

Evaluation of Residues of Benfuracarb and Carbosulfan in *Spergularia marina*

Yeon Young Lee , Seung Won Lee , Ji Yu Kim , Seon Hwa Kim  and In Seon Kim 

Department of Agricultural Chemistry, Chonnam National University, Gwangju 61186, Korea

* Correspondence: mindzero@chonnam.ac.kr

Abstract: The residues of benfuracarb and carbosulfan required for insect control in *Spergularia marina* were evaluated to investigate basic data for their registration with safe use standards. *S. marina* grown in soil treated with benfuracarb or carbosulfan was harvested and subjected to LC/MS/MS analysis equipped with a modified QuEChERS method for quantitative and qualitative analyses of benfuracarb, carbosulfan and their metabolites carbofuran and 3-hydroxycarbofuran. The methods for sample preparation and instrumental analysis were established to meet the CODEX guidelines. Total residues of benfuracarb were found in the range of 0.01~0.02 mg/kg in samples of *S. marina* grown in soil treated with benfuracarb. The low total levels of benfuracarb were suggested by the rapid degradation of benfuracarb in soil and plant. Total residues of carbosulfan were in the range of 0.02~0.39 mg/kg in samples of *S. marina* grown in soil treated with carbosulfan. Carbosulfan was degraded to carbofuran and 3-hydroxycarbofuran at higher levels than those in benfuracarb-treated samples. The higher total levels of carbosulfan than those of benfuracarb were suggested by an increase in the total amount translocated to plant. The residues of carbosulfan and its metabolites increasing with harvest time at twice the recommended dose suggested continuous uptake and translocation occurred during plant growth. Considering the total residues of benfuracarb and carbosulfan higher than 0.01 mg/kg, the Positive List System level, our study suggests that the establishment of safe use standards for benfuracarb and carbosulfan in *S. marina* is necessary.

<https://doi.org/10.5338/KJEA.2025.44.23>

Agric. Environ. Sci. 2025, 44, 220-229

Received: May 2, 2025

Revised: May 30, 2025

Accepted: June 13, 2025

Published: June 20, 2025

Online ISSN: 2233-4173

Print ISSN: 1225-3537



© The Korean Society of Environmental Agriculture 2025



This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<https://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Keywords: Benfuracarb, Carbofuran, Carbosulfan, *Spergularia marina*

Introduction

Spergularia marina (L.) is a one- to two-year old salt-tolerant herbaceous plant of the Caryophyllaceae family that grows in saline locations, such as near salt flats, along the coast [1]. It grows in reclaimed rice fields on the west and south coasts of Korea [2] and is also distributed in Russia, South Asia, North Africa, Europe and North America [Plants of the World Online, 2025, <https://powo.science.kew.org/>]. It is known as tetrapod because of the similarity of its slender, long leaves to those of a tetrapod squid and is characterized by its semi-cylindrical, row-like leaves that grow in multiple nodes and have pointed tips [3].

In Korea, according to an unofficial report from the Korea Agriculture, Fisheries and Food Distribution Corporation, more than 96% of the total product

of *S. marina* is cultivated in Jeollanamdo coasts from October to May, including Muanangun, Youngkwanggun, Sinangun, and Hampyeonggun. *S. marina* can be grown in outdoors in winter due to its high resistance to cold and drought, thus saving heating costs (production costs) when grown in facilities. As a result, it is increasingly being grown as an alternative crop to increase farmers' income in winter when other crops grow relatively poorly. *S. marina* contains high amounts of functional components such as choline, β -carotene, betaine, phenolic acids and flavonoids and natural minerals such as calcium, magnesium and potassium, which may exert anti-aging, antioxidant and anti-inflammatory effects [4,5]. *S. marina* is attracting attention as one of the functional food ingredients in the food service industry as it is known to be used as a salt substitute to reduce high sodium intake [6].

It is expected that the cultivation of *S. marina* in Korea will continue to increase due to its economic crop status as mentioned above. However, the cultivation of *S. marina* is threatened by a number of insects such as black cutworm, aphids, mode cricket and mites. Especially the black cutworm is one of the typical insects that cause a significant reduction in the production of *S. marina*. The black cutworm feeds mainly on the leaves of *S. marina*, which is the main source of income for the farmers. According to the Pesticide Safety Information Database of the Rural Administration of Agriculture (RDA), only bifenthrin is registered as a typical pesticide for the control of black cutworm in *S. marina*. The RDA has recently received a number of requests from farmers for additional pesticide registrations that can be used to better control black cutworm in *S. marina*. Therefore, there is a need to investigate safe use criteria for additional pesticides that may be used to control insects in *S. marina*.

