Effect of Biochar on the Degradation Dynamics of Chlorantraniliprole and Acetochlor in *Brassica chinensis* L. and Soil under Field Conditions

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**ABSTRACT:** Although biochar is a promising soil enhancement material, we have limited understanding of its effect on certain pesticide in soils and plants under field conditions. The aim of this study was to examine the impact of walnut shell biochar (WSB), which is rich in benzylic ring C and lignin charcoal, on the degradation dynamics of chlorantraniliprole (CAP) and acetochlor in *Brassica chinensis* L. fields. The functional group structure, aromatic ring structure, and crystallite size of the WSB were determined by thermogravimetric analysis and derivative thermogravimetry analysis (TGA−DTG), NMR, Raman spectroscopy, and X-ray diffraction, respectively. With WSB applications of 5% (v/v) in root soil, *B. chinensis* L. growth was facilitated. Degradation dynamic analysis showed that the half-life of CAP on *B. chinensis* L. and in soil did not change greatly. For acetochlor, the half-life in soil was 6.93 days with WSB application and 9.90 days without WSB application. The WSB application increased bioconcentration factor values more significantly for acetochlor than for CAP. These results show that WSB has a greater impact on acetochlor than on CAP when used for pesticide degradation in the field.

1. **INTRODUCTION**

Pesticides can prevent large crop losses and play an important role in agriculture. However, pesticide overuse causes ill effects in both humans and environment and is therefore a cause for concern. Increasing adoption of agrochemical-based crop production practices has considerably increased persistent organic contamination in the food chain and the surrounding environment, which has raised public concerns for the environment and human health. According to statistics, China uses almost 30% of total global pesticides, applied to only 9% of the total global pesticide-treated land. This low use efficiency coupled with a high proportion of pesticide loss leads to environmental pollution and contamination of surrounding aquatic ecosystems. Thus, it is important to find a reasonable method to control pesticide pollution.

Chlorantraniliprole (CAP), synthesized by the DuPont Crop Protection Company, belongs to the class of anthranilic diamide insecticides and has been extensively used in crop farming. CAP is registered in China for use on many crops such as rice, corn, beans, and apples for control of many lepidopteron species. It is reported that CAP made up nearly 30% of the total pesticides used and 70% of the insecticides. Wide spread use of CAP causes great concern regarding potential pollution of the surrounding environment.

Acetochlor is a member of the class of chloroacetanilide herbicides and is widely used on crops such as corn, soybeans, cotton, and peanuts in China, with an annual use of more than 10,000 tons. Studies have reported that acetochlor has been detected in soils, drinking water sources, and streams in the Midwestern United States and China. The structures and physiochemical properties of CAP and acetochlor are shown in Table 1.

Biochar generally refers to the carbon-rich solid produced by the pyrolysis of biomass in oxygen-limited conditions. As biochar has a strong adsorption ability, a large specific surface area, abundant functional groups, and a rich source of nutrients and organic matter for crops, it is a promising material for soil enhancement, which can reduce pesticide leaching at diffuse and point sources, such as agricultural ditches and drainage systems, and in areas where concentrated pesticides are handled and potentially spilled. Walnut shell biochar (WSB) is an abundant resource in China, especially in Zhejiang Province. Walnuts are a cash crop in China and are planted widely in Zhejiang Province. Walnut processing has been reported to produce more than 0.5 million ton of walnut.
shells as a byproduct each year. The application of WSB on soil and crop yields has been studied, and it has been found that it increased nitrification rates and plant-available nutrient concentrations.

Field trials have found that the addition of biochar to soil can improve the bioavailability of pesticides and reduce the plant uptake of pesticides. Wang et al. (2012) found that soil improvement by biochar leads to a decrease in the bioavailability of soil CAP for earthworms. The degree of bioavailability reduction with the same application of biochar differed depending on different soil properties. Martin et al. (2012) showed that the application of two biochars (one from paper mill sludge and one from poultry litter) significantly increased soil sorption capacity for atrazine and diuron and

| Items                  | CAP                  | Acetochlor           |
|-----------------------|----------------------|----------------------|
| CAS Registry Number   | 500008-45-7          | 34256-82-1           |
| Molecular formula     | C₃H₁₂BrC₆N₃O₂        | C₃H₁₇OCINO₂           |
| Molecular weight      | 483.152              | 269.8                |
| Melting point (°C)    | 208-210              | <0°C                 |
| Vapor pressure (25°C, Pa) | 2.1×10⁻¹⁴          | 4.6×10⁻¹²            |
| Solubility (mg/L)     | 1.023                | 222.8 (in methanol)  |
| LogKₜₐ₂            | 2.76                 | 4.14                 |

