Determination of glufosinate-ammonium residue in wheat and soil by ultra-performance liquid chromatography-tandem mass spectrometry

Xiaoyun She, Yu Gao, Yan Shi*

Dryland-Technology Key Laboratory of Shandong Province, College of Agronomy, Qingdao Agricultural University, Qingdao City, China

***Corresponding Author:** Yan Shi, Dryland-Technology Key Laboratory of Shandong Province, College of Agronomy, Qingdao Agricultural University, Qingdao City, China. Email: yanshi@qau.edu.cn

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RESEARCH ARTICLE

Abstract

The worldwide use of glufosinate-ammonium has dramatically increased, but concern over its impact on plants and soil is also increasing. With the aim of clarifying whether the application of glufosinate-ammonium will generate residue in wheat *(Triticum aestivum* L.) and soil, ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was used to detect wheat plants, grains, and soil. Under experimental conditions, no residue of glufosinate-ammonium was detected in wheat plants and grains during each growth period. The residual level of glufosinate decreased gradually with the increment of soil layer during the same reproductive period. In the same soil layer, the sequence of glufosinate residues in the reproductive period were wintering, recovering, jointing, and heading stage. The residues of glufosinate after 2.0 times applied amount was significantly greater than the 1.0 times applied amount. During the wintering period, the residuals after 2.0 times application of glufosinate were 1.50 and 28.27 times higher than 1.0 times application in the field and soil column experiment, respectively, in the 0–20 cm soil layer. No residue of glufosinate was detected in the different soil layers of each treatment during the flowering, filling, and maturation stages of wheat. The residues of glufosinate-ammonium in wheat and soil were far less than 0.2 ng kg^{-1} in all treatments. It shows that the application of glufosinate-ammonium is safe for wheat field soil and the next crop under the spraying rate of this experiment.

Keywords: glufosinate-ammonium; grains; residual; soil; UPLC-MS/MS; wheat

Introduction

Wheat is the most widely distributed food crop in the world. It is also one of the three major food crops in China, and its output and sown area account for about one-third of the world's food and food production. As one of the principal wheat-producing areas in China, Shandong Province has a significant comparative advantage in wheat production (Wang and Li, 2010). Weeds compete with crops for water, nutrients, space, and light, and are also the hiding place of pests, which is one of the factors restricting wheat production. Herbicide application is still the main method to control weeds (Gaba *et al.*, 2016; Shennan, 2008).

There are more than 60 species of weeds in the wheat fields in Shandong (Gao *et al.*, 2014). Glufosinate-ammonium is a broad-spectrum nonselective herbicide commonly used for the control of weeds in agricultural systems (Dayan *et al.*, 2009; Norizah and Kuntom, 2013). However, glufosinate-ammonium is rarely used in crop weed control, so the residual characteristics of

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glufosinate-ammonium in wheat field soil and its effect on wheat and other gramineous crops are still unclear.

Glufosinate-ammonium is a contact-killing herbicide. It is sprayed on the soil immediately after sowing the wheat as a pre-emergence herbicide, so the wheat will not be directly poisoned by glufosinate-ammonium. However, it is still unclear whether glufosinate-ammonium at an excessively high concentration is adsorbed by the soil, and whether it will be transported to the whole body of the wheat through the root system in the subsequent life activities of the wheat. As the main source of food in the world, the safety of wheat is of utmost importance. Existing studies have identified that glufosinate-ammonium in the soil is mainly dissipated through the oxidation, transamination, and acetylation reactions of soil microorganisms, with a short half-life and no adverse effects on the ecological components of crops and soil microorganisms (Bartsch and Tebbe, 1989, Wibawa *et al.*, 2010). However, the adsorption of glufosinate-ammonium is associated with biological activity, soil pH, organic matter, clay content, and cation exchange capacity (Tayeb *et al.*, 2019). Therefore, soils with different physical and chemical properties exert various effects on the adsorption of glufosinate-ammonium, and the residual amount of glufosinate-ammonium in wheat fields needs to be tested.

