# Fate of endosulfan in ginseng farm and effect of granular biochar treatment on endosulfan accumulation in ginseng

Deuk-Yeong Lee[a,†], Geun-Hyoung Choi[b,†], Young-Suk Bae[c], Sung-Woo Lee[c], Sang-Kuk Kim[c], Ji-Yeon Bae[a], A-Reum Song[b], Bo-Yeon Moon[b], David Megson[d], Kyeong-Yeol Oh[a], Jin-Hyo Kim[a,*]

[a] *Department of Agricultural Chemistry, Institutes of Agriculture and Life Science (IALS), Gyeongsang National University, Jinju, 52828, Republic of Korea*
[b] *Chemical Safety Division, National Institute of Agricultural Sciences, RDA, Wanju, 55365, Republic of Korea*
[c] *Department of Herbal Crop Research, National Institute of Horticultural and Herbal Science, RDA, Eumsung 27709, Republic of Korea*
[d] *Ecology and Environment Research Centre, Manchester Metropolitan University, Manchester, M15GD, United Kingdom*

[†] Lee DY and Choi GH equally contributed as first author

[*] Corresponding author; Kim J-H,
E-mail: jhkim75@gnu.ac.kr, Tel.+82-55-772-1961, Fax. +82-55-772-1969
ORCID: orcid.org/0000-0002-0341-7085

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## Abstract

Endosulfan was widely used as an insecticide in the agricultural sector before its environmental persistence was fully understood. Although its fate and transport in the environment have been studied, the effects of historic endosulfan residues in soil and its bioaccumulation in crops are not well understood. This knowledge gap was addressed by investigating the dissipation and bioaccumulation of endosulfan in ginseng as a perennial crop in fresh and aged endosulfan-contaminated fields. In addition, the effect of granular biochar (GBC) treatment on the bioaccumulation factor (BAF) of endosulfan residue in ginseng was assessed. The 50% dissipation time ($DT_{50}$) of the total endosulfan was over 770 days in both the fresh and aged soils under mulching conditions.; This was at least 2-fold greater than the reported (6->200 days) in arable soil. Among the endosulfan congeners, the main contributor to the soil residue was endosulfan sulfate, as observed from 150 days after treatment. The BAF for the 2-year-old ginseng was similar in the fresh (1.682-2.055) and aged (1.372-2.570) soils, whereas the BAF for the 3-year-old ginseng in the aged soil (1.087-1.137) was lower than that in the fresh soil (1.771-2.387). The treatment with 0.3 wt% GBC extended the $DT_{50}$ of endosulfan in soil; however, this could successfully suppress endosulfan uptake, and reduced the BAFs by 66.5-67.7% in the freshly contaminated soil and 32.3-41.4% in the aged soil. Thus, this adsorbent treatment could be an effective, financially viable and sustainable option to protect human health by reducing plant uptake of endosulfan from contaminated soils.


**Keywords:** Endosulfan, Carbonaceous adsorbent, Ginseng, Perennial crop, Bioaccumulation

## Introduction

Endosulfan is an organochlorine pesticide with a broad insecticidal spectrum that has been used widely in the agricultural field since the 1950s (Lubick 2010; Weber et al., 2010). It is present in the environment in the form of two stereoisomers (α- and β-endosulfans) and a biological metabolite (endosulfan sulfate) (Kapsi et al., 2019; Vaikosen et al., 2019). The Stockholm Convention has classified endosulfan as a persistent organic pollutant (POPs) due to its persistence, long-range transport, and high bioaccumulation properties (Bruce-Vanderpuije et al., 2021; Choi et al., 2021; Sathishkumar et al., 2021). Most countries have banned the production and use of endosulfan a decade ago, however, it is still frequently detected in the air, water, and soil environment (Oh et al., 2020; Bruce-Vanderpuije et al., 2021). The reported 50% dissipation time ($DT_{50}$) in soil is 4 to 75 days, 4 to 376 days, 26 to 200 days, and 6 to >200 days for α-endosulfan, β-endosulfan, endosulfan sulfate, and total endosulfan, respectively (Ntow et al., 2007; Weber et al., 2010; Vaikosen et al., 2019). Although the underlying reasons behind the wide ranges of the $DT_{50}$ in soil are unclear, the reason was believed to be the leaching potential and varying microbial degradation activity in different soils and crop cultivation practices (Ghadiri et al., 2001; Grondona et al., 2014; Oh et al., 2020; Singh and Singh 2008). Among the crop cultivation practices, tillage and mulching are directly affected to the soil condition. Mulching which is prevalent in arable crop cultivation to prevent nutrient erosion and weed development can change the soil environment such as temperature, moisture, microbial, and leaching of nutrients and pollutants (Abbas et al., 2020; Chalise et al., 2020; Mwango et al., 2016; Parsottambhai and Rawat, 2020). However, the mulching effect during crop cultivation was not accounted for in the $DT_{50}$ and bioaccumulation of organic pollutants, such as endosulfan and other POPs.

Environmental residues of endosulfan and accumulation in food crops are important potential points to enter the human food chain. However, the residue safety in crops has not previously been considered deeply.This may be because the residue had been supervised as the registered pesticide before the ban and the exposure risk from the environmental contamination would be underestimated due to the low estimated bioaccumulation factor (BAF) in crops (Mitton et al., 2016; Vaikosen et al., 2019). To date, the BAFs has been reported at <0.001 in grains, 0.013–0.047 in leafy vegetables, 0.008–0.285 in root vegetables and 0.001–0.136 in fruit vegetables (Choi et al., 2017, 2018a, 2018b; Hwang et al., 2015, 2016, 2018; Vaikosen et al., 2019). These values are comparatively lower than BAFs in animals, such as 2628–3278 in plankton, 2429–11583 in fish, and 0.53–2.62 in chickens (Brinati et al., 2016; DeLorenzo et al., 2002; Fang et al., 2018; Negro et al., 2012; Sathishkumar et al., 2021; Toledo and Jonsson 1992). Existing studies have focused on short-term cultivated crops however, the BAF of endosulfan in a perennial crops needs establishing as these have along exposure period and potent biological stability (Kim et al. 2018; Oh et al. 2020). Kim et al. (2018) reported the BAF (1.238–4.570) of endosulfan in the root of ginseng in freshly applied farm soil, and Oh et al. (2020) reported the field-surveyed plant uptake factor of endosulfan (0.243–1.708) in ginseng root. However, these reported BAFs in crops were mostly studied in freshly contaminated soil; hence, the aging factor of historic endosulfan in the environment was not considered (Hwang et al., 2018, 2020; Mukherjee. 2012; Ntow et al., 2007; Tariq et al., 2006). The ban on the use of endosulfan, which was implemented a decade ago, may lead to variations in the liability, half-life, and BAFs of endosulfan in fresh and aged endosulfan-contaminated soils. Such variations necessitate research to establish the fate and bioaccumulation of legacy endosulfan during perennial crop cultivation.