**Figure 1.** Characterization of WSB (a. TGA−DTG curves of WSB, b. NMR curve of WSB, c. Raman curve of WSB, and d. XRD curve of WSB).
that sorption-desorption hysteresis was prominent in the soil amended with fresh biochar.\textsuperscript{17} Yu et al. (2011) found that the addition of wood chip biochar to soils could significantly increase the sorption of acetamiprid, and the dissipation of acetamiprid in soils enhanced with biochar was delayed compared to soils without biochar enhancement.\textsuperscript{16} Li et al. (2018) found that the addition of aged biochar to soil and its uptake in maize seedlings could increase the bioaccumulation of acetochlor in plants.\textsuperscript{18}

As most studies were conducted on soils amended with biochars in laboratories and pot experiments, the impact of biochars on the bioavailability of pesticides in plants and soils under field conditions was limited. Mutual impacts such as pesticide properties, biochar characteristics, and crop species can influence the persistence of pesticides applied to crops and soils. It is necessary to know how biochar affects the persistence of pesticides and the relationship between its physical and chemical properties and its effect on field trials. Given this background, the aims of this study were (1) to evaluate the influence of WSB on the degradation of CAP and acetochlor in \textit{Brassica chinensis} L. (\textit{B. chinensis} var \textit{chinensis}) residue and soil and (2) to quantitatively compare the differences in biochar effects on CAP and acetochlor pesticides.

2. RESULTS AND DISCUSSION

2.1. Characterization of WSB. WSB characteristic results are shown in Figure 1a—d. Figure 1a shows the thermogravimetric analysis and derivative thermogravimetry analysis (TGA−DTG) change of WSB with temperature. It can be concluded that large and dramatic weight loss occurred between 300 and 500 °C with a peak at 403.2 °C. Weight loss then became much more gradual before becoming approximately constant above 700 °C. Walnut shells are composed of lignin, cellulose, and hemicelluloses and decompose easily at a temperature of approximately 400 °C. Generally speaking, the decomposition temperature of lignin was 250 to 500 °C, and the decomposition temperatures of celluloses and hemicelluloses were 325 to 375 °C and 225 to 350 °C, respectively. For WSB produced at the highest treatment temperature of 550 °C, the weight decrease was progressive but mild. The result was in accordance with the values reported.\textsuperscript{19}

Figure 1b shows the NMR curve of WSB. As outlined previously, the frequencies of interunit linkages in each biochar sample were calculated from then on acetylated and acetylated spectra. The spectrum can be subdivided into regions of interest to obtain information about the overall structure of WSB. The chemical shifts between 0 and 45 ppm were likely related to alkyl carbon, and those between 45 and 93 ppm were likely related to methoxy carbon and carbohydrate. Aromatic carbon was present between 93 and 165 ppm, and carbonyl carbon was present between 165 and 280 ppm. The predominant region was the methoxyl carbon and carbohydrate (45−93 ppm), which was consistent with the low H/C ratios. Specifically, the peak in this region appeared at 75 ppm. It probably had more benzylic ring C than carbonyl C, respectively. For WSB produced at the highest treatment temperature of 550 °C, the weight decrease was progressive but mild. The result was in accordance with the values reported.\textsuperscript{19}

Figure 1c shows the Raman spectroscopy results of WSB. There were two major shifts around 1379.1 and 1571.5 cm\textsuperscript{-1}, commonly called the “D” and “G” bands, respectively. These two bands corresponded to the in-plane vibrations of sp\textsuperscript{2}-bonded carbon structures with structural defects (D band) and to the in-plane vibrations of the sp\textsuperscript{2}-bonded graphitic carbon structures (G band), respectively. The characteristics of the Raman bands’ position and band width indicate that the carbon order degree of biochar progressively increases with the increase of pyrolysis temperature and that the detailed chemical structures of biochars from different raw biomasses can significantly differ from each other.\textsuperscript{20}