Considerable efforts have been made to detect glufosinate residue in plants and soil. Glufosinate-ammonium has the characteristics of strong polarity, strong water solubility, low volatility, and insoluble inorganic solvents (Yang *et al.*, 2019). Detection methods such as gas chromatography-quadrupole mass spectrometry (GC-MS) and gas chromatography-flame photometric detector (GC-FPD) are used, but they are time-consuming and labor-intensive to apply (Royer *et al.*, 2000, Tseng *et al.*, 2004). In addition, ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) with high sensitivity, accuracy, and efficiency has been applied for the determination of glufosinate residues in some plants (Dong *et al.*, 2015, Wu *et al.*, 2015, Yang *et al.*, 2019), but there is hardly any paper showing the application of this method for the determination of glufosinate residues in wheat.

In this experiment, an UPLC-MS/MS method was developed to investigate the residues of glufosinate at different dosages [0 times the recommended dosage (CK), 0.5 times the recommended dosage (T1), 1.0 times the recommended dosage (T2), 1.5 times the recommended dosage (T3), and 2.0 times the recommended dosage (T4)] in wheat plants, grains, and different soil layers (0–20, 20–40, 40–60 cm soil layers in field experiment, and 0–20, 20–40, 40–60, 60–80, 80–100 cm soil layers in soil column experiment). The results are of important implications for promoting safe wheat production.

Materials and Methods

Experimental materials

The compound fertilizer is Ruimin compound fertilizer (12-15-10 of N-P_2O_5-K_2O, Ruimin Fertilizer Co., Ltd., Kaifeng, China). Glufosinate-ammonium was provided by Yongnong Biological Science Co., Ltd. (Kaifeng, China), the active ingredient content of 20%. Glufosinate-ammonium standard product (99% purity) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Sodium borate, ethyl acetate, methanol, and Fmoc-Cl were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Experimental design

The study was divided into field experimental and soil column experimental, and it was conducted from October 2015 to June 2016. Apply glufosinate ammonium spray to the wheat field immediately after sowing. The dosage of ammonium phosphate was 0.5 times (T1), 1.0 times (T2), 1.5 times (T3), and 2.0 times (T4) of the recommended dosage of the commercial preparations, respectively. The spraying of water was used as a control (CK). The field was sprayed with a hand-held sprayer, and the soil column test was sprayed with a small watering can. For treatment, the specific dosage of ammonium phosphate was shown in Table 1.

The field test was carried out at Baoshan Test Base (36.02°N, 119.85°E) in Huangdao District, Qingdao. A randomized block design was adopted in the field, with five treatments and three repetitions in the experiment. The area of each plot is 3*18 m^2, and the isolation area is 1 m. Apply 750 kg/hm^2 compound fertilizer as base fertilizer before sowing. The wheat was sown on October 14, 2015, with a sowing rate of 187.5 kg/hm^2, and harvested on June 8, 2016.

The soil column experiment was conducted in the experimental base of Qingdao Agricultural University (36.30 ° N, 120.36 ° E). Five treatments were set up with

Table 1. Herbicide design of each treatment of experiment.

Treatments	Application rate of field (mL/hm^2)	Application rate of soil column (μL/column)
CK	0	0
T_1	2001	6.28
T_2	4002	12.56
T_3	6003	18.84
T_4	8004	25.12

Table 2. The basic information of the experiment site.

	pH	Organic matter (%)	Available phosphorus (mg/kg)	Available potassium (mg/kg)	Total nitrogen (%)	Available nitrogen (mg/kg)
Field experiment	6.57	1.1	—	—	1.3	87.5
Soil column experiment	7.35	1.1	41.3	103.6	1.1	89.8

12 repetitions, and 4 wheat plants were planted per column. Field soil was selected, removed from debris such as rocks, plant materials, wood blocks, and other with a 1-cm soil sieve, and then moved into soil columns that were 20 cm in diameter and 60 cm in height. The compound fertilizer was applied into the soil layer of 5–35 cm and mixed evenly with the soil. On October 12, 2015, the wheat seeds were applied to the germination trays, and water was added to promote germination. On October 16, 2015, the healthy sprouting wheat seeds were selected and planted into the 5 cm soil layer in the soil column, and the sowing distance was maintained. The basic information of the experiment site is shown in Table 2.

