Exposure Assessment of a Novel Pesticide Fufenozide in a Dryland Field Ditch and Pond

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Abstract

A semi-field test was conducted to assess the risk of exposure to fufenozide in a ditch and pond adjacent to an agricultural area. To support the investigation, a fast, highly selective, and sensitive method was developed to determine the residue of fufenozide in water, sediment, and soil through high performance liquid chromatography-tandem mass spectrometry. The recoveries were in the acceptable range of 85.6% to 99.3% in the three matrices, with the associated relative standard deviations at 1.2% to 7.8%. The results indicate that the surface water-sediment system could be exposed to fufenozide through runoff after application, which dissipated rapidly in the aquatic ecosystem. The toxicity exposure ratio showed no risk of fufenozide exposure to the fish in the aquatic ecosystem close to the agriculture field.

Introduction

Pesticides are widely used for their benefits in increasing the yield of agricultural products; however, they have been reported to increase eco-toxicological effects and give rise to potential risks to the ecosystem [1]. Pesticides have long presented risks to aquatic environments through several modes (e.g., spray drift deposition on crops, surface soil, and water bodies; discharge into surface water through runoff or drainage; and so on).The environmental pollution attributed to pesticides is a major concern in the safety of ecosystems [2-4], particularly that of aquatic ecosystems. For instance, risk assessment and risk mitigation of pesticides in ponds have been performed in different studies [5-7].

Fufenozide (Fig. 1) [2, 3-dihydro-2, 7-dimethyl-2-(3, 5-dimethylbenzoyl)-2-(1, 1-dimethylethyl)-hydrazide] is a novel nonsteroidal ecdysone agonist that binds to the ecdysone receptor complex of insects to compete with ecdysteroids, thus interfering with the gene expression of cuticle secretion and inducing precocious and incomplete molt [8, 9]. Fufenozide was developed by Jiangsu Pesticide Research Institute Company Ltd., China (development code JS118, CAS registry number 467 427-81-1, and China patent number ZL 01108161.9). Fufenozide is currently registered to control such lepidopterous insects as diamondback moth, armyworm, and tea geometrid on vegetables, tea, and forests in China [10-13]. Although nonsteroidal ecdysone agonists are reportedly safe for mammals, a number of studies remain focused on the toxicology and ecotoxicology effects of nonsteroidal ecdysone agonists on mammals and non-target organisms [14, 15].

In the high rainfall area of southern China, dryland agricultural fields typically surround a pond. Fufenozide will typically enter the pond through runoff after being sprayed on the fields. Although the toxicity of fufenozide to aquatic organisms and non-target plants remains unclear, the risk of

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exposure to fufenozide for dryland aquatic ecosystems must be investigated to ensure environmental safety. To support the study, it is necessary to develop a residue analysis approach for soil, surface water, and sediments.

To date, a few studies have conducted a residue analysis method for fufenozide in soil [16-18]. However, none have reported on a fufenozide residue analysis method suitable for surface water and sediments. In published papers, fufenozide was detected via high performance liquid chromatography-ultraviolet detection (HPLC-UV) or HPLC-diode array detection (HPLC-DAD) [16-21].The sensitivity and the specificity of these methods do not meet the requirements for the determination of fufenozide residue in sediments and surface water. Owing to recent technical developments, HPLC-mass spectrometry (HPLC-MS) has recently been used to detect polar and thermally labile pesticides. In particular, the tandem mass technique (HPLC-MS/MS) is a useful tool for pesticide analysis because of its high precision, sensitivity, and selectivity [22-24]. To the best of our knowledge, ours is the first study on the risk assessment of fufenozide in dryland aquatic systems; and is the first study on the use of a residue detection method of fufenozide in sediments and surface water utilizing HPLC-MS/MS to meet sensitivity and specificity requirements.

The present study aims to investigate the exposure risk of fufenozide to adjacent ditches and ponds and access the ecotoxicological risk of fufenozide to fish in dryland aquatic systems. In support, an HPLC-MS/MS approach was developed to determine fufenozide exposure levels in soil, water, and sediments.
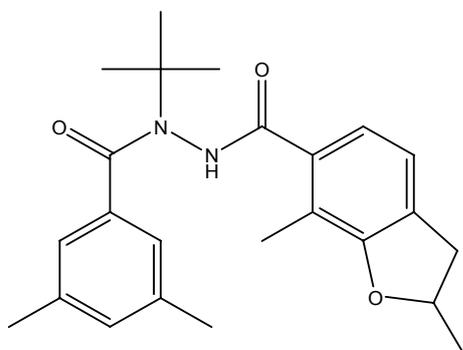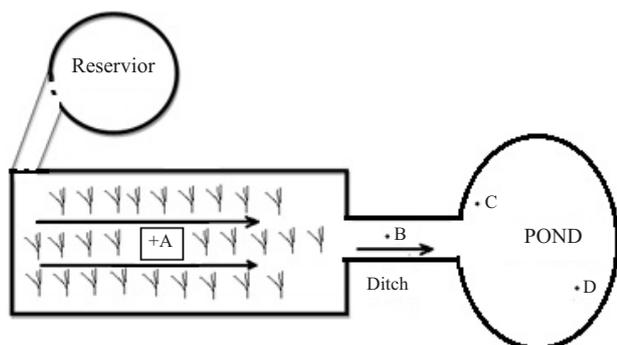

Fig. 1. Fufenozide structure.