Benfuracarb and carbosulfan are carbamate insecticides widely used to control black cutworm in variable crops. They exert their insecticidal action by inhibiting the function of acetylcholinesterase, an enzyme that hydrolyzes the neurotransmitter acetylcholine in insect bodies [7,8]. Benfuracarb and carbosulfan are known for their low persistence relative to their efficacy, which contributes to their widespread use in continuous leaf-harvest crops such as *S. marina*. Considering the potential threat of insects to the productivity of *S. marina* and the requests for pesticide registration from farmers, the Korean government has recognized the need for pesticides that can be used to control black cutworm. Therefore, this study was conducted to evaluate the residues of benfuracarb and carbosulfan, which can be used to control black cutworm and aphids, which are major problems in the greenhouse cultivation of *S. marina*. For this purpose, sample preparation and analytical methods were optimized according to the CODEX guidelines for pesticide residue analysis [9], and the optimized methods were used to evaluate the residues of benfuracarb and carbosulfan in samples of *S. marina*, which will provide basic data for pesticide registration with establishment of safe use standards.

Results

Method Validation

The method for the analysis of the test chemical components was established by considering the ion ratio difference of the components, the sample matrix effect, the linearity of the matrix-matched calibration and limit of quantitation (LOQ).

The ion ratio difference was automatically calculated by the instrument sequence setting program to accept the actual detection of the target compound (benfuracarb, carbosulfan, carbofuran, 3-hydroxycarbofuran) only when the ion ratio difference meets the level of $\pm 30\%$ in reference to the SANTE/SANCO European Food Safety Agency guidelines [10]. The ion ratio differences of benfuracarb, carbosulfan, carbofuran and 3-hydroxycarbofuran between the solvent-matched calibration and the matrix-matched calibration were similar in the range of $\pm 30\%$ (Fig. 1), indicating that the residues of the target compounds detected in this study were obtained by the method that meets the international guidelines as mentioned above, and the error of the detection method can be considered insignificant.

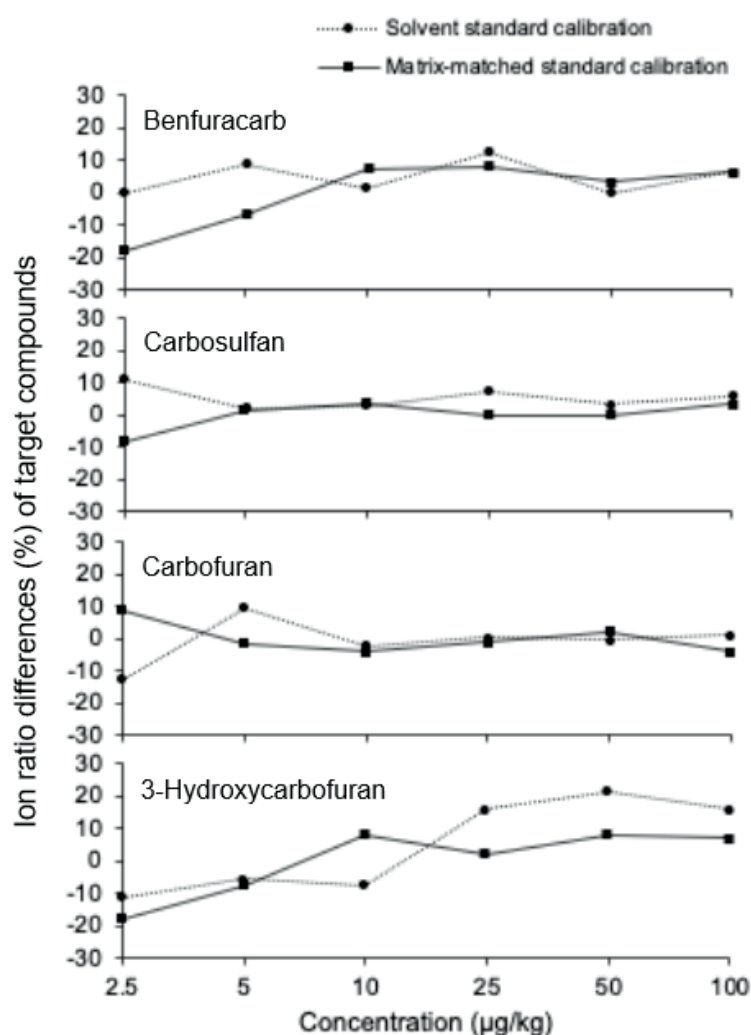


Fig. 1. Ion ratio difference patterns of the target compounds at different concentrations prepared in organic solvent or control sample matrix. Ion ratio differences are the averages of triplicates.

The sample matrix effect ranged from -39.820 to -10.479% for the target compounds, and the suppression and enhancement of ion intensity were within $\pm 40\%$ (Table 1). It is known that there is no significant difference between the matrix-matched calibration and the solvent-matched calibration when the test substance is quantified with the matrix effect within $\pm 10\%$ [11,12]. Therefore, in this study, benfuracarb and carbosulfan were quantitatively analyzed based on the matrix-matched calibration curve, considering the matrix of the sample to ensure the reliability of the method.

The matrix-calibration curve showed good linearity with the coefficient of determination (R^2) ranging from 0.9970 to 0.9995 for all samples (Table 2). The curve showed a LOQ of 0.01 mg/kg of the target compound and more than 75% recovery of back-calculation efficiency at 0.005 mg/kg, indicating that the sample matrix did not interfere with the calibration of the target compounds in all samples.