Sampling methods

The plant samples were taken at the wintering stage, recovering stage, jointing stage, heading stage, flowering stage, filling stage, and maturing stage, and then stored directly in −20°C freezer. Soil samples were collected at the wintering stage, recovering stage, jointing stage, heading stage, flowering stage, filling stage, and maturing stage, then screened by 20 mesh sieve and stored in −20°C freezer. During the harvest period, the harvested wheat was dried, ground, and stored in −20°C freezer. The plant, ground soil, and wheat grain samples were used for the determination of glufosinate residue.

Sample pretreatment methods

The sample pretreatment methods were adopted by Jian *et al*. (2015) and Zhu *et al*. (2015), with minor modifications.

Exactly 4.0 g of the sieved soil samples was weighed in a 100 mL conical flask and extracted with THZ-92C oscillator using 20 mL of ultrapure water for 1.5 h. The extraction solution was filtered through a 0.45 μm water system microporous membrane for derivatization. Filtered solution (1.5 mL) was fully mixed with 0.2 mL of 0.125 mol L^{-1} sodium borate solution and 1 mL of 200 mg L^{-1} Fmoc-Cl solution. The mixed solution was placed at room temperature for 30 min, then extracted with ethyl acetate (5 mL by three times), and the water layer was taken for injection.

Weighed wheat plant or grain sample 2.0 g was mixed in 10 mL of 0.05 mol L^{-1} KOH solution in a 50 mL centrifuge tube and shaken at THZ-92C oscillator for 30 min, then made to stand and filtered. Add 20 μl of 5 mol L^{-1} HCl solution to 5 mL of the filtrate, shake evenly, and filter again. Filtrates were subsequently purified with 3 mL Oasis HLB column (first rinse with 2 mL of methanol and then activate with 2 mL of water) by gravity flow. Around 0.2 mL of 0.125 mol L^{-1} sodium borate buffer solution was added to the purified solution and shaken well, then 1 mL of 1.0 g L^{-1} Fmoc-Cl derivatization reagent was mixed, shaken evenly, and made to stand for 2 h. The derivatized liquid sample was then filtered through a 0.22 μm water filtration membrane before being used for UPLC-MS/MS analysis.

Measurement condition

Extracts of samples and calibration standards were analyzed on an Agilent 1290 ultra-high pressure liquid chromatograph (Agilent Technologies Inc., American) coupled to Agilent 6460 QQQ mass spectrometer (Agilent Technologies Inc., American) equipped with electrospray ion source (ESI).

Analytical separation was achieved using the Agilent ZORBAX Extend C18 (2.1 mm * 100 mm, 1.8 μm) column. Isocratic elution was achieved with a mobile phase of DI water (2% formic acid)—methanol (98:2) at a flow rate of 4 mL/min. The sample injection volume was set at 5 μl and the column temperature was kept at 30°C.

The mass spectrum condition and parameters were as follows: scanning method, positive ion source; spray voltage, 80V; capillary voltages, 4kV (+) and 3.5kV (−); desolvation temperature, 375°C; sheath gas flow, 11 L/min; nebulizer pressure, 40 psi; detection mode, multiple reaction monitoring (MRM); qualitative ion pair(m/z), 404/136; retention time, 3.33s.

Method verification

Calibration curve

Using the peak area as the ordinate (Y) and the injection mass concentration as the abscissa (X), the standard curve equation was Y = 115995X−498.06 (Figure 1).

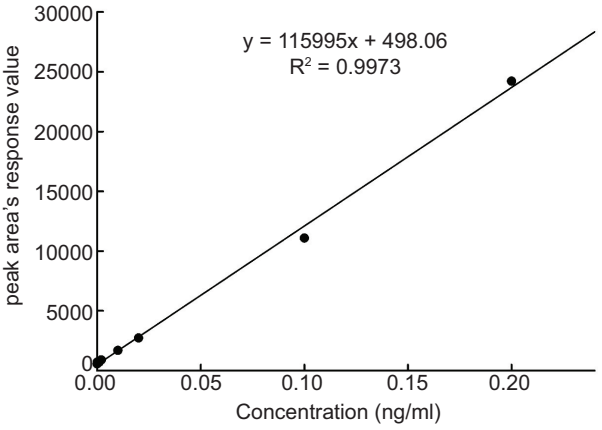

Figure 1. Standard curve of glufosinate-ammonium.