Fig. 2. Dryland aquatic ecosystem scheme and sampling site A in testing field, B in ditch, C and D in pond.

Experimental Procedures

Semi-Field Test

The semi-field test was conducted in Hu Zhou, Zhejiang Province, China. The site is a dryland aquatic ecosystem comprising a reservoir, a testing field, a ditch, and a pond (Fig. 2). The testing field has an area of 733 m^2, whereas that of the pond was 500 m^2 with a 70 cm water depth. The ditch was 20 m long. Fufenozide was applied once at a dose of 150 g a.i./ha (the maximum recommended manufacturer dose). Using the water from the reservoir, rainfall was simulated at 24 hr after fufenozide was sprayed. 36.65 tons of water was pumped from the aqueduct connected with the reservoir, whereas the rainfall was mimicked by 6 stretcher-mounted sprayers, equaling 50 mm precipitation. This rainfall could carry the fufenozide through the ditch into the pond. Samples were collected before the fufenozide was sprayed, 1 hr and 26 hr after application (after the artificial rainfall and all the surface water in the field had entered the pond), and 5 days and 7 days after application. In the research period, the daily average temperature ranged from 23.6 to 27.2ºC, whereas only one shower occurred 2 days after application, which did not induce runoff. The samples included a test field soil sample collected from sampling site A, ditch water and ditch sediment samples collected from sampling site B, and pond water and pond sediment samples collected from sampling sites C and D (Fig. 2).

The water, sediment and soil samples were collected according to environmental monitoring sampling approaches [25, 26]. All the samples were refrigerated (-20ºC) until analysis.

Chemicals

A formulation of 10% fufenozide SC (suspension concentrates) was used for field application. This formulation is widely used in China. The analytical standards of fufenozide (99.6% purity) were obtained from the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA), Beijing, China and then stored in a freezer at -20ºC. Ethyl acetate, methanol, formic acid, and acetonitrile were all of analytical grade and purchased from Beijing Chemical Plant. HPLC-grade methanol was purchased from Jack Johnson (USA), and ultra pure water was purchased from Wahaha, Inc. (Jiangsu, China). The solid phase extraction (SPE) C_{18} bonded porous silica (500 mg) with a 6 mL capacity cartridge was obtained from VARIAN (USA), and the SPE of the 300 and 500 mg Graphitized Carbon Black cartridges (GCB absorbent, 100 to 200 mesh, Jilin Chemical Industry Co., China) with 6 mL capacity were prepared in our laboratory.

The 1,000 mg/L standard stock solution of fufenozide was prepared in methanol and then serially diluted in methanol to prepare the working standard solutions used for a calibration curve (10, 50, 100, 500, and 750 µg/L). Matrix-matched standard solutions were prepared by adding a concentrated blank sample extract (water, soil, and

sediment matrices) to each serially diluted standard solution. All the standard solutions were stored in the dark in a refrigerator at -20ºC, and no degradation or reaction was observed over 6 months. Matrix-matched standard solutions were freshly prepared before use.

Analysis Procedure

Extraction and Clean Up

Water samples: The fufenozide residue in the water samples was extracted using C_{18} cartridges preconditioned with 5 mL methanol and 5 mL ultra pure water before use. The 100 mL samples were loaded into the cartridge at a flow rate of 2 mL/min. The cartridge was washed with 10 mL ultra pure water and dried in air for 30 min. Fufenozide was eluted from the cartridges with 40 mL methanol and ethyl acetate (1:1, V/V) and then concentrated to nearly 1 mL using a rotary evaporator (Yarong Biochemical Instrument, Inc., Shanghai, China) at 35ºC, followed by drying with nitrogen gas. The sample was then dissolved in a 1 mL methanol and ultrapure water solution (80:20, V/V). Finally, the sample was filtered through a 0.2 μm polyvinylidene difluoride (PVDF) syringe filter and stored for chromatographic injection. The soil and sediment samples also were filtered with the 0.2 μm PVDF syringe filter prior to injection.