Overall, the method established as described above complies with the CODEX guidelines [9], indicating that the method in our study is suitable for the determination of the target compounds in samples of *S. marina*.

Table 1. Sample matrix effects on the calibration linearity of the target compounds

Target compounds	Sample matrix effects (%) [*]
Benfuracarb	-14.337
Carbosulfan	-39.820
Carbofuran	-10.479
3-Hydroxycarbofuran	-20.205

^{*} [(Slope of linearity curve in matrix – slope of linearity curve in solvent only) / (slope of linearity curve in solvent only)] × 100%.

Table 2. Correlation factors of determination (R²) of matrix-matched calibration curves of the target compounds

Test pesticides	R ² factors of the target compounds in sample matrices			
	Benfuracarb	Carbosulfan	Carbofuran	3OH-carbofuran
Benfuracarb	0.9973	-	0.9985	0.9993
Carbosulfan	-	0.9970	0.9995	0.9988

Recovery and Selectivity of Established Method

The established method for the target compounds was verified by recovery test according to the CODEX guidelines [9]. The LC-MS/MS analysis detected benfuracarb, carbosulfan, carbofuran and 3-hydroxycarbofuran at retention times of 3.38, 3.80, 2.89~2.91 and 2.65~2.66 minutes, respectively, without any interfering peaks on their chromatograms in the control sample at these retention times. The difference in retention time of the target compound detected in the sample was less than 0.6% compared with the retention time of the standard, which met the 2.5% recommended by the European Community guideline (2002/657/EC). In addition, peaks considered to be the target compound were observed in the control sample at times close to the retention times of the target compound in the sample, but these were not accepted as the same substance because they deviated significantly from the ±30% ion ratio difference value set in the instrument sequence program. These results indicated that the established method had selectivity between samples.

The mean recoveries of benfuracarb, carbosulfan, carbofuran and 3-hydroxycarbofuran ranged from 79.5 to 108.4% and from 93.5 to 106.5% at 10 times the LOQ level (Table 3). The percentages of coefficient of variation (%CV) ranged from approximately 1.7~10.3% at the LOQ level and approximately 2.3~13.0% at 10 times the LOQ level. In a separate preliminary experiment, the chemical stability of the target compound in the samples during storage was investigated. The target compound was added to the control samples at 0.1 mg/kg and stored at -20°C in a refrigerator until analysis. The mean recoveries of the target compound ranged from 80.3 to 111.9% with %CV less than 4.8%, indicating that the target compound was chemically stable during

Table 3. Recovery values of the test compounds from spiked plant samples

Test pesticide	Target compounds	Recovery (%) [*]	
		Spiked levels (mg/kg)	
		0.01 (LOQ)	10 x LOQ
Benfuracarb	Benfuracarb	87.6 ± 6.8	94.2 ± 12.2
	Carbofuran	104.9 ± 10.8	103.5 ± 4.9
	3OH-carbofuran	93.8 ± 1.6	93.5 ± 8.7
Carbosulfan	Carbosulfan	79.5 ± 4.7	102.1 ± 2.3
	Carbofuran	108.3 ± 4.3	106.5 ± 4.8
	3OH-carbofuran	108.4 ± 1.7	99.8 ± 4.6

^{*} Data are means ± standard deviation of triplicates.

the test period. Overall, the above results met the guidelines for pesticide residue analysis recommended by the CODEX.

Residues of Benfuracarb and Carbosulfan in Harvested Samples

The above established method was used to determine the residues of benfuracarb and carbosulfan in samples of *S. marina* grown in greenhouse. The residues of benfuracarb and carbosulfan were calculated on the basis of the total carbofuran residue converted as described in the Materials and Methods section.

In samples treated with benfuracarb, the residues of benfuracarb and 3-hydroxycarbofuran were found to be less than 0.01 mg/kg in all samples, while carbofuran was found at levels of 0.02 mg/kg and 0.01 mg/kg at the recommended dose and twice the recommended dose, respectively (Table 4). Thus, the total residues of benfuracarb were calculated to be 0.01~0.02 mg/kg.

In samples treated with carbosulfan, carbosulfan, carbofuran and 3-hydroxycarbofuran were found at levels of 0.11 mg/kg, 0.06 mg/kg and 0.03 mg/kg, respectively, 37 days after treatment at the recommended dose (Table 5), and their residues decreased to levels of 0.01~0.02 mg/kg 44 days after treatment. Carbosulfan, carbofuran and 3-hydroxycarbofuran were found at levels of 0.14 mg/kg, 0.11 mg/kg and 0.03 mg/kg, respectively, 37 days after treatment at twice the recommended dose, these residue levels were 0.44 mg/kg, 0.11 mg/kg and 0.02 mg/kg, respectively, 44 days after treatment. Thus, the total residues of carbosulfan calculated as described above were 0.22~0.39 mg/kg, higher than in the samples treated with benfuracarb.