Figure 1d shows the X-ray diffraction (XRD) curve of WSB. We analyzed the results using jade 6.0 software, which showed that the hkl values were 113, 300, 401, 511, and 452 for 2θ values of 21, 27.5, 40, 50, and 68, respectively. The weak diffraction was expected for non-graphitizable carbonized cellululosics, and the broader peaks at 21 and 27.5° that were obtained were consistent with the presence of amorphous carbon and/or the presence of nanoparticles. The XRD analysis results showed that WSB consists of a large amount of lignin charcoal other than crystalline carbon.\textsuperscript{21}

2.2. Growing Status of \textit{B. chinensis} L. The height of \textit{B. chinensis} L. in the control plot (CK) without WSB and in the plot containing 5% v/v WSB was recorded from 5 to 30 days after planting. The height was recorded for five samples, and the mean value is shown in Figure 2.

The results show that \textit{B. chinensis} L. grown with amendments of WSB grew faster than in the control plot. This shows that WSB can facilitate the nutrient substance absorption and that \textit{B. chinensis} L. grows faster when WSB is added. These results are in accordance with former studies that concluded that biochar directly affects rhizosphere microorganisms and influences plant growth.\textsuperscript{14}

2.3. Degradation of CAP and Acetochlor in the Field Experiment. 2.3.1. CAP Degradation. The dynamic residue of CAP on \textit{B. chinensis} L. with a low dose of 41.25 g a.i.ha\textsuperscript{-1} or a high dose of 61.87 g a.i.ha\textsuperscript{-1}, with and without application of WSB, and pesticide residue analysis was recorded for three samples, and the mean value is shown in Figure 3. All data were fitted to a first-order equation to estimate half-lives of CAP degradation in different treatments (Table 2 and Table S1).

When CAP was applied on \textit{B. chinensis} L., the initial residue on concentrations were 2.75−2.83 mg kg\textsuperscript{-1} at the low dose and 3.72−4.17 mg kg\textsuperscript{-1} at the high dose. The initial residue
concentrations correlated with the application dosage but showed no significant relationship with the application of WSB. Thus, for the same application conditions and sampling points, the residue level increased concurrently with the applied dose. Over time, the residue concentrations declined to 0.0444–0.0576 mg kg\(^{-1}\) at the low dose and 0.0600–0.0800 mg kg\(^{-1}\) at the high dose on the 28th day. For the same application conditions, the final residues of CAP on \(B.\ chinensis\) L. amended with WSB were less than the values without WSB application. The half-life of CAP on \(B.\ chinensis\) L. was 5.33–5.77 days both with and without WSB application. For the degradation dynamics of CAP in soil, the initial residue concentrations were 0.108–0.119 mg kg\(^{-1}\) at the low dose and 0.124–0.129 mg kg\(^{-1}\) at the high dose. Overtime, the residue concentrations declined to 0.0262–0.0268 mg kg\(^{-1}\) at the low dose and 0.0242–0.0316 mg kg\(^{-1}\) at the high dose on the 28th day. For the same application conditions, the final residues of CAP in soil with WSB were higher than the values without WSB application. The half-life of CAP in soil was 17.3 days both with and without WSB application. For CAP, the amendment of WSB with 5% (v/v) did not have a significant effect on the degradation rate in soil and on \(B.\ chinensis\) L. A former study suggested that soil microbial degradation is the main factor that leads to the loss of pesticides in soil, while on plants, factors such as sunshine and rainfall affected pesticide degradation.\(^{22}\) Our results showed that WSB addition did not change CAP degradation dynamics greatly.

### 2.3.2. Acetochlor Degradation

The dynamic residue of acetochlor on \(B.\ chinensis\) L. with a low dose of 675 g a.i.ha\(^{-1}\) or a high dose of 1012.5 g a.i.ha\(^{-1}\), with and without application of WSB, and pesticide residue analysis was recorded for three samples, and the mean value is shown in Figure 4.

The degradation dynamics of acetochlor on \(B.\ chinensis\) L. and soil followed a first-order equation. The half-lives of different conditions were estimated (Table 3 and Table S2).