Table 3. The accuracy and precision of glufosinate-ammonium analytical methods.

Sample	Adding level (mg/kg)	Average fortified recoveries (%)	RSD (%)
Soil	0.05	85.3	2.04
	0.10	85.5	2.16
	1.00	86.8	1.72
Plant	0.05	83.5	1.95
	0.10	84.2	2.18
	1.00	85.1	2.21
Grains	0.05	80.7	2.83
	0.10	81.3	2.09
	1.00	82.6	1.99

Within the concentration range of 0.00002–0.2 ng/mL, a correlation coefficient (R^2) of 0.9973 indicates good linearity between concentration and area. The minimal limit of detection was 0.1 ng/kg.

Accuracy and precision

To identify the accuracy and precision of UPLC-MS/MS used in this experiment, glufosinate standard solutions at three levels of 0.05, 0.10, and 1.00 mg/kg were added to the blank samples of wheat soil, plant, and grain, respectively, and the above steps were repeated five times. The recovery of glufosinate standard solution was determined by ultra-high pressure liquid chromatography tandem mass spectrometry, and the average addition recovery and relative standard deviation were calculated. The test results were shown in Table 3.

The average recoveries ranged from 80.7 to 86.8%, and their RSDs were within 2.83% (Table 3). The results showed that the accuracy and precision were acceptable.

Data processing

Microsoft Excel 2019 and SigmaPlot 14.0 software were used for data processing and figure drawing, respectively. One-way ANOVA was performed with SPSS 26.0, and post hoc multiple comparisons were performed using Tukey test ($P < 0.05$).

Results and Discussion

Residual characteristics of glufosinate-ammonium in soil

As shown in Table 4, during the growth period of wheat, glufosinate-ammonium has residue in different soil layers of field wheat, but the amount of residue is very small. No residue of glufosinate-ammonium was detected in the 0–60 cm soil layer of each treatment during the flowering, filling, and maturing stages of wheat. In the same growth period, the residual amount of glufosinate-ammonium showed a gradually decreasing trend with the increase of soil thickness. Glufosinate has strong water solubility, and the glufosinate sprayed on the surface of the soil will leach to the deeper soil with the rain. During this process, glufosinate-ammonium will be gradually adsorbed by clay particles in the soil. Therefore, the residual amount of glufosinate in the surface soil is greater than the residual amount in the deep soil.

In the same soil layer, the sequence of glufosinate residues in the reproductive period were wintering, recovering, jointing, and heading stage. Temperature will affect the adsorption of glufosinate to soil. There are studies indicating that the Kd value tended to decrease with the increase of temperature under the condition of neutral soil (Dinehart *et al*., 2009, Kah and Brown, 2006). From the wintering stage to the heading stage, with the increase in temperature, the adsorption amount of glufosinate-ammonium decreased continuously, and the desorption trend increased. The most predominant is that glufosinate-ammonium desorbs and leaches into the soil solution, and is degraded by soil microbial activities, causing the biological loss of glufosinate-ammonium. The harm of organic chemical herbicides to soil microorganisms is limited to a short time after application. Subsequently, microorganisms participate in the degradation of herbicides and use them as the biological source of their own physiological processes. Correspondingly, the residual concentration of the herbicide and its toxic effect gradually decreases with the biological activities of soil microorganisms until the half-life (Bera and Ghosh, 2013). However, excessive application of herbicides will cause too much harm to soil microorganisms in a short time, and the recovery cycle of microbial biological activities will become longer.

During the wintering stage, the glufosinate residues of T4 were significantly higher than those of T1, T2, and T3 in the 0–20 cm soil layer, which were 1.63, 1.50, and 1.48 times higher than those of T1, T2, and T3, respectively.

Table 4. The glufosinate-ammonium residue in wheat soil (field).