Ginseng is a widely cultivated perennial root vegetable known as a healthy food crop (Oh et al., 2014; Pan et al., 2021; Song et al., 2019). On a farm, one-year-old ginseng is transplanted and cultivated for more than three years under shade (Fig. S1). The root growth in 4-year-old ginseng was approximately 80% of the 6-year-old root (Choi et al., 2007; Jin et al., 2009; Kim et al., 2020), and 3- and 4-year-old ginseng is typically available commercially. However, endosulfan is one of the most frequently detected pesticide and a big concern due to the persistent historic residues in soil and the relatively high BAF in ginseng (Kim et al., 2018; Oh et al., 2020). The best option for the reduction of endosulfan residue in ginseng would be the reduction and removing the residue in soil environment, however, it is not practical or financially feasible in agriculture. Hence, the need for investigations on immobilization practices to reduce the uptake of endosulfan residues from soils and facilitate an environmental-friendly and economically viable residue reduction in perennial crops.

The application of carbonaceous adsorbents, such as activated carbon and biochar, in farmland has been considered a priority to reduce the uptake of organic contaminants by crops (Khan et al., 2015; Kroulikova et al., 2019; Mishra and Patel, 2008; Ponnam et al., 2020). Some researchers have demonstrated the positive effect of carbonaceous adsorbent treatment to suppress endosulfan uptake in short-term cultivated crops (Choi et al., 2018b; Hwang et al., 2020; Lee et al., 2021). Since carbonaceous adsorbents can adsorb endosulfan, it will also inhibit leaching and increase the retention of residues in the soil (Ahmad, 2019; Choi et al., 2018b; Qian et al., 2017; Hwang et al. 2020). The use of adsorbents may also result in differences in bioaccumulation by the perennial and short-term cultivated crops.

This manuscript aims to better understand the effects of granular biochar (GBC) treatment on endosulfan accumulation in a perennial crop (ginseng). This was achieved by; assessing the dissipation of endosulfan residues in a ginseng cultivation farm soil with or without GBC, determining the endosulfan residues and the BAF in ginseng grown in soil with or without GBC, and establishing the effect of biochar treatment on the BAF of endosulfan in ginseng. Studies were also preformed to understand how these factors varied based upon whether the endosulfan was recently, or historically applied to the soil.

## Materials and Methods

### *Chemicals and Standards*

The analytical standards for the quantitative analysis for α-endosulfan, β-endosulfan and endosulfan sulfate were from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Technical endosulfans as 3% dustable powder (FarmHannong, Seoul, Korea) for field trials and 35% emulsifiable concentrate (SG Hankook Samgong, Seoul, Korea) for the adsorption kinetics were used. Acetone, acetonitrile, n-hexane, dichloromethane (DCM), sodium chloride (NaCl), magnesium sulfate ($MgSO_4$) anhydrous, trisodium citrate, and dispersive solid phase extraction (dSPE) for primary-secondary-amine (PSA) and $C_{18}$ were purchased from Merck (Darmstadt, Germany).

### *Physico-chemical property analysis of the granular biochar (GBC)*

Thermally activated oak biochar was purchased from Hongcheon-Charcoal Co. (Hongcheon, Korea) and 0.5-2 mm size of the GBC was used for the experiment. The GBC was dried at 120 $^{o}$C for 72 h before the adsorption experiment and the application to soil. EC and pH of the GBC were measured using a pH meter (Jenway 3540, Bibby Scientific Ltd., UK) and an EC meter (WalkLAB, Trans Instruments, Singapore) with a 5.0 g of the GBC suspended solution in 100 mL $dH_2O$. The total pore volume and the surface areas of the GBC were analyzed with ASAP2020 (Micromeritics Instrument Co., Norcross, GA, USA). The GBC's CHNO element was analyzed by dry combustion (CHN628, Leco Co., MI, USA). The analyzed properties of the GBC were described in Table 1.

***Soil preparation for plant uptake experiment***

The ginseng cultivation soil was spiked with endosulfan to a concentration of 0.15 mg $kg^{-1}$ and 1.5 mg $kg^{-1}$ with 3% dustable powder of the commercial endosulfan. These low (0.15 mg $kg^{-1}$) and high (1.5 mg $kg^{-1}$) endosulfan residue test plots were classified into two subgroups; with soil aging or without soil aging for eight months. The fresh test plots for FLL (fresh low level) and FHL (fresh high level) were prepared without soil aging and the young ginseng was transplanted right after endosulfan spike, while the aged test plots for ALL (aged low level) and AHL (aged high level) were prepared for eight months after endosulfan treatment with mixing and ploughing the field then transplanted the young ginseng in March. All the plots were covered with dried rice straw and installed plastic shade after the transplantation (Fig. S1). The endosulfan residue for the initial concentration was analyzed with the soil sample at the ginseng transplanting day. Each replication plot size for the ginseng cultivation was 1.62 $m^2$ (1.8 m × 0.9 m), and 30 replicates were performed for the test plot. The 0.3wt% GBC treated plots were prepared with 2.9 kg of the dried GBC for each plot, and the GBC was treated on the same day on the endosulfan treatment for the fresh plot and five months later from the endosulfan treatment for the aged plot.