When acetochlor was applied on \(B.\ chinensis\) L., the initial residue concentrations were 14.7–15.0 mg kg\(^{-1}\) at the low dose and 37.9–45.8 mg kg\(^{-1}\) at the high dose. The results showed that the initial residue on \(B.\ chinensis\) L. increased when acetochlor dosage increased. As time passed, acetochlor residue on \(B.\ chinensis\) L. decreased. On the 28th day, the residue was 0.25–0.36 mg kg\(^{-1}\) at the low dose and 0.35–0.56 mg kg\(^{-1}\) at the high dose. The half-life of acetochlor was 4.62 days both with and without WSB application for both low and high dosages. For the residue in soil, the initial residue concentrations were 1.176–1.99 mg kg\(^{-1}\) at the low dose and 1.607–2.51 mg kg\(^{-1}\) at the high dose. Over time, the residue concentrations declined to 0.053–0.182 mg kg\(^{-1}\) at the low dose and 0.059–0.258 mg kg\(^{-1}\) at the high dose on the 28th day. With WSB applied, acetochlor residue was much lower than that without WSB application. The half-life of acetochlor in soil was 6.93 days with WSB application and 9.90 days without WSB application. Acetochlor degraded more easily in soil when WSB was applied, and the half-life was shorter with both low and high dosages. As acetochlor was hard to dissolve in water and its solubility in methanol was 222.8 mg L\(^{-1}\), the results showed that the addition of WSB promoted microbial degradation of acetochlor in soil. For acetochlor degradation on \(B.\ chinensis\) L., the addition of WSB had no great effect.

### 2.4. Effect of WSB on the Bioavailability of CAP and Acetochlor in \(B.\ chinensis\) L.

The bioconcentration factor of CAP is shown in Figure 3. The concentrations of CAP in soil and on \(B.\ chinensis\) L. with and without amendment of WSB and with different application dosages (a. low dosage in soil, b. high dosage in soil, c. low dosage on \(B.\ chinensis\) L., and d. high dosage on \(B.\ chinensis\) L.).

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c04268)
Table 2. Half-Lives of CAP in Soils and B. chinensis L. with and without Amendment of Biochar

| Time days | without WSB | with WSB | without WSB | with WSB |
|-----------|-------------|----------|-------------|----------|
| 1         | 61.87 g a.i.ha⁻¹ | 41.25 g a.i.ha⁻¹ | 61.87 g a.i.ha⁻¹ | 41.25 g a.i.ha⁻¹ |
|           | C = 2.54 e⁻⁴ | C = 2.95 e⁻⁴ | C = 2.54 e⁻⁴ | C = 2.95 e⁻⁴ |
|           | R² = 0.960 | R² = 0.913 | R² = 0.960 | R² = 0.913 |
|           | T₁/₂ = 5.77 | T₁/₂ = 7.30 | T₁/₂ = 5.77 | T₁/₂ = 7.30 |

"T₁/₂" mean half-life days.

As the pesticides were applied during the late growing stage of B. chinensis L., it is obvious that CAP and acetochlor concentrations in B. chinensis L. were significantly higher than those in soil. CAP degraded faster in B. chinensis L. than in soil, and as the aging time increased, the BCF decreased in most conditions. With low and high dosages and a 14 day aging period, the bioaccumulation of CAP in WSB-amended soil was not obvious, as the BCF value with WSB was lower than that without WSB at low dosages, while at high dosages, the BCF value with WSB was greater than that without WSB. For example, the concentration of CAP was 0.046 mg kg⁻¹ in soil and 0.543 mg kg⁻¹ in B. chinensis L. with WSB and a low dosage application, and without WSB, the values were 0.0382 mg kg⁻¹ in soil and 0.679 mg kg⁻¹ in B. chinensis L. These were attributed to the CAP sorption ability of WSB in soil being different at low and high CAP dosage. With a 21 day aging period, the BCF value with WSB was greater than that without WSB at both low and high CAP dosages, while at a 28 day aging period, the BCF value with WSB was lower than that without WSB. This indicate that WSB sorption of CAP had taken effect.

Acetochlor degraded faster in B. chinensis L. than in soil. With a 14 day aging period, the BCF values were 4.90 and 6.92 with WSB applied at low and high acetochlor dosages, respectively, while without WSB application, the BCF values were 3.16 and 4.15 at low and high acetochlor dosages, respectively. With a 28 day aging period, the BCF values were 4.71 and 5.93 with WSB applied at low and high acetochlor dosages, respectively, while without WSB application, the BCF values were 1.97 and 2.17 at low and high acetochlor dosages, respectively. The BCF value for acetochlor was higher when WSB was applied, which indicated that acetochlor degraded faster in soil with amendment of WSB.