Treatment	Soil-layer thickness (cm)	Residual amount of glufosinate-ammonium (ng/kg)						
		Wintering stage	Recovering stage	Jointing stage	Heading stage	Flowering stage	Filling stage	Maturing stage
CK	0–20	ND	ND	ND	ND	ND	ND	ND
	20–40	ND	ND	ND	ND	ND	ND	ND
	40–60	ND	ND	ND	ND	ND	ND	ND
T_1	0–20	59.51 ± 2.29^{b}	13.91 ± 1.66^{b}	2.13 ± 0.14^{b}	ND	ND	ND	ND
	20–40	26.26 ± 2.46^{c}	2.7 ± 0.43^{c}	0.07 ± 0.01^{c}	ND	ND	ND	ND
	40–60	13.03 ± 1.98^{b}	0.43 ± 0.13^{b}	ND	ND	ND	ND	ND
T_2	0–20	64.87 ± 2.51^{b}	15.94 ± 0.87^{b}	3.96 ± 0.23^{b}	ND	ND	ND	ND
	20–40	29.44 ± 1.65^{bc}	3.73 ± 0.58^{bc}	0.79 ± 0.08^{b}	ND	ND	ND	ND
	40–60	16.79 ± 1.56^{b}	0.38 ± 0.07^{b}	ND	ND	ND	ND	ND
T_3	0–20	66.48 ± 1.80^{b}	27.03 ± 1.45^{a}	7.25 ± 0.52^{a}	1.68 ± 0.11^{a}	ND	ND	ND
	20–40	31.99 ± 1.15^{ab}	5.19 ± 0.26^{b}	1.01 ± 0.18^{ab}	ND	ND	ND	ND
	40–60	24.91	1.87 ± 0.45^{a}	ND	ND	ND	ND	ND
T_4	0–20	97.23 ± 2.16^{a}	30.38 ± 1.10^{a}	9.24 ± 0.91^{a}	1.89 ± 0.16^{a}	ND	ND	ND
	20–40	36.18 ± 1.38^{a}	7.24 ± 0.71^{a}	1.4 ± 0.21^{a}	ND	ND	ND	ND
	40–60	26.61 ± 1.38^{a}	1.92 ± 0.27^{a}	ND	ND	ND	ND	ND

ND indicates that glufosinate-ammonium's residue was not detected under the chromatography/mass spectrometry conditions.

And in the 20–40 cm and 40–60 cm soil layers, the glufosinate residues of T4 were significantly higher than those of T2, while there was no significant difference between T3 and T2. At the jointing stage, the residual amount of glufosinate in T4 was significantly higher than that in T1 and T2 in the 0–20 cm and 20–40 cm soil layers. And, no glufosinate residue was detected in 40–60 soil layers of all treatments. At the heading stage, only the residue of glufosinate in 0–20 cm soil layer of treatment T3 and T4 were detected, which were 1.68 ng/kg and 1.89 ng/kg, respectively. No glufosinate residue was detected in all soil layers of each treatment at the flowering stage.

From Table 5, it can be seen that the determination results of glufosinate residue in soil column experiment were similar to those in the field experiment. No residues of glufosinate were detected in the soil of T1, T2, T3, and T4 at flowering, filling, and maturing stage of wheat. During the wintering stage, the residues of glufosinate in T4 were significantly higher than those in T1, T2, and T3 in the 0–20 cm soil layer, which were 90.27, 28.27, and 5.64 times higher than those in T1, T2, and T3, respectively. During the jointing stage, glufosinate residues were significantly greater in T3 and T4 than those in T1 and T2 in the 0–20, 20–40, and 40–60 cm soil layers. No glufosinate residues were detected in the 60–100 cm soil layer in T1, and glufosinate residues were significantly higher in T3 and T4 than those in T2. At the heading stage, no glufosinate residue was detected in the 0–100 cm soil layer of treatments T1 and T2. T3 and T4 still have glufosinate residues in the 40–60 cm soil layer, but no glufosinate was detected in the 40–60 cm soil layer of T3 and T4 in the field experiment at this stage. It may be because the field soil is weakly acidic soil, and the soil selected for the soil column experiment is weakly alkaline. Generally, the adsorption of glufosinate-ammonium was higher at higher pH (Küsters and Gerhartz, 2015). The increase in pH leads to the loss of H^+ ions on the surface of clay particles and the increment in the negative charge of the quantity of the surface charge, resulting in the elevation of Kd value and the adsorption capacity of glufosinate (Corbett *et al*., 2004; Tayeb *et al*., 2015).