A total of 2 kg of soil was collected at a depth of 20 cm from three randomly selected points in each of the test plots. The soil was homogenized after the drying under fume hood for 5 days, then the analytical sample was taken from below 2 mm. The physicochemical soil properties of the test plot were measured, and the results were described in Table 2. The 3 kg root of ginseng was harvested once a year. The ginseng was gently washed under running water to remove soil then blended with dry ice. The ground samples were stored at -20 °C before extraction and sample preparation for endosulfan analysis.

***Endosulfan adsorption properties for GBC***

The adsorption characteristics of GBC to endosulfan were evaluated using Langmuir adsorption isotherm equations. 35% emulsifiable concentrate of endosulfan was used for the adsorption experiment. GBC (0.05 g) was added to a 100 mL solution of different initial concentrations of endosulfan (50 - 350 mg $L^{-1}$) and equilibrated at 24°C for 24 h at 150 rpm. The equilibrated endosulfan solution (50 mL) was extracted three times with DCM then concentrated under nitrogen. The concentrated solution was redissolved in 1.0 mL acetone and analyzed by GC-MS. The endosulfan adsorption property of GBC was fitted by Langmuir equation (Lee et al. 2021). The linearization of the equation can be expressed in the following equation (Eq.1) :

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{Kq_{max}} \qquad \text{(Eq. 1)}$$

$C_e$ (mg $L^{-1}$) is equilibrium concentration, $q$ (mg $g^{-1}$) is the amount of adsorbate on the per gram of the adsorbent at equilibrium, $q_{max}$ is the maximum adsorption capacity (mg $g^{-1}$), K is the constant related to the energy of adsorption (L $mg^{-1}$).

***Endosulfan Residue Analysis***

The analysis of endosulfan residues in soil and ginseng was followed the previously reported method by Bruce-Vanderpuije et al. (2021). For the soil sample, 5.0 g sample was added 2.0 g $MgSO_4$, 0.5 g NaCl, and 0.5 g trisodium citrate and extracted with 10 mL acetonitrile by shaking at 180 rpm for two hours with sonication for 15 min. The extracts were centrifuged, and 6.0 mL supernatant was taken and concentrated under nitrogen. The concentrate was redissolved with 1.0 mL of acetonitrile. 150 mg $MgSO_4$, 25 mg $C_{18}$ and 25 mg PSA were added to the redissolved solution then vortexed and filtered with 0.22 μm syringe filter. The filtered solution was analyzed with GC-μECD (Agilent 7890B, Agilent Technologies, Inc. Santa Clara, CA, USA) and the instrument conditions were described in Table S1. For the ginseng sample, 10.0 g of ground ginseng was added 4.0 g $MgSO_4$, 1.0 g NaCl and 1.0 g trisodium citrate, then shaked at 200 rpm with 10 mL of acetonitrile for two hours and sonicated for 15 min. The extract was centrifuged then 5.0 mL of the supernatant was concentrated under nitrogen. The concentrate was redissolved with 1.0 mL acetonitrile and extracted with the mixture of 150 mg $MgSO_4$, 50 mg PSA, and 50 mg $C_{18}$. The extract was filtered with 0.22 μm syringe filter, and analyzed by GC-MS (QP-2020, Shimadzu Co., Kyoto, Japan). The instrument conditions of GC-MS were described in Table S2. The endosulfan residue analysis in soil and ginseng was performed in triplicate.

***Method validation for endosulfan analysis***

The accuracy of the analytical method was evaluated by determining recoveries associated with relative standard deviation (% RSD) of the target analyte, α-endosulfan, β-endosulfan, and endosulfan sulfate fortified at 0.01 mg $kg^{-1}$ and 0.1 mg $kg^{-1}$ in soil and fresh ginseng, respectively. The recoveries ranged from 81-92% for all the analytes and the RSD was below

15%. The linearities ($R^2$) of a series of working solutions were over 0.999 for all the analytes. The method limit of quantitations (mLOQ) of α-endosulfan, β-endosulfan, and endosulfan sulfate for soil and ginseng were 0.001 mg kg$^{-1}$ and 0.002 mg kg$^{-1}$ for all endosulfans, respectively (Table S3 in the supporting materials).

### *Calculation on BAF of endosulfan in ginseng*

The BAF is represented as the ratio between concentrations of the total endosulfan concentration in fresh ginseng and the initial concentration of the dried soil; it can be expressed as follows equation (Eq. 2):

$$BAF = \frac{Concentration\ in\ fresh\ ginseng}{Concentration\ in\ dried\ soil} \qquad \text{(Eq. 2)}$$

## Results and discussion

### *Dissipation of endosulfan residue in a ginseng cultivation farm soil with or without GBC*

The dissipation of endosulfan residues in soil was investigated on the fresh and aged endosulfan-contaminated plots during ginseng cultivation. In fresh endosulfan-applied test plots, the initial total endosulfan residue for FLL was 0.157 mg kg$^{-1}$ $^{-}$on the transplanting day and 0.107 mg kg$^{-1}$ on the final harvest day. For FHL the initial total endosulfan residue was 1.297 mg kg$^{-1}$ on transplanting day and 0.855 mg kg$^{-1}$ on the final harvest day (Table 3). The $DT_{50}$ of the total endosulfan was estimated at 866 days in both FLL and FHL soils. The α-endosulfan residue in the soil of the fresh plots was drastically decreased for 150 days after the transplantation (DAT) ($DT_{50}$ = 39-61 days), whereas the β-endosulfan residue ($DT_{50}$ = 267–433 days) was more stable. This difference is likely due to the isomerization of α-endosulfan to β-endosulfan (Zhao et al., 2013). The concentration of endosulfan sulfate, a metabolite of α- and β-endosulfans, in the soil increased over time and appeared to peak at 150 DAT before becoming constant for the rest of the ginseng cultivation period (Fig. 1). The concentration of endosulfan sulfate residues in the soil depended on the decrease in α- and β-endosulfans in the soil and closely followed the Michaelis-Menten equation, as previously reported by Shivaramaiah et al. (2005).