Martin et al. found that the sorption capacity of biochar decreased as the aging time increased. With the decreased sorption capacity, part of the absorbed contaminations could be released into the soil and taken up by plants. Therefore, the influences of WSB on the environmental behavior of CAP must be further investigated.

The sorption mechanism of organic pollutants in biochars is complicated because of the sorption behavior being influenced by aromaticity, polarity, surface area, and micropore volume of the biochar as well as the soil properties. It is possible that minerals and organic matter in the soil may cover the reactive surface of the biochar, thereby masking the true sorption capacity of the biochar for organic compounds such as pesticides. Previous studies have proposed that the sorption sites of organic matter such as charcoal can be blocked by interactions with soil components, particularly organo-mineral interactions in soils.

3. CONCLUSIONS

This study showed that the effects of WSB application in soil under field conditions for CAP and acetochlor pesticide degradation are influenced by factors including pesticide characteristics, soil characteristics, and field conditions, and it was in accordance with the former studies. The application of WSB did not change the degradation rate of residue or half-life for CAP both in soil and on plants, while for acetochlor, the half-life in soil was shorter with WSB application than without WSB. The application of WSB (BCFs) of CAP and acetochlor in B. chinensis L. amended with WSB are shown in Table 4.
increased BCF values more markedly for acetochlor than for CAP. In soil, biochar will incorporate with soil and could change the bioavailability of pesticides and the plant uptake of pesticides from contaminated soils. Thus, more research is required to establish guidelines for the field application of biochar in order to maintain its outstanding ability to absorb pesticides and promote its efficient use.

4. EXPERIMENTAL METHODS

4.1. Reagents and Materials. The commercial CAP product (5% SC) was supplied by DuPont Co. Ltd., USA. Commercial acetochlor (90% EC) was supplied by Ryan Plant Protection Co. Ltd, Beijing. For high-performance liquid chromatography (HPLC) detection, analytical-grade CAP and acetochlor (99% chemical purity) were obtained from Green Agricultural Science and Technology Group Co. Ltd. (Beijing, China). HPLC grade methanol was supplied by Sinopharm Chemical Reagent Co.Ltd. Guaranteed reagent grade acetoni-trile and toluene were purchased from Merck (Darmstadt, Germany). HPLC-grade water was supplied by Wahaha (Hangzhou, China). All other chemicals were of analytical reagent grade. *B. chinensis* L. seed was supplied by the Vegetable Institute, Zhejiang Academy of Agricultural Sciences.

4.2. WSB and Soils. WSB (with a BET surface area of 1645 m² g⁻¹) derived from walnut shells was supplied by the Wotu Ecology and Technology Company, Zhejiang Province. WSB was produced at the highest treatment temperature of 550°C and at a heating rate of 5–10 °C min⁻¹. A field without detectable CAP and acetochlor was chosen as a sampling site, and the upper 10 cm soil was sampled and passed through a 2 mm sieve for analysis. Soil and biochar chemical analyses were undertaken at HCITQSAGMP (Hangzhou Center for Inspection and Testing for Quality and Safety of Agricultural and Genetically Modified Products) laboratory, certified by the Ministry of Agriculture, P. R. China accredited to ISO 17025. The pH was measured in 0.01 M CaCl₂ (1:5). Ash content was measured by combusting WSB at 750°C for 4 h. Elemental N, P, and K abundances were analyzed by a Varion EL analyzer (Germany). The Brunauer–Emmett–Teller surface area was analyzed by a JW-BK224 surface area analyzer. Cation exchange capacity (CEC) was assessed using exchange into 1 M NH₄OAc.

The physical and chemical properties of WSB and soil are provided in Table 5. The results showed that WSB contained a large amount of total organic content (TOC) (93.9%) and had a pH value of 6.78. This was in accordance with earlier findings that most biochars were alkaline in nature. The CEC of WSB was 40.23 cmol kg⁻¹, while the value of soil was 13.7. This agreed with the results of earlier studies.