Table 4. Residues of the test compounds in the samples of harvested plant grown in soil treated with benfuracarb

Treated levels (mg/kg)	Target compounds	Residues (mg/kg) ¹⁾	
		37 DAT ²⁾	44 DAT
0.12 kg a.i./10a	Benfuracarb	<0.01	<0.01
	Carbofuran	0.02 ± 0.01	0.01 ± 0.01
	3OH-carbofuran	<0.01	<0.01
	Total carbofuran	0.02 ± 0.01	0.01 ± 0.01
0.24 kg a.i./10a	Benfuracarb	<0.01	<0.01
	Carbofuran	0.02 ± 0.01	0.02 ± 0.01
	3OH-carbofuran	<0.01	<0.01
	Total carbofuran	0.02 ± 0.01	0.02 ± 0.01

¹⁾ Data are means±standard deviation of triplicates.

²⁾ DAT: day after treatment.

Table 5. Residues of the test compounds in the samples of harvested plant grown in soil treated with carbosulfan

Treated levels (mg/kg)	Target compounds	Residues (mg/kg) ¹⁾	
		37 DAT ²⁾	44 DAT
0.18 kg a.i./10a	Carbosulfan	0.11 ± 0.01	<0.01
	Carbofuran	0.06 ± 0.01	0.02 ± 0.01
	3OH-carbofuran	0.03 ± 0.01	<0.01
	Total carbofuran	0.15 ± 0.01	0.02 ± 0.01
0.36 kg a.i./10a	Carbosulfan	0.14 ± 0.03	0.44 ± 0.01
	Carbofuran	0.11 ± 0.01	0.11 ± 0.02
	3OH-carbofuran	0.03 ± 0.01	0.02 ± 0.01
	Total carbofuran	0.22 ± 0.02	0.39 ± 0.02

¹⁾ Data are means±standard deviation of triplicates.

²⁾ DAT: day after treatment.

Discussion

In this study, the residue patterns of benfuracarb and carbosulfan were investigated in *S. marina* grown in greenhouse soil treated with the test pesticides at the recommended dose and double dose, respectively. The methods for sample preparation and instrumental analysis were successfully optimized and established according to the CODEX guidelines in order to quantitatively and qualitatively evaluate the residues of the target compounds in the samples.

Total residues of benfuracarb were found at levels of 0.01 mg/kg and 0.02 mg/kg in samples of *S. marina* grown in soil treated with benfuracarb, which were significantly low as compared to the treated level. The levels of carbofuran were higher than those of benfuracarb, suggesting that benfuracarb was degraded to carbofuran during the experiment. The detection of 3-hydroxycarbosulfan indicated that carbofuran was also degraded to 3-hydroxycarbofuran. The low total levels of benfuracarb were suggested by the rapid degradation of benfuracarb in soil. It has been reported that benfuracarb degrades mostly to with carbofuran as the major degradation product within 7 to 10 days after soil treatment [13]. Benfuracarb has also been reported to degrade rapidly in an upland soil to 74% of the treated level within 5 days with carbofuran as the major degradation product [14]. Benfuracarb, in particular, is known to be significantly degraded to carbofuran and other products by sunlight in plant and soil [15]. In our study, *S. marina* was harvested 37 days and 44 days after soil treatment with benfuracarb, which is longer than the above time period known to degrade most of the treated benfuracarb. Given the degradation behaviour of benfuracarb, the length of time that *S. marina* was grown was likely sufficient for significant degradation of benfuracarb. Benfuracarb is a systemic carbamate insecticide that translocates from the treated part to the whole plant and is metabolized to carbofuran and 3-hydroxycarbofuran [16]. Benfuracarb has been reported to persist for 7 to 12 days in the brinjal crop, with 50% reduction in applied residue within 3 to 5 days after foliar spraying at rates of 0.25 mg/kg and 0.5 mg/kg [17]. The metabolism of ¹⁴C-labeled benfuracarb in cotton, bean, and corn plants demonstrated the rapid degradation of benfuracarb to carbofuran and 3-hydroxycarbofuran and carbofuran phenol as major metabolites following foliar application [18]. Benfuracarb is known to be mostly immobile in soil after soil treatment [19], which may contribute to the amount of benfuracarb translocated to the plant depending on its levels in the soil. Soil-treated benfuracarb is known to be absorbed at the root level and translocated via the apoplast pathway to the aerial parts of the plant where it is distributed and accumulated at low levels in the plant body [20]. These observations in previous studies may explain the low levels of benfuracarb in *S. marina* in our study.