The aged test plots for ginseng were prepared with the same amount of endosulfan that was used for preparing the fresh test plots, eight months before the transplantation. In the aged endosulfan-applied test plots for ALL, the initial total endosulfan residue was 0.044 mg $kg^{-1}$ on transplanting day and 0.034 mg $kg^{-1}$ on the final harvest day (Table 3). For AHL, the initial total endosulfan residue was 0.273 mg $kg^{-1}$ on transplanting day and 0.271 mg $kg^{-1}$ on the final harvest day. The $DT_{50}$ of the total endosulfan was 770 days for ALL and >1200 days for AHL in the aged soil. The $DT_{50}$ of the congeners in the aged plots was 178-210 days for α-endosulfans and 198-385 days for β-endosulfan, whereas endosulfan sulfate showed a constant concentration. The $DT_{50}$ for the total endosulfan was higher than that reported for other arable crop soils (half-life = 6-138.6 days) (Hwang et al., 2018). The prolonged $DT_{50}$ of endosulfan in ginseng farmland soil could be due to the unique cultivation environment, with shade and rice straw mulching on the soil surface. This shading and mulching would protect the soil structure and reduce the degradation of endosulfan by sunlight (Chalise et al., 2020; Mwango et al., 2016; Parsottambhai and Rawat, 2020), For reference, an image showing the ginseng cultivation environment is presented in Fig. S1.

In order to investigate the effect of GBC treatment on the DT50 in the farmland soil, the GBC was treated with 0.3 wt% of soil in the fresh and aged plots, and the $DT_{50}$ of the total endosulfan showed a similar trend to the untreated plots. However, the $DT_{50}$ of α- and β-endosulfans was greater and calculated as 210-248 days and 630-866 days, respectively, in the fresh and aged plots. The endosulfan sulfate contribution ratio in the fresh plots was reduced to 43.9%, which was less than that from the GBC untreated soil (57.5%). On the other hand, the contribution of α-endosulfan increased to 25.3% on the final harvesting day (Fig. 2). This can be explained by the GBC adsorbing endosulfan, thereby protecting it from hydrolysis and biological oxidation. The estimated maximum residue of endosulfan sulfate by the Michaelis-Menten equation was found to be 0.354 mg kg$^{-1}$, which was lower than the GBC untreated plot (0.947 mg kg$^{-1}$). Thus, a potent carbonaceous adsorbent could successfully adsorb and immobilize endosulfan in the soil environment. However, a potential downside of the adsorbent treatment is that whilst endosulfan is immobilized its residence times in these soils would be increased.

***Endosulfan residues and the BAF in ginseng root***

In the freshly applied endosulfan plots the total endosulfan concentration in the 2-year-old (183 DAT) ginseng was 0.264 mg kg$^{-1}$ for FLL and 2.67 mg kg$^{-1}$ for FHL. In the 3-year-old (554 DAT) ginseng the concentrations were 0.278 mg kg$^{-1}$ for FLL and 3.10 mg kg$^{-1}$ for FHL.. The results show that the concentrations were slightly greater in 3-year-old ginseng than the 2-year old ginseng (Fig. 3). The average total endosulfan in the 2-year-old root was 0.660 µg root$^{-1}$ for FFL and 6.66 µg root$^{-1}$ for FHL. In the 3-year-old ginseng roots the average total endosulfan concentration was 2.64 µg root$^{-1}$ for FFL and 29.4 µg root$^{-1}$ for FHL. The total endosulfan in the 3-year-old ginseng was at least four times higher than that recorded in the 2-year-old ginseng in the fresh plots.

This trend was less pronounced in the aged plots where the total endosulfan concentration in the ginseng in the 2-year-old (206 DAT) plots was 0.050 mg kg$^{-1}$ (ALL) and 0.700 mg kg$^{-1}$

(AHL) compared with 0.040 mg kg$^{-1}$ (ALL) and 0.310 mg kg$^{-1}$ (AHL) in the 3-year-old (577 DAT) plots. The average total endosulfan concentrations in the 2-year old roots were 0.141 µg root$^{-1}$ (ALL) and 1.95 µg root$^{-1}$ (AHL) and 0.444 µg root$^{-1}$ (ALL) and 3.47 µg (AHL) for the 3-year old roots. The endosulfan uptake in each root of ginseng in the aged plots increased by 1.8-3.1 times, whereas the root growth rate increased by 3.9-4.0 times. Thus, the effective concentration of endosulfan in ginseng decreased after a year of cultivation owing to the growth effect. The rate of uptake of endosulfan in ginseng after a year of cultivation in the aged plots was lower than that in the fresh plots, which might be attributed to the different levels of the water-extractable contaminants in both soil environments (Gonzalez et al., 2010; Huang et al., 2015; Zhang et al., 2011).

The BAFs of endosulfan were calculated from the initial residue in the soil of test plots and the residue in the harvested ginseng. The BAFs of the total endosulfan for the ginseng were 1.682-1.771 in the FLL plot, 2.055-2.387 in the FHL plot, 1.087-1.372 in the ALL plot, and 1.137-2.570 in the AHL plot. These values were closely related to the previous reports (Kim et al., 2018; Oh et al., 2020). The differences may be explained by different soil organic matter contents used in each experiment because an increase in soil organic matter content could suppress the organic pollutant uptake to crop (Lee et al., 2021; Oh et al., 2020). The main endosulfan congener identified in the ginseng root was endosulfan sulfate. This comprised 61–84% of the total endosulfan from the fresh plots and 80–93% from the aged plots.

The BAFs for α- and β-endosulfans in the fresh plots, and for endosulfan sulfate, in the aged plots because the residues of α- and β-endosulfans in the ginseng of the aged plot and the initial endosulfan sulfate residue in the soil of the fresh plot were not detected. The calculated BAFs were 0.141–0.771, 0.493–0.914, and 1.509–3.522 for α-endosulfan, β-endosulfan, and endosulfan sulfate, respectively. The residue dissipation ratio of each endosulfan congener in the fresh soils between the harvesting days for the 2-year-old and the 3-year-old was 47.5-69.9% for α-endosulfan and 10.0–37.8% for β-endosulfan. Further, the residues in the ginseng root were reduced similarly by 44.9-59.3% for α-endosulfan and 12.8-19.5% for β-endosulfan. The endosulfan sulfate concentrations decreased by only 9.9-14.6% in the soil, while the residue in the ginseng root increased by 17.7-46.5% during the same period. In the aged plots that had the low contribution ratio of α- and β-endosulfans there was a decrease of 4.0-18.9% of endosulfan sulfate in the soil. The concentration of endosulfan sulfate in the ginseng of the aged plots decreased by 20.7-57.1%, unlike the ginseng of the fresh plot which showed an increase. This increase of the endosulfan sulfate in ginseng in the fresh plot could be explained by the biological oxidation of α- and β-endosulfans in the ginseng.

