosulfan (total) in the specimen of the root of ginseng collected in June 2013 was higher than that of the treatment in soil (5.0 mg kg⁻¹). During the period from the transplantation of seedling of ginseng to June is a season provided with the best conditions of temperature and light for the growth phase of ginseng by which the foliage in stem and

development in root are actively realized (Poong-gi Ginseng Cultivation Field, Agricultural Research Institute, Gyeongsangbukdo Province, 2011). Thus, the high level of retention of endosulfan (total) in the root of ginseng was concluded to be attributable to the co-translocation and co-absorption of the endosulfan (total) with lots of nutrients into the root of ginseng by the active growth phase of ginseng. In addition, the low solubility in water and high coefficient of adhesion of endosulfan (total) together with poor drainage in the cultivation pot comparing to general conditions of the cultivation of ginseng were also concluded to be attributable to the continuous retention of endosulfan (total) adsorbed into soil around the root of ginseng away from the eluviation of endosulfan (total) to the underground.

The increase in the ratio of endosulfan-sulfate appeared during the cultivation period in 2013 (the first year) was concluded to be attributable to its physicochemical properties lengthening half-life through metabolism [22,23]. The retention of agrochemicals is expressed by the amount of agrochemical per weight of specimen and thereby, the level of retention of agrochemicals would be diluted with the thickening growth of specimens [25,26]. Also, in the case of disturbed growth of crops, the agrochemicals absorbed into crops would be concentrated and thereby could affect the concentration of agrochemicals to be detected. Park et al. have examined the translocation and absorption of endosulfan into crops and reported that larger amount of agrochemicals had translocated and detected from small sized crops experienced delayed growth comparing to other crops of which biomass grew rapidly. The level of growth of crops with the concentration of endosulfan (total) in soil of 0.5 mg kg^{-1} by the treatment was 74.2% comparing to that of crops from the soil of non-treatment of endosulfan (total), and the growth of crops became gradually reduced along with the increase in concentration of endosulfan (total). Ginseng is one of the perennial growing slowly by which the weights of root measured during the first year of growth under test cultivation were 0.78 g (April), 1.63 g (June), 2.80 g (September), and 2.45 g (December) and these measurements also revealed the slightly decreasing trend of weight on entering into the resting stage (November~March). The dilution effect of endosulfan (total) in the root of ginseng owing to the thickening growth would be insignificant but the decrease in moisture content in the resting stage might have influenced on the detected concentration of endosulfan (total). The measured level of retention of endosulfan (total) in the root of ginseng varied during the period of 2014 (the second year from transplantation) showed significant decrease from 19.27 mg kg^{-1} (March 2014) to 5.30 mg kg^{-1} (September 2014). This was concluded to be attributable to the weight gain typically seen in the growth phase of ginseng from the second to the third year together with the internal decomposition of endosulfan (total).

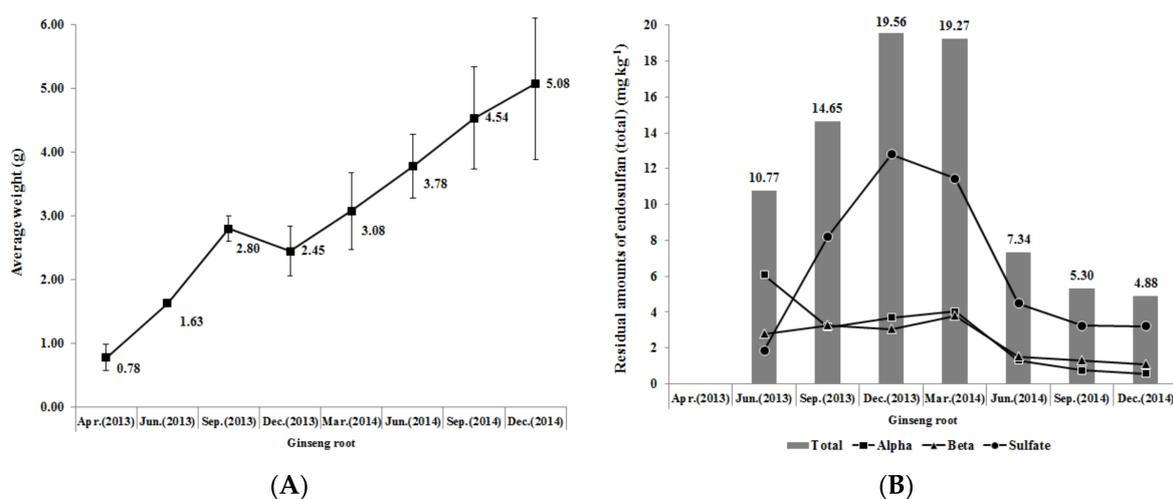


Figure 5. (A) Variation of ginseng root samples weight during experimental periods; and (B) residual amounts of endosulfan in ginseng root samples. Total: alpha (mg kg^{-1}) + beta (mg kg^{-1}) + sulfate (mg kg^{-1}).

4. Conclusions

Endosulfan (total) is the non-systemic agrochemical and has been known to be mainly present within 10 cm in depth of soil layer [27,28] with its value of Koc of 7100~12,100 to soil that corresponds to the non-mobile class (Koc > 4000) in the standard of classification of mobility specified by the SSLRC (Soil Survey and Land Research Center, Cranfield, UK). It also corresponds to the immobile class (Koc > 5000) in the standard of classification of mobility specified according to values of Koc by McCall, Swann, Laskowski, Unger, Vrona, and Dishburger [29] which is typically regarded as one of the most immobile agrochemicals [28]. Therefore, by the low immobility of endosulfan (total) owing to its high adsorption to soil [28,30,31], the probability of direct translocation of endosulfan (total) to crops would be low. However, according to previous studies examined the translocation of endosulfan in soil to crops, the cases of translocation of endosulfan to crops were reported [14,27,32]. In this study, the translocation characteristics of endosulfan (total) in soil to ginseng (leaf, stem, and root) were assessed and found the level of retention of α -endosulfan and β -endosulfan in soil has decreased along with time together with the level of retention of the endosulfan-sulfate in soil, the main metabolite, tended to be increasing gradually in the soil along with time and then consequently translocated into ginseng. The endosulfan (total) was detected from specimens of leaf and stem of ginseng away from the contact with ground and thereby evidenced the translocation of endosulfan (total) remained in the soil to the crop definitely. The use of endosulfan (total) has been prohibited since 1994 but still, the maximum residue limit (MRL) of endosulfan (total) in ginseng is not defined yet thus the ginseng correspond to cases of the detection of endosulfan (total) has to be classified into an inappropriate agricultural product. Therefore, the level of residual concentration of endosulfan (total) in soil that is unable to be detected from ginseng through potential translocation should be identified in advance to produce ginseng safely from endosulfan (total) remaining in soil. This could also contribute to the safe control of endosulfan (total) in soils of fields predetermined for the cultivation of ginseng.

Furthermore, the present study suggests that the pollutant from soil accumulator plants (plant-based bioremediation techniques) can be employed for decontamination of endosulfan and other pesticides in polluted sites.

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Conflicts of Interest: The authors declare no conflict of interest.

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