Soil samples: 3 g of soil was extracted with 30 mL ultra pure water/methanol (5:1, V/V) using a Vortex-Genie 2 shaker for 0.5 min and via ultra-sound extraction for 60 min at 50ºC in sequence. The extract solution was centrifuged at 4,000 r/min for 10 min. The supernatant was transferred into a flask, and the residue was re-extracted with 30 mL acetonitrile. The supernatant was then mixed in the flask and was concentrated to approximately 2 mL to 3 mL using a rotary evaporator. The concentrated sample solution was loaded into 300 mg GCB cartridges preconditioned with 3 mL methanol and 3 mL pure water, in sequence, before use. Fufenozide was eluted with 15 mL methanol and 10 mL ethyl acetate, concentrated to nearly 1 mL using a rotary evaporator, dried with nitrogen gas, and dissolved in a 1 mL methanol and ultra pure water solution (80:20, V/V).

Sediment samples: 20 g of sediment sample was extracted twice with 40 mL acetone/ethyl acetate (60/40, V/V) using a Vortex-Genie shaker for 1 min and ultra-sound for 20 min with a water bath set to 50ºC, in sequence. The extract was centrifuged at 4,000 r/min for 10 min. The supernatant was collected and then concentrated to remove the acetone/ethyl acetate using a rotary evaporator. The liquid phase was extracted with 40, 30, and 30 mL dichloromethane, in sequence. The dichloromethane phases were combined and concentrated to nearly 1 mL, followed by drying with nitrogen gas flux and dissolution with 3 mL methanol. The extract solution was loaded onto a 500 mg GCB cartridge. Fufenozide was eluted with 20 mL methanol and concentrated using a rotary evaporator, followed by drying with nitrogen gas flux and dissolution with a 1 mL solution of methanol and ultrapure water (80/20, V/V).

HPLC-MS/MS Conditions

The chromatographic system comprised a Shimadzu separation module (Shimadzu, Japan) equipped with a binary solvent delivery system, a degasser, an autosampler, and a column heater. Chromatographic separation was performed using a VARIAN Pursuit XRs Ultra 2.8 n C_{18} 50 mm × 2.0 mm analytical column (Varian, USA) at 40ºC to reduce viscosity. The mobile phase was a 70% methanol and water solution (containing 0.2% formic acid) at 0.2 mL/min. The injection volume was 5 μL.

Fufenozide was detected using a linear ion trap mass spectrometer LTQ XL (Thermo-Fisher, USA) equipped with an electrospray ionization (ESI) source. The nebulizer gas was 99.999% nitrogen, whereas the collision gas was 99.999% helium gas. MS/MS detection was performed in the positive ion mode. The monitoring conditions were: spray voltage, 4.0 kV; sheath gas flow rate, 30 arb; aux gas flow rate, 10 arb; capillary voltage, 45 V; and capillary temp, 350ºC. Selected reaction monitoring (SRM) was used to detect fufenozide. The m/z 417 $[M+Na]^+$ is the precursor ion and its product ions (m/z 245 and m/z 267) were monitored at collision energy 20. Among these ions, the most intense (m/z267) was used for quantification. The scan time was set at 30 ms. Under these conditions, the retention time of fufenozide was approximately 2.9 min.

Quantification and Identification

The fufenozide retention time and the relative intensity ratio of the mass ions (m/z 245 and m/z 267) were used for peak identification. The presence of fufenozide in a sample was verified based on the following criteria:
(1) the signal-to-noise (S/N) ratio of each SRM chromatogram must be 3/1 or higher
(2) the retention time in each SRM chromatogram must not exceed 5%, relative to the standard
(3) the relative abundance ratio obtained from the product ions in the sample must match the comparison standard within ± 10% [27].

Method Validation

A conventional validation procedure was employed to validate the developed method performance by evaluating specificity, linearity, limit of detection (LOD), limit of quantization (LOQ), accuracy, and precision. The linearity of the HPLC-MS/MS system was evaluated by analyzing the standard solvent solution and the standard matrix-matched solutions. Blank samples were analyzed to estimate the interference from different matrices. The LODs were generated based on the lowest fortified level in the present research, and the LOQs were estimated from the S/N ratio of 10 according to the mass chromatogram.

Five replicates of the fortified samples were prepared at two fortification levels (0.1 and 10 μg/L for water, 3.3 and 330 μg/kg for soil, and 2.5 and 500 μg/kg for sediments). Fufenozide was extracted and purified according to the described method.

Table 1. Solvent standard calibration curve of fufenozide and matrix-matched calibration curves.