***Effect of biochar treatment on the BAF of endosulfan in ginseng***

To achieve the BAF reduction effect on the treatment of carbonaceous adsorbent the adsorption property of endosulfan on GBC was first investigated. The physicochemical properties are described in Table 1 and were selected as they were similar to previously reported biochars (Bae et al., 2019; Choi et al., 2018b). The adsorption property of GBC for endosulfan as a carbonaceous adsorbent was investigated in aqueous conditions before the soil treatment was performed, and the adsorption isotherm of endosulfan fitted the Langmuir equation (Fig. 4). The maximum adsorption capacity ($q_{max}$) of GBC for endosulfan was calculated to 625.0 mg $g^{-1,}$ and the constant related to the energy of net enthalpy of adsorption was 0.800 g $L^{-1}$ ($p$ <0.01). This adsorption potential was weaker than the previously reported active carbon, but was comparable with the reported biochars as a potential endosulfan adsorbent (Hwang et al. 2020, Choi et al. 2018b).

GBC (0.3 wt%) treatment in the soil showed no physiological effect on the ginseng growth during the cultivation period (Table S4 in the supporting materials). The concentrations of the total endosulfan for the ginseng in the GBC treated plots were 0.790 mg kg$^{-1}$ for 2-year-old ginseng (183 DAT) and 0.951 mg kg$^{-1}$ for 3-year-old ginseng (554 DAT) in the fresh plot. In the aged plots the concentrations of the total endosulfan were 0.539 mg kg$^{-1}$ for 2-year-old ginseng (206 DAT) and 0.207 mg kg$^{-1}$ for 3-year-old ginseng (577 DAT). The GBC treatment suppressed the uptake of endosulfan and effectively reduced the BAFs from 2.055-2.387 to 0.664-0.799 in the fresh plot and from 1.137-2.570 to 0.666-1.739 in the aged plot (Table 4). This may be because the leachable amount of endosulfan in the GBC treated soil would lower than the GBC non-treated soil (Gonzalez et al., 2010; Sun et al., 2020; Zhang et al., 2011). The BAF suppression effect of 0.3 wt% GBC treatment was higher in the fresh plot (66.5-67.7%) than in the aged plot (32.3-41.4%). The BAF suppression effect for each endosulfan congener by the GBC treatment was 71.3-73.8% for α-endosulfan and 56.9-63.3% for β-endosulfan, and 35.0-40.4% for endosulfan sulfate. The isomerization and the biotransformation may explain this difference. Hwang et al. (2020) reported that the desorption concentration of endosulfan sulfate on powdered activated carbon was approximately 2-fold higher than α- and β-endosulfans; thus, the different desorption properties could lead to the BAF suppression effect by GBC treatment as well.

## Conclusion

Ginseng is a perennial crop cultivated under unique cultivation environment with shading and mulching during whole cultivation period for several years. Thus, the soil residue and the bioaccumulation properties differ from short-term cultivated crops that have been more widely investigated. This study established that the $DT_{50}$ of the total endosulfan was drastically increased to >770 days in the ginseng cultivation soil when compared with the previously reported $DT_{50}$ in agricultural soil. In addition, the BAFs of endosulfan in ginseng as a perennial crop (1.087-2.570) were approximately over 10-fold higher values than the short-term cultivated crops due to the extended $DT_{50}$ in soil, the exposure period, and the high stability in ginseng root. The decrease in BAF according to the extension of cultivation period in the aged soil was shown by the higher growth ratio of ginseng than the increase in endosulfan. The decrease was not prominent in the freshly applied endosulfan soil due to the higher uptake ratio in the fresh soil than in the aged soil. Thus, the crop uptake investigation of environmental pollutants should consider the aging effect in the soil environment. Furthermore, the carbonaceous adsorbent treatment successfully reduced the BAF of endosulfan in ginseng root, even though the $DT_{50}$s were extended in the soils. When the Positive List System was considered for the security of the crop safety from the prohibited pesticides like organochlorine POPs, the residue guideline for the agricultural soil could be suggested below 0.005 mg $kg^{-1}$. Due to widespread historical endosulfan contamination, it may not always be possible or financially practical to achieve this target. Therefore, other methods should be investigated that can limit the transfer of endosulfan (and other POPs) from contaminated soils to crops. This study shows that the carbonaceous adsorbent treatment in the contaminated farmland soil can be used effectively to reduce crop uptake and has the potential as a tool to help protect human health in a more sustainable and cost-effective manner.

## Appendix. Supplementary data

Supplementary data related to this article can be found at Supporting Information

**Credit authorship statement**

Lee DY and Bae JY performed the field experiment, adsorption experiment and the quantitative analysis; Oh KY, Lee SW, Bae YS, Kim SK, Song AR, Moon BY and Choi GH performed the field experiments; Megson D and Choi GH discussed the results; Kim JH designed and supervised all the experiments and wrote the manuscript. All authors read and approved the final manuscript.

**Data availability**

Not applicable.

**Competing interests**

The authors declare that they have no competing interests.

**Ethics approval and consent to participate**

This is an observational study. Not applicable.

**Consent for publication**

Not applicable.