Determination of glufosinate residue in wheat

In each growth period of wheat, no residue of glufosinate-ammonium was detected in the plants of wheat in the field and soil column experiments (Tables 6 and 7).

It can be seen from Table 8 that under the detection method of UPLC-MS/MS in this experiment, no residue of glufosinate was detected in the grains of field wheat and soil column wheat treated with CK, T1, T2, T3, and T4.

Under the normal field rate, the absorption of glufosinate-ammonium occurs mainly through intercellular diffusion, and the absorption rate depends on

Table 5. The glufosinate-ammonium residue in wheat soil (soil column).

Treatment	Soil-layer thickness (cm)	Residual amount of glufosinate-ammonium (ng/kg)						
		Wintering stage	Recovering stage	Jointing stage	Heading stage	Flowering stage	Filling stage	Maturing stage
CK	0–20	ND	ND	ND	ND	ND	ND	ND
	20–40	ND	ND	ND	ND	ND	ND	ND
	40–60	ND	ND	ND	ND	ND	ND	ND
	60–80	ND	ND	ND	ND	ND	ND	ND
	80–100	ND	ND	ND	ND	ND	ND	ND
T_1	0–20	11.59 ± 1.11^c	3.66 ± 0.28^c	0.24 ± 0.02^c	ND	ND	ND	ND
	20–40	10.16 ± 0.92^c	1.82 ± 0.15^c	0.16 ± 0.01^c	ND	ND	ND	ND
	40–60	7.53 ± 0.75^c	0.91 ± 0.13^c	0.13 ± 0.01^c	ND	ND	ND	ND
	60–80	5.29 ± 0.33^d	0.53 ± 0.05^c	ND	ND	ND	ND	ND
	80–100	4.22 ± 0.41^c	0.27 ± 0.04^c	ND	ND	ND	ND	ND
T_2	0–20	32.44 ± 1.70^c	6.01 ± 0.62^c	1.46 ± 0.06^c	ND	ND	ND	ND
	20–40	27.41 ± 0.91^c	5.29 ± 0.22^c	0.96 ± 0.06^c	ND	ND	ND	ND
	40–60	18.35 ± 1.71^c	4.08 ± 0.30^c	0.23 ± 0.01^c	ND	ND	ND	ND
	60–80	17.36 ± 0.45^c	3.90 ± 0.23^c	0.11 ± 0.01^c	ND	ND	ND	ND
	80–100	12.22 ± 1.02^c	2.58 ± 0.17^c	ND	ND	ND	ND	ND
T_3	0–20	162.49 ± 4.21^b	27.36 ± 1.09^b	9.82 ± 0.50^b	1.01 ± 0.09^b	ND	ND	ND
	20–40	131.02 ± 4.09^b	23.92 ± 1.28^b	8.16 ± 0.21^b	0.92 ± 0.10^b	ND	ND	ND
	40–60	110.19 ± 3.20^b	16.83 ± 1.38^b	7.02 ± 0.12^b	0.56 ± 0.07^b	ND	ND	ND
	60–80	82.41 ± 2.80^b	11.76 ± 0.18^b	4.34 ± 0.20^b	0.32 ± 0.05^b	ND	ND	ND
	80–100	40.15 ± 1.91^b	10.16 ± 0.25^b	1.92 ± 0.09^b	ND	ND	ND	ND
T_4	0–20	917.17 ± 14.22^a	158.44 ± 1.81^a	21.58 ± 1.55^a	6.58 ± 0.17^a	ND	ND	ND
	20–40	714.09 ± 10.62^a	133.61 ± 3.76^a	19.37 ± 1.25^a	4.42 ± 0.18^a	ND	ND	ND
	40–60	499.9 ± 12.93^a	116.37 ± 3.76^b	16.23 ± 1.04^a	2.72 ± 0.21^a	ND	ND	ND
	60–80	273.28 ± 4.93^a	103.77 ± 3.67^a	10.18 ± 0.87^a	1.53 ± 0.17^a	ND	ND	ND
	80–100	183.16 ± 8.53^a	94.80 ± 2.54^a	9.58 ± 0.46^a	0.96 ± 0.06^a	ND	ND	ND

ND indicates that glufosinate-ammonium's residue was not detected under the chromatography/mass spectrometry conditions.