Total residues of carbosulfan were in the range of 0.02~0.39 mg/kg in samples of *S. marina* grown in soil treated with carbosulfan, which were higher than those of benfuracarb. The detection of carbofuran and 3-hydroxycarbofuran indicated that carbosulfan was degraded to these degradation products at higher levels than those in benfuracarb-treated samples. The higher total levels of carbosulfan than those of benfuracarb may be due to a difference in the rate of degradation between them, considering that the rate of degradation of carbosulfan is lower than that of benfuracarb in soil [13,14]. The slower degradation of carbosulfan and its products in soil may contribute to an increase in the total amount translocated to the plant. Soil-treated carbosulfan is known to be taken up by the plant and translocated via the apoplast pathway, distributed and accumulated in cell walls and in roots [21,22]. It is also metabolized to carbofuran and 3-hydroxycarbofuran in plant leaves, roots and shoots [23]. These observations suggest that the residue patterns of soil-treated carbosulfan in the plant may need to be considered for carbosulfan and its metabolites, as their levels are higher than those in benfuracarb-treated samples. The residue levels of carbosulfan and its metabolites decreased with harvest time in the samples treated at the recommended dose, but their residue levels increased with harvest time in the samples treated at twice the recommended dose, suggesting that continuous uptake and translocation of the compounds occurred during plant growth after treatment at twice the recommended dose. These observations are consistent with a previous study showing that carbofuran residue levels in plants increase with treatment levels [24]. Carbosulfan treated in different growth stages (sowing, seedling, and podding) of cowpea demonstrated that the risk of acute dietary intake of the total residues of carbosulfan, including carbosulfan, carbofuran, and 3-hydroxycarbofuran, was higher than 100% in the seedling and podding stages, 10 days after foliar application [25]. It was also reported that the pre-harvest

interval should be strictly considered for 7 days after foliar application on cucumber to ensure the safety of dietary intake [26]. These observation together our study suggest that the total residues of carbosulfan are needed to carefully follow the pre-harvest interval after soil treatment and foliar application to ensure.

In this study, the total residues of benfuracarb and carbosulfan based on the residues of carbofuran in *S. marina* were found to be in the range of 0.01~0.39 mg/kg. The total residues of carbosulfan were higher than those of benfuracarb, which may be due to the differences in water solubility and LogP values between them. Carbosulfan has about 0.3 mg/kg of water solubility and 5.4 of LogP value, while benfuracarb has about 0.8 mg/kg of water solubility and 4.3 of LogP value, suggesting more hydrophobicity for carbosulfan than benfuracarb, which may contribute to the differences in the total residues in *S. marina*. Considering the total residues of benfuracarb and carbosulfan higher than 0.01 mg/kg, the Positive List System level, our study suggests that the establishment of safe use standards for benfuracarb and carbosulfan in *S. marina* is necessary. Based on the OECD MRL calculator (<http://www.oecd.org/env/pesticides>), the residues of benfuracarb and carbosulfan that could be proposed as temporary MRLs (maximum residue limits) in *S. marina* are estimated to be 0.06 mg/kg and 0.8 mg/kg, respectively.

Materials and Methods

Chemicals

The test products of benfuracarb and carbosulfan were 3% granular formulations (GRs) commercially available in Korea. Standard stock solutions of benfuracarb, carbosulfan, carbofuran and 3-hydroxycarbofuran (Fig. 2) were purchased from Kemidas (Gunpo, Gyeonggi-do, Korea) at a concentration of 1,000 mg/L dissolved in acetonitrile. Organic solvents used were of HPLC grade purchased from J.T. Baker (Phillipsburg, NJ, USA). Formic acid (99%) was purchased from Sigma-Aldrich (St. Louis, USA). All other chemicals were reagent grade purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan), unless otherwise stated. The QuEChERS kit used for sample preparation was purchased from Agilent (San Francisco, CA, USA).

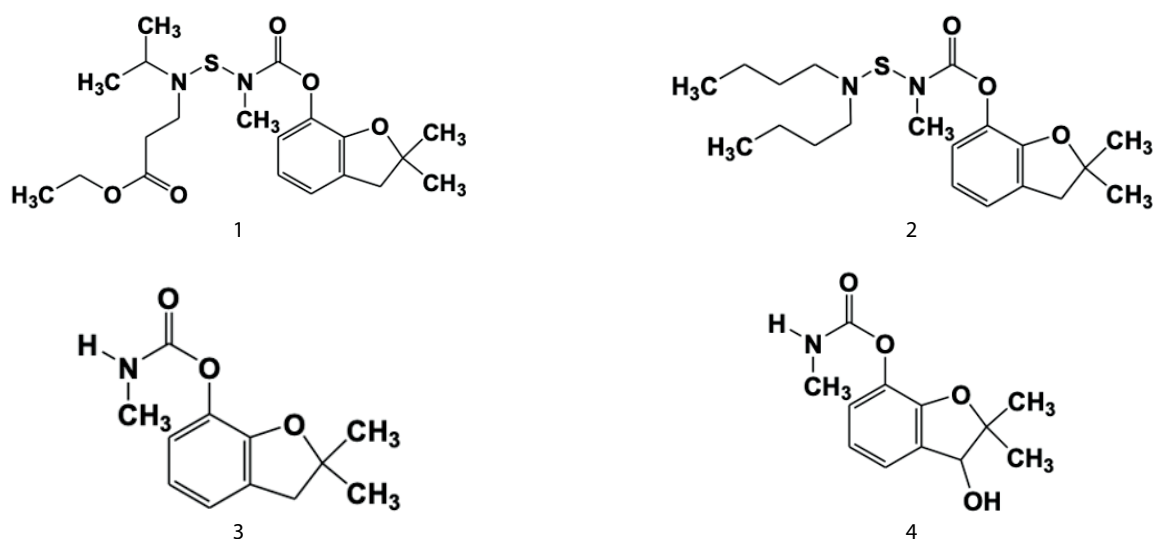


Fig. 2. Chemical structures of benfuracarb (1), carbosulfan (2), carbofuran (3) and 3-hydroxycarbofuran (4) test in this study.