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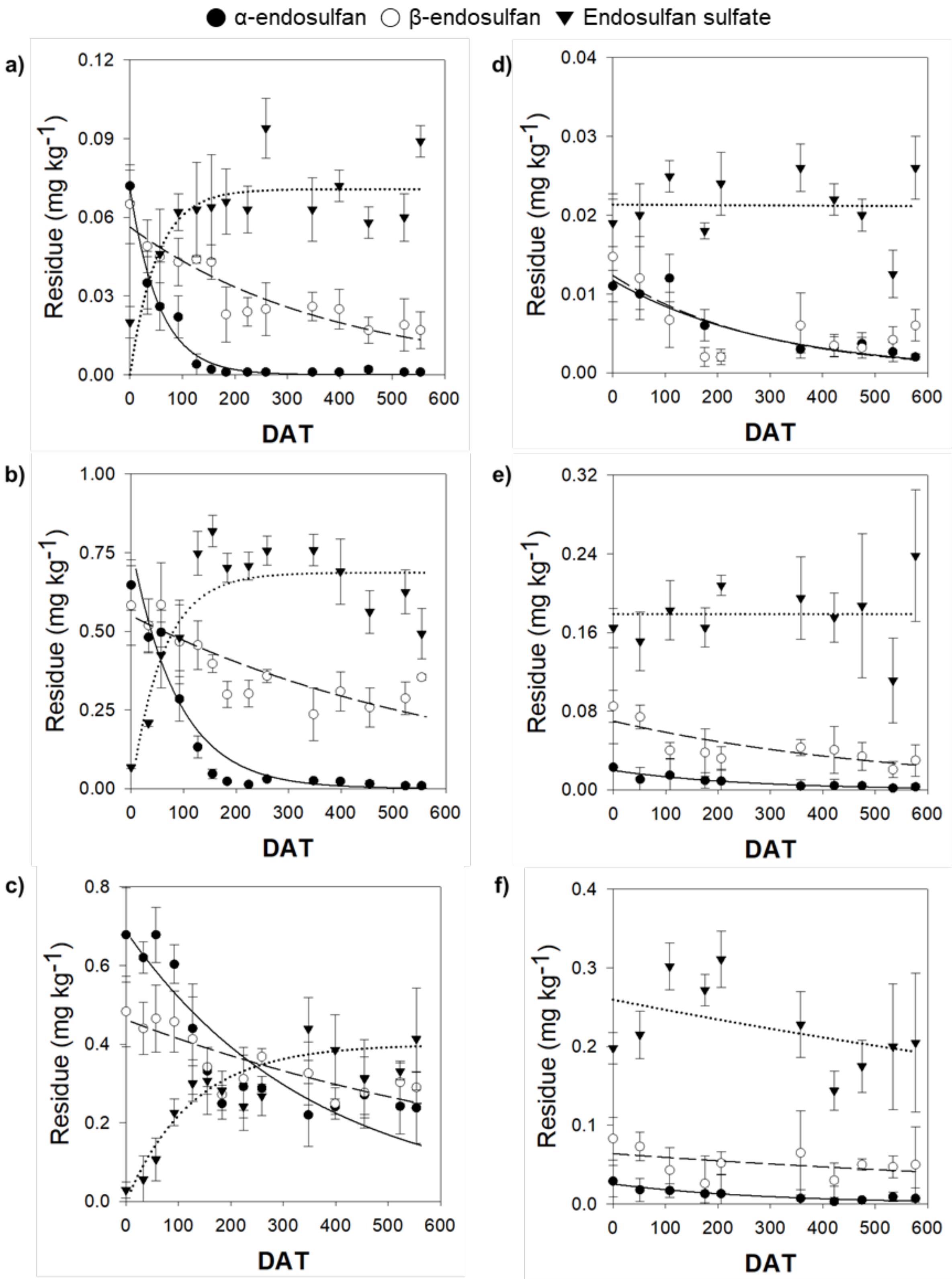
Figure captions

**Fig. 1.** Dissipation of α-endosulfan, β-endosulfan, and endosulfan sulfate in ginseng cultivated soil of the test plots; (a) Fresh lower level (FLL), (b) Fresh higher level (FHL), (c) Fresh higher level with 0.3 wt% GBC (FHL+GBC), (d) Aged lower level (ALL), (e) Aged higher level (AHL), and (f) Aged higher level with 0.3wt% GBC (AHL+GBC).

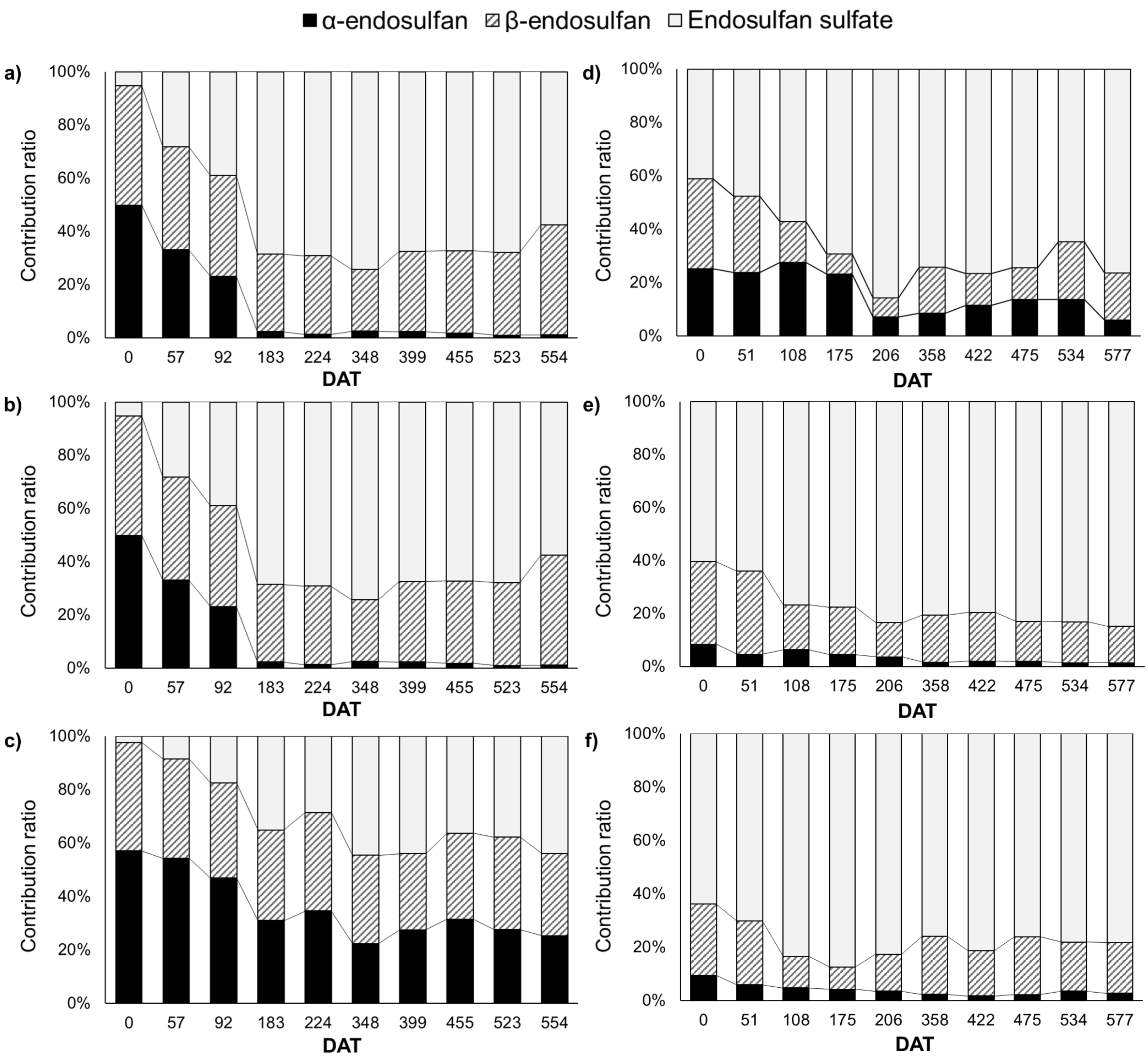
**Fig. 2.** The contribution of endosulfan congeners in the FLL (a), FHL (b), FHL+0.3wt% GBC (c), ALL (d), AHL (e), and AHL+0.3wt% GBC (f) plots.