Table 6. The glufosinate-ammonium residue in wheat plant (field).

Treatment	Residual amount of glufosinate-ammonium (ng/kg)						
	Wintering stage	Recovering stage	Jointing stage	Heading stage	Flowering stage	Filling stage	Maturing stage
CK	ND	ND	ND	ND	ND	ND	ND
T_1	ND	ND	ND	ND	ND	ND	ND
T_2	ND	ND	ND	ND	ND	ND	ND
T_3	ND	ND	ND	ND	ND	ND	ND
T_4	ND	ND	ND	ND	ND	ND	ND

ND indicates that glufosinate-ammonium's residue was not detected under the chromatography/mass spectrometry conditions.

the concentration gradient inside and outside the cell (Takano *et al.*, 2020). During the period from spraying glufosinate-ammonium to the germination of wheat, glufosinate-ammonium was partially adsorbed by soil and partially degraded by microbial activity. Glufosinate-ammonium has high hydrophilicity, it is difficult to distribute in high-lipid solid phase, and it is unlikely to move between lipophilic layers (Takano *et al.*, 2019). Part of the glufosinate-ammonium dissolved in the soil solution may be absorbed by wheat roots through cell proliferation. However, no residue of glufosinate-ammonium was detected in the wheat plants from the wintering

Table 7. The glufosinate-ammonium residue in wheat plant (soil column).

Treatment	Residual amount of glufosinate-ammonium (ng/kg)						
	Wintering stage	Recovering stage	Jointing stage	Heading stage	Flowering stage	Filling stage	Maturing stage
CK	ND	ND	ND	ND	ND	ND	ND
T_1	ND	ND	ND	ND	ND	ND	ND
T_2	ND	ND	ND	ND	ND	ND	ND
T_3	ND	ND	ND	ND	ND	ND	ND
T_4	ND	ND	ND	ND	ND	ND	ND

ND indicates that glufosinate-ammonium's residue was not detected under the chromatography/mass spectrometry conditions.

Table 8. The glufosinate-ammonium residue in wheat grains.

Treatment	Residual amount of glufosinate-ammonium (ng/kg)	
	Field	Soil column
CK	ND	ND
T_1	ND	ND
T_2	ND	ND
T_3	ND	ND
T_4	ND	ND

ND indicates that glufosinate-ammonium's residue was not detected under the chromatography/mass spectrometry conditions.

stage to the maturing stage. This may be due to the low content of glufosinate-ammonium in the soil solution, and only a very small amount of glufosinate-ammonium is absorbed by the wheat roots through cell diffusion. At the same time, glufosinate-ammonium does not have favorable systemic capacity, and it is difficult to quickly transport from the root of wheat to other parts (Takano and Dayan, 2020). Besides, the uptake of glufosinate by wheat cells is very low, and some of the absorbed glufosinate is metabolized to 4-methyl-phosphinico-butyric acid in wheat cells (Komossa and Sandermann, 1992), so the residual amount of glufosinate in wheat plants is insignificant.

The U.S. Federal Law stipulates that the residue of glufosinate-ammonium in wheat straw is less than or equal to 0.4 mg/kg. In Japan, the final residue of glufosinate-ammonium in wheat should be less than or equal to 0.20 mg/kg. Furthermore, the maximum residue limit (MRL) of glufosinate-ammonium in wheat grain is regulated to be 0.1 mg/kg in the European Union. However, the results of this experiment showed that in the mature period of wheat, the residual amount of glufosinate-ammonium in the wheat soil was much less than 0.2 ng/kg in all treatments. Glufosinate-ammonium was not detected in wheat plants and grains at each growth stage. It shows that the application of glufosinate-ammonium is safe for wheat grains, wheat soil, and next crops under the spraying rate of this experiment.

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Conflicts of Interest

The author declares that there is no conflict of interest.

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