Field Trials

Field trials were conducted in a greenhouse in Sinangun, Jeollanamdo. *S. marina*, which had grown in the greenhouse during the winter season, was conventionally cut to a height of less than 1 cm before treatment with the test granular formulations (GRs). The test GRs were thoroughly mixed with soil at a ratio of 1 to 100 (g/g) in polyvinyl bags and applied evenly to the greenhouse soil plot (2 m × 5 m) at the recommended doses of 4 kg/10a for benfuracarb and 6 kg/10a for carbosulfan and twice their recommended doses. Greenhouse soil plots were designed and prepared in triplicate as described in a previous study [27]. *S. marina* was conventionally cultivated under greenhouse conditions and harvested 37 days and 44 days after the GRs treatments. The average temperature and humidity during the field trials were 4.5~16.6°C and 52.8~90.1%, respectively. The harvested samples were chopped into small pieces, then ground using a high-speed homogenizer with dry ice. All samples were then stored at -20°C until analysis.

Sample Preparation

A modified QuEChERS method was used for sample preparation. A 10 g sample from above was added to a 50 mL centrifuge tube with 10 mL of acetonitrile containing 6.0 g of anhydrous MgSO₄, 1.5 g of CH₃COONa and vortexed vigorously for 2.0 min. The mixture was then centrifuged at 4,500 rpm for 5.0 min to obtain the supernatant. A 1.0 mL aliquot of the supernatant was transferred to a 2 mL micro-centrifuge tube containing anhydrous MgSO₄ (150 mg), PSA (25 mg) and GCB (7.5 mg), mixed and centrifuged at 8,000 rpm for 3.0 min. The resulting supernatant was passed through a 0.2 µm syringe membrane filter (PTFE-H) and used for LC/MS/MS analysis. In a separate study, the chemical stability of the test compounds in the samples during storage at -20°C was examined by calculating the recovery data of the standards spiked at a level of 0.1 mg/L in the control samples. The chemical stability of the target compounds was tested at -20°C for the same period as the field samples until analysis. The residues of benfuracarb and carbosulfan were calculated on the basis of the total carbofuran residue converted as follows:

- 1) The total carbofuran residue (mg/kg) in the samples treated with benfuracarb = carbofuran residue (mg/kg) + [conversion factor I × benfuracarb residue (mg/kg)] + [conversion factor II × 3-hydroxycarbofuran (mg/kg)]
- 2) The total carbofuran residue (mg/kg) in the samples treated with carbosulfan = carbofuran residue (mg/kg) + [conversion factor III × carbosulfan residue (mg/kg)] + [conversion factor II × 3-hydroxycarbofuran (mg/kg)]
- 3) The conversion factors are; I. Molecular weight of carbofuran/molecular weight of benfuracarb, II. Molecular weight of carbofuran/molecular weight of 3-hydroxycarbofuran, III. Molecular weight of carbofuran/molecular weight of carbosulfan.

Method Validation

The ion ratio, calibration linearity, sensitivity, precision and accuracy of the analytical methods were subjected to method validation tests according to the guidelines of the European Commission document SANTE/11813/2017 [10]. The ion ratio difference was automatically calculated by the instrument sequence setting program as a level of ±30% in the reference. A qualitative ion ratio was used to indicate the presence of interferences, which was calculated as the ratio of the peak area for the quantifier transition to the peak area of the qualifier transition in the calibration standard and sample matrix solutions. The selected ions used to calculate the ion ratio are as follows: precursor ion m/z 411.5 and product ions m/z 195.1 and m/z 158.4 for benfuracarb, precursor ion m/z 381.2 and product ions m/z 118.0 and m/z 160.1 for carbosulfan, precursor ion m/z 222.0 and product ions m/z 165.1 and m/z 123.0 for carbofuran, and precursor ion m/z 238.0 and product ions m/z 181.2 and m/z 163.0 for 3-hydroxycarbofuran. The linearity of matrix-matched standard calibration curve was obtained by diluting serially their stock solutions (100 mg/L) with the extracts of control samples into their working solutions ranged from 5.0 to 200 µg/L. The sensitivity of the method was evaluated by the quantification of limit (LOQ) at the signal to noise of 10:1. The LOQ was calculated as:

$$\text{LOQ (mg/kg)} = [\text{minimum detectable amount (ng)} \times \text{final sample volume (mL)}] / [\text{injection volume (}\mu\text{L)} \times \text{sample amount (g)}]$$