4.3. Characterization of WSB. We have performed TG, NMR spectra analysis, Raman spectroscopy, and XRD to characterize the WSB. TG analysis was conducted using a Shimadzu TA-60 WS. The WSB was heated from 30 to 1000°C at the rate of 10 °C min⁻¹ under an N₂ atmosphere, and the DTG curve was calculated by derivative weight loss. The pyrolysis characteristics of WSB were elucidated by TGA–DTG curves. NMR experiments were performed on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 150.9 MHz. ¹³C CP/MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 14 kHz. A contact time of 2 ms and a cycle delay of 3 s were used for the 1H-13CP/MAS measurement. Raman spectroscopy (HR 800 Lab RAM, HORIBAJobin Yvon, France) with an excitation
4.4. Field Experimental Design. The field experiment was conducted in a greenhouse trial field of Zhejiang Academy of Agricultural Sciences, located in Shao Xing, Zhejiang Province, China, from May 2019 to August 2019. *B. chinensis* L. was planted in May 2019, and pesticide was applied during July 2019. Field trials were conducted under greenhouse conditions in separate plots, each measuring 40 m², with three replicates. The plots were separated by blank experimental plots 1 m in width. The field plots were enhanced with WSB in May 2019 at the rate of 25 t ha⁻¹ (equivalent to 5% v/v following incorporation to 15 mm), and the WSB was mixed with the root soil before the experiment. In July 2019, CAP and acetochlor were sprayed in the field during the late growing stage of *B. chinensis* L. at low and high doses. The dosage of CAP was 41.25 g a.i.ha⁻¹ for the low dose treatment and 61.87 g a.i.ha⁻¹ for the high dose treatment, while acetochlor used was 675 g a.i.ha⁻¹ for the low dose treatment and 1012.5 g a.i.ha⁻¹ for the high dose treatment. The trial plots were divided into five types: (i) three plots without WSB and low doses of pesticides, (ii) three plots without WSB and high doses of pesticides, (iii) three plots with WSB and low doses of pesticides, (iv) three plots with WSB and high doses of pesticides, and (v) two blank plots without WSB. Thus, the total plots numbered 14. The height was recorded for five samples, and the mean value is shown in Figure 2.

Field management was conducted in accordance with the pesticide use guide, with the pesticide dose applied to each experimental plot and plots arranged in an orderly fashion. During the period of pesticide application, the daily air temperature minimum and maximum values were 28 and 36 °C, respectively, while the relative humidity ranged from 80 to 94%.

Samples were collected at 0 (2 h), 1, 3, 5, 7, 14, 21, and 28 days. For the sample collection, 200 g of *B. chinensis* L. was collected from each experimental plot and stored at −20 °C after being homogenized by a blender (Philips, China). Soil was collected at the same time and stored at −20 °C.

4.5. Pesticide Residue Analysis. LC−MS/MS was used for pesticide analysis using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method for the extraction and purification of *B. chinensis* L. samples. For *B. chinensis* L. extraction treatment, samples from each experimental plot were naturally defrosted from −20 °C for about 20 min and

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Table 4. BCF of CAP in *Brassica chinensis* L. with and without WSB for Selected Aging Time

| days after CAP/acetochlor application with WSB without WSB with WSB without WSB | low dosage | high dosage |
|----------------------------------|-------------|-------------|
| CAP                              | 14          | 13.37       | 18.51       | 16.25       | 11.68       |
|                                  | 21          | 12.16       | 7.71        | 16.30       | 8.29        |
|                                  | 28          | 1.656       | 2.19        | 1.89        | 3.30        |
| acetochlor                       | 14          | 4.90        | 3.16        | 6.92        | 4.15        |
|                                  | 21          | 4.12        | 2.79        | 4.59        | 2.69        |
|                                  | 28          | 4.71        | 1.97        | 5.93        | 2.17        |
homogenized for extraction. *B. chinensis* L. samples of 5.00 g were weighed into a 50 mL polypolyethylene centrifuge tube with a plug. Then, 10 mL of acetonitrile was added, and the tube was shaken at 2500 rpm for 1 min by a vortex mixer. Then, 4.00 g of sodium chloride and 1.00 g of a hydrous magnesium sulfate were added to the centrifuge tube, and the tube was shaken for 3 min. The mixture was shaken at 2500 rpm for 30 s by a vortex mixer and then centrifuged at 8000 rpm (Thermo/PrimoR) for 3 min and prepared for purification.