**Fig. 3.** Bioaccumulated endosulfan residues in the cultivated ginseng of the test plots; FLL (a), FHL (b), FHL+0.3wt% GBC (c), ALL (d), AHL (e), and AHL+0.3wt% GBC (f).

**Fig. 4.** Adsorption isotherms of endosulfan on GBC. $C_e$ (mg $L^{-1}$) is the equilibrium concentration of endosulfan in the water, and $q$ (mg $g^{-1}$) is the adsorption amount of GBC. The dashed line is the fitted Langmuir isotherms.

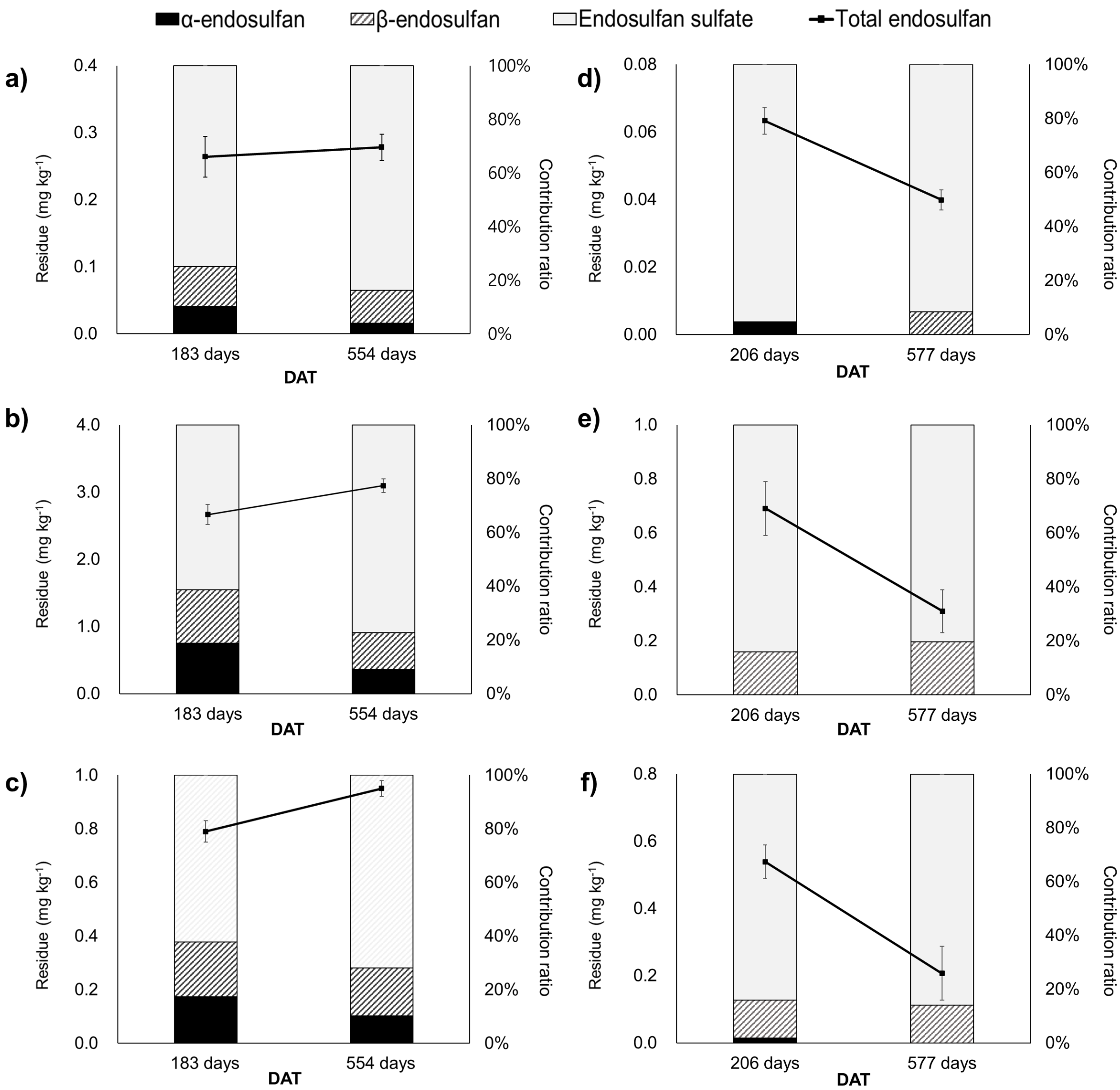

α-endosulfan β-endosulfan Endosulfan sulfate
a)
b)
c)
d)
e)
f)
Residue (mg kg$^{-1}$)
DAT