The precision and accuracy of the methods were evaluated by the recovery data using the standards spiked in the control samples at levels of LOQ and $10 \times \text{LOQ}$. The recovery data were acceptable in the range of 70~120% with the relative standard deviation (RSD) less than 20% according to the guidelines of the European Commission document SANTE/11813/2017 [10]. The recovery was conducted in triplicate and calculated as:

$$\text{Recovery (\%)} = (\text{the concentration detected in the sample}) / (\text{the spiked concentration}) \times 100.$$

Instrumentals

A Waters model Xevo TQD-XS triple quadrupole LC/MS/MS equipped with a Waters model ACQUITY™ UPLC system was used. An Acquity BEH C₁₈ stainless steel column (100 × 2.1 mm, 1.7 μm thickness) was used for the sample separation. The mobile phase was consisted of water (A) and acetonitrile (B) containing 0.1% (v/v) formic acid, and its isocratic and gradient were performed as follows: isocratic 100% solvent A for 1.0 min, linear gradients 100% solvent B for 2.0 min, isocratic 100% solvent A for 5.0 min, flow rate 0.3 mL/min. Electron spray ionization (ESI) mode was used for LC/MS/MS spectra. LC/MS/MS conditions were routinely optimized at desolvation gas flow 10.8 mL/min (N₂), capillary gas flow 0.4 mL/min, capillary voltage 3.5 KV, ion source temperature 150°C and desolvation temperature 350°C.

Data Availability: All data are available in the main text or in the Supplementary Information.

Author Contributions: Lee YY, conducted the experiments; Lee SW and Kim JY, investigation and data curation; Kim SH, wrote original draft; Kim IS, designed, supervised, edited all draft, and financed the research.

Notes: The authors declare no conflict of interest.

Acknowledgments: This work was supported by the Rural Development Administration of Republic of Korea (No. 02073033).

Additional Information:

Supplementary information The online version contains supplementary material available at <https://doi.org/10.5338/KJEA.2025.44.23>

Correspondence and requests for materials should be addressed to In Seon Kim.

Peer review information Korean Journal of Environmental Agriculture thanks the anonymous reviewers for their contribution to the peer review of this work.

Reprints and permissions information is available at <http://www.korseaj.org>

References

1. Augusthy S, Nizam A, Kumar A (2024) The diversity, drivers, consequences and management of plant invasions in the mangrove ecosystems. *Science of the Total Environment*, 945, 173851. <https://doi.org/10.1016/j.scitotenv.2024.173851>.
2. Hyun JO, Na HR, Kim YS, Han BW (2018) Floristic study of Aphaedo island in Shinangun, Jeollanam-do, Korea. *Korean Journal of Plant Taxonomy*, 48, 65-99. <https://doi.org/10.11110/kjpt.2018.48.1.65>.
3. Heo BK, Park YJ, Park YS, Im MH, Oh KT, Cho JY (2009) Distribution status, physicochemical composition, and physiological activity of *Spergularia marina* cultivated the western region in Jeon-Ra-Nam-Do. *Korean Journal of Community Living Science*, 20, 181-191. <https://doi.org/10.1410-ECN-0101-2009-522-018498095>.
4. Kim HS, Kim JA, Karadeniz F, Ahn BN, Kong CS (2014). Radical scavenging and anti-inflammatory effects of the halophyte *Spergularia marina* Griseb. *Zeitschrift für Naturforschung C*, 69, 425-433. <https://doi.org/10.5560/znc.2014-0098>.