For soil extraction treatment, samples from each experimental plot were naturally defrosted from −20 °C for about 20 min. Soil samples of 5.00 g were weighed into a 50 mL polypolyethylene centrifuge tube with a plug. Then, 5 mL of water was added, and the solution was allowed to stand for 30 min before 5 mL of acetonitrile was added, and the tube was shaken at 2500 rpm for 1 min by a vortex mixer. The mixture was extracted using the ultrasonic wave technique for 20 min. Following this, 4.00 g of sodium chloride and 1.00 g of anhydrous magnesium sulfate were added to the centrifuge tube, and the tube was shaken for 3 min. The mixture was shaken at 2500 rpm for 30 s by a vortex mixer and then centrifuged at 8000 rpm (Thermo/PrimoR) for 3 min and prepared for purification.

For purification of *B. chinensis* L. and soil, 1 mL of supernatant from the centrifuge tube was transferred to a Cleanert MAS-Q, which contained 50 mg of PSA, 50 mg of C18, and 150 mg of MgSO4. The mixture was shaken and filtered through a 0.22 μm membrane and transferred into a glass vial for HPLC–MS/MS determination.

HPLC–MS/MS detection was conducted by the TSQ Quantum Discovery mass spectrometer system (Thermo Fisher Scientific, USA), equipped with a triple-quadrupole ion trap hybrid mass detector in the MRM positive electrospray ion (ESI) mode. Thermo Fisher Xcalibur 2.0.7 software was used to control the instrument and to analyze the data. Separation was conducted on a chiral column Lux Cellulose-1[cellulose *tris*(3,5-dimethylphenylcarbamate)] supplied by Phenomenex (Torrance, USA). The mobile phase consisted of 90% (v/v) 0.1% for mic acid acetonitrile and 10% (v/v) 0.1% for mic acid water solution, with a flow rate of 0.25 mL min⁻¹. The column oven temperature was set at 30 °C, and the auto sampler temperature was set at 4 °C. The injection volume was 5 μL, and the total run time was 5 min. The spray voltage was set at 4.0 kV. The capillary temperature was set at 400 °C. The auxiliary and sheath gas used was normal nitrogen. The collision gas used was high-purity argon at a set pressure of 0.2. For CAP, pain collision cell transitions of m/z 484 > 452 and m/z 484 > 285 were used for quantification and confirmation, respectively. The retention time (Rf) of acetochlor was approximately 1.535 min.

Pesticide residue analysis was recorded for three samples, and the mean value is shown in Figures 3 and 4.

### 4.6. Quality Control and Data Analysis

With this method, linear correlation was obtained for the *B. chinensis* L. and soil extracts with a correlation coefficient (R²) at five concentrations (0.002, 0.01, 0.5, 1, and 5 mg kg⁻¹) with three replicates. Relative standard detection (RSD) was obtained for three spikes (0.05, 2.00, and 5.00 mg kg⁻¹) with five replicates. The limit of detection and the limit of quantitation were defined as the concentrations giving a signal-to-noise ratio of 3 and 10, respectively. A blank analysis was performed to check for interference from the matrix. The slope ratios of the linear calibration functions were calculated to differentiate between the extraction efficiency and matrix-induced signal suppression/enhancement (SSE) (Table S3).

In field experiments, the pesticide dissipation process followed first-order kinetics. The degradation rate constant and half-lives were calculated using the first-order rate equation

$$C_t = C_0 e^{-kt},$$

where $C_t$ represents the concentration of the pesticide residue at time $t$, $C_0$ represents the initial concentration after application, and $k$ is the degradation rate constant (days⁻¹). The half-life ($t_{1/2}$) was calculated from the $k$ value for each experiment ($t_{1/2} = \ln 2 / k$).²⁵,³¹

The extent of pesticide accumulation was expressed using the BCF:

$$BCF = \frac{C_{\text{plant}}}{C_{\text{soil}}}$$

where $C_{\text{plant}}$ and $C_{\text{soil}}$ are the concentrations of CAP and acetochlor in plants (dry weight) and soil (dry weight), respectively.

**CCC**

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c04268.

Comparison of matrix-matched calibration and solvent calibration (2–1000 μg L⁻¹), degradation dynamics of CAP on *B. chinensis* L. and soil, and degradation dynamics of acetochlor on *B. chinensis* L. and soil (PDF)

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Notes
The authors declare no competing financial interest.

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