574 **Fig. 1.**



α-endosulfan
β-endosulfan
Endosulfan sulfate
a)
b)
c)
d)
e)
f)
Contribution ratio
DAT
0% 20% 40% 60% 80% 100%
0 57 92 183 224 348 399 455 523 554
0 51 108 175 206 358 422 475 534 577


576 **Fig. 2.**


α-endosulfan
β-endosulfan
Endosulfan sulfate
Total endosulfan
a)
b)
c)
d)
e)
f)
Residue (mg kg-1)
Contribution ratio
DAT
183 days
554 days
206 days
577 days
0%
20%
40%
60%
80%
100%

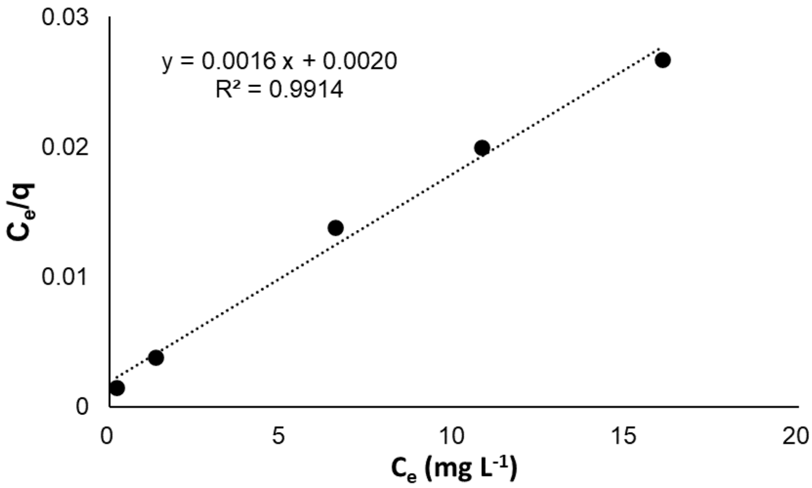

y = 0.0016 x + 0.0020
R² = 0.9914
0.03
0.02
0.01
0
0
5
10
15
20
Ce/q
Ce (mg L-1)

**Table 1** Physico-chemical properties of the tested GBC

| pH (1:20) | EC (dS $m^{-1}$) | Elemental composition (%) | | | | | | | Surface area ($m^2$ $g^{-1}$) | Pore volume ($cm^3$ $g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | O | S | H/C | O/C | | |
| 10.2 | 12.1 | 91.6 | 2.3 | 0.5 | 2.0 | 0.2 | 0.30 | 0.02 | 378 | 0.17 |

**Table 3.** The endosulfan residue in the tested plots and estimated half-lives of the total endosulfan in ginseng cultivation soil

| | Residue (mg $kg^{-1}$) at the planting day | | | | Residue (mg $kg^{-1}$) at final harvest day | | | | $DT_{50}$ (days) |
|---|---|---|---|---|---|---|---|---|---|
| | α-EN[a)] | β-EN[b)] | ENS[c)] | Total | α-EN[a)] | β-EN[b)] | ENS[c)] | Total | |
| FLL | 0.078 | 0.069 | 0.010 | 0.157 | 0.001 | 0.017 | 0.089 | 0.107 | 866 |
| FHL | 0.647 | 0.582 | 0.068 | 1.297 | 0.009 | 0.354 | 0.492 | 0.855 | 866 |
| FHL+GBC[d)] | 0.678 | 0.483 | 0.029 | 1.190 | 0.238 | 0.290 | 0.413 | 0.941 | 1155 |
| ALL | 0.011 | 0.015 | 0.018 | 0.044 | 0.002 | 0.006 | 0.026 | 0.034 | 770 |
| AHL | 0.023 | 0.085 | 0.165 | 0.273 | 0.003 | 0.030 | 0.238 | 0.271 | >1200 |
| AHL+GBC[d)] | 0.029 | 0.083 | 0.198 | 0.310 | 0.005 | 0.050 | 0.154 | 0.209 | 1155 |

[a)] α-EN is α-endosulfan, [b)] β-EN is β-endosulfan, [c)] ENS is endosulfan sulfate, [d)] 0.3 wt% GBC was treated in the soil.

**Table 2** Physico-chemical properties of the plantation soil for the experiment

| | Texture | SOM (g $kg^{-1}$) | pH (1:5) | EC (dS $m^{-1}$) | Available $P_2O_5$ (mg $kg^{-1}$) | Exchangeable cations ($c$mol$_c$ $kg^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | K | Ca | Mg |
| FLL | Sandy loam | 9.4 | 6.41 | 0.78 | 266 | 0.21 | 4.63 | 1.05 |
| FHL | | 9.8 | 6.53 | 0.76 | 262 | 0.20 | 4.53 | 1.00 |
| ALL | | 9.8 | 6.33 | 0.77 | 161 | 0.28 | 3.95 | 1.18 |
| AHL | | 8.7 | 6.58 | 0.75 | 151 | 0.22 | 1.12 | 1.22 |

**Table 4** The endosulfan residue in the root of ginseng and the BAF values in the tested plots

| | Endosulfan residue (mg $kg^{-1}$) | | BAF | |
|---|---|---|---|---|
| | 2-year-old | 3-year-old | 2-year-old | 3-Year-old |
| FLL | 0.264 | 0.278 | 1.682 | 1.771 |
| FHL | 2.665 | 3.096 | 2.055 | 2.387 |
| FHL+GBC[a)] | 0.790 | 0.951 | 0.664 | 0.799 |
| **BAF reduction ratio by GBC** | | | **67.7%** | **66.5%** |
| ALL | 0.060 | 0.048 | 1.372 | 1.087 |
| AHL | 0.701 | 0.310 | 2.570 | 1.137 |
| AHL+GBC[a)] | 0.539 | 0.207 | 1.739 | 0.666 |
| **BAF reduction ratio by GBC** | | | **32.3%** | **41.4%** |

[a)] GBC was treated to 0.3wt% of dried soil