5. Park YJ, Lee JJ (2020) Comparison of nutritional components and antioxidative effects of *Spergularia marina* according to different drying methods. Korean Journal of Community Living Science, 31, 51-63. <https://doi.org/10.1410-ECN-0101-2020-590-000420078>.
6. Kim DS, Lee SM, Joo N (2016). Quality characteristics and optimization of rice cookies prepared by substituting salt with *Spergularia marina* L. Griseb. Korean Journal of Food and Cookery Science 32, 279-289. <https://doi.org/10.9724/kfcs.2016.32.3.279>.
7. Stehrer-Schmid P, Wolf HU (1995) Effects of benzofuran and seven benzofuran derivatives including four carbamate insecticides in the *in vitro* porcine brain tubulin assembly assay and description of a new approach for the evaluation of the test data. Mutation Research, 339, 61-72. [https://doi.org/10.1016/0165-1110\(94\)00015-5](https://doi.org/10.1016/0165-1110(94)00015-5).
8. Eren Y, Erdogmus SF, Akyil D, Ozkara A (2016) Mutagenic and cytotoxic activities of benfuracarb insecticide. Cytotechnology, 68, 637-643. <https://doi.org/10.1007/s10616-014-9811-3>.
9. Codex Alimentarius (2009) Guidelines for the design and implementation of national regulatory food safety assurance programme associated with the use of veterinary drugs in food producing animals CAC/GL 71. Available online: http://www.fao.org/imput/download/standards/11252/CXG_071e_2014.pdf (accessed on 24 April 2025).
10. SANTE Guidance Document on Analytical Quality Control and Validation Procedures for Pesticide Analysis in Food and Feed; SANTE/12682/2019, Implemented by 01.01.2020; European Commission Directorate General for Health and Food Safety: Brussels, Belgium, 2020.
11. Yoon JH, Lim DJ, Kim SW, Kim IS (2022) Evaluation of residues of fungicide azoxystrobin in radish based on plant back interval experiment. Korean Journal of Environmental Agriculture, 41, 1-8. <https://doi.org/10.5338/KJEA.2022.41.1.1>.
12. Dong M, Nie D, Tang H, Rao Q, Qu M, Wang W, Han L, Song W, Han Z (2015) Analysis of amicarbazone and its two metabolites in grains and soybeans by liquid chromatography with tandem mass spectrometry. Journal of Separation Science, 38, 2245-2252. <https://doi.org/10.1002/jssc.201500265>.
13. Xue N, Yang R, Xu X, Seip HM, Zang Q (2006) Adsorption and degradation of benfuracarb in three soils in Hunan, People's Republic of China. Bulletin of Environmental Contamination and Toxicology, 76, 720-727. <https://doi.org/10.1007/s00128-006-0979-x>.
14. Lee YD, Choi JH (1995) Evolution of carbofuran in soils treated with its aminothio derivatives, carbosulfan, furathiocarb and benfuracarb. Korean Journal of Environmental Agriculture, 14, 179-185.
15. Katagi T (2004) Photodegradation of pesticides on plant and soil surfaces. Reviews of Environmental Contamination and Toxicology, 182, 1-195. <https://doi.org/10.1007/978-1-4419-9098-31>.
16. Umetsu N, Tanaka AK, Fukuto TR (1985) Absorption, translocation and metabolism of the insecticide benfuracarb in plants. Journal of Pesticide Science, 10, 501-511. <https://doi.org/10.1016/B978-0-323-99427-9.00004-5>.
17. Osaki N, Yasudomi N, Aoki Y, Umetsu N (1992) Studies on the insecticidal properties of benfuracarb as a soil treatment. Applied Entomology and Zoology, 27, 261-268. <https://doi.org/10.1303/aez.27.261>.
18. Tanaka AK, Umetsu N, Fukuto TR (1985) Metabolism of benfuracarb in young cotton, bean, and corn plants. Journal of Agriculture and Food Chemistry, 33, 1049-1055. <https://doi.org/10.1021/jf00066a010>.
19. Chandra R, Srivastava A, Srivastava PC (2009) Fate of benfuracarb insecticide in mollisols and brinjal crop. Bulletin of Environmental Contamination and Toxicology, 83, 348-351. <https://doi.org/10.1007/s00128-009-9710-z>.
20. European Food Safety Authority (2006) Conclusion regarding the peer review of the pesticide risk assessment of the active substance benfuracarb. EFSA Scientific Report, 89, 1-81. <https://doi.org/10.2903/j.efsa.2006.89r>.
21. Shi L, Lang H, Shen J, Shen F, Song J, Zhang L, Fand H, Yu Y (2022) Absorption, metabolism and distribution of carbosulfan in maize plants (*Zea mays* L.). Pest Management Science, 79, 3926-3933. <https://doi.org/10.1002/ps.758>.
22. Meher H, Ghanendra TG, Kamra A, Chawla G (2010) Persistence and nematocidal efficacy of carbosulfan, cadusafos, phorate, and triazophos in soil and uptake by chickpea and tomato crops under tropical conditions. Journal of Agricultural and Food Chemistry, 58, 1815-1822. <https://doi.org/10.1021/jf903609d>.
23. Clay VE, Fukuto TR (1984) Metabolism of carbosulfan in Valencia orange tree leaves and fruit. Archives of Environmental Contamination and Toxicology, 13, 53-62. <https://doi.org/10.1007/BF01055646>.
24. Kamala IM, Kennedy JS (2017) Dissipation dynamics and risk assessment of carbosulfan in brinjal (*Solanum melongena* L.) fruits. Journal of Entomology and Zoology Studies, 5, 1353-1357.
25. Wang D, Di SS, Wang XQ, Zhang CP, Wang XU, Wang M (2021) Degradation of carbosulfan after its application in different growth stage of cowpea. Acta Agriculturae Zhejiangensis, 32, 2050-2058. <https://doi.org/10.3969/j.issn.1004-1524.2020.11.16>.
26. Song W, Jia C, Jing J, Zhao E, He M, Chen L, Yu P (2018) Residue behavior and dietary intake risk assessment of carbosulfan and its metabolites in cucumber. Regulatory Toxicology and Pharmacology, 95, 250-253. <https://doi.org/10.1016/j.yrtph.2018.03.023>.
27. Kim YE, Kim SW, Lim DJ, Kim IS (2020) Residue analysis of acetamiprid, boscalid, imidacloprid and pyraclostrobin in the minor crop mustard green under greenhouse conditions for evaluation of their potentiality of PLS violation. Korean Journal of Environmental Agriculture, 39, 214-221. <https://doi.org/10.5338/KJEA.2020.39.3.25>.