Standard sample	Concentration (µg/L)	Calibration equation	R^2
Solvent standard	10-750	y = 0.00023x − 34.6432	0.9949
Water-matched standard	10-750	y = 0.00012x + 1.7525	0.9927
Soil-matched standard	10-750	y = 0.00024x − 51.5423	0.9917
Sediment-matched standard	40-750	y = 0.00059x + 0.2416	0.9961

TER Method

Effect data (LC_{50}, EC_{50}, NOEC, and so on) for fish were divided according to exposure levels to generate the TER [28-30]. Given that fish are the subject, the acute TER values (TERst) and long-term TER values (TERlt) can be considered. TERs are compared with the trigger values in 91/414 Annex VI. A TERst < 100 or a TERlt < 10 indicates high risk for fish.

$$TERa = \frac{acute\ LC_{50}\ (mg\ a.\ s./L)}{realistic\ worst\text{-}case\ PECsw\ (initial\ or\ short\text{-}term,\ mg\ a.\ s./L)}$$

$$TERlt = \frac{chronic\ NOEC\ (mg\ a.\ s./L)}{long\text{-}term\ PECsw\ (mg\ a.\ s./L)}$$

Results and Discussion

HPLC-MS/MS Parameterization

HPLC was performed using a VARIAN Pursuit XRs Ultra 2.8 n C_{18} 50 mm × 2.0 mm analytical column and then optimized to achieve minimal run time. Comparing the HPLC-MS/MS chromatograms of the blank sample with that of the matrix-matched standard (Fig. 3), no interference peak was observed in the region of the fufenozide peak. The retention time of fufenozide was 2.9 min, and the total HPLC analysis time was 5.5 min. The present detection method was faster than the reported HPLC-UV and HPLC-DAD methods in which the retention time and analysis time was at least 6 and 10 min, respectively [16-21].

Fufenozide analysis was performed in the SRM mode. Compared with the ESI negative model, the ESI positive mode was chosen for its high response signals. Fig. 4 shows the product ion mass spectrogram of fufenozide.

Method Validation

Linearity, Matrix Effect, and LODs

The matrix effect may enhance or suppress the response of the target compound detected [31]. Comparing the calibration curves of the standard solution with the matrix-matched standards (Table 1), the matrix effects in the water, soil, and sediments were investigated, although both samples had high linearity (R^2>0.991). The result indicates that significant matrix effects were observed for fufenozide in the sediment and water matrices. Hence, the matrix-matched standards of all matrices were used for the quantitative calculations to reduce the matrix effects. The minimum LODs were 3.3 µg/kg, 2.5 µg/kg, and 0.1 µg/L for the soil, sediment, and water samples, respectively. Comparing with the published approaches [16-18], the detection for soil was the most sensitive method.

Accuracy and Precision (Recovery Experiments)

The recovery and repeatability of the LC-MS/MS method were determined in all three matrices at two fortification levels with five replicates to evaluate the method (Table 2). Matrix-matched calibrations were introduced to calculate the recoveries of fufenozide at different concentration levels. The average recovery values were within
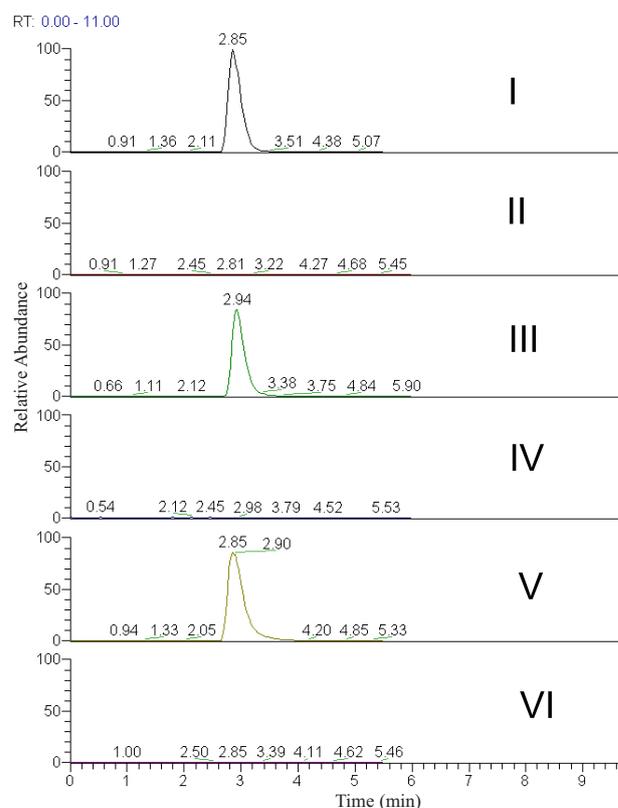

Fig. 3. HPLC-MS/MS chromatograms of (I) water matrix-matched standard of fufenozide, (II) water blank, (III) soil matrix-matched standard of fufenozide, (IV) soil blank, (V) sediment matrix-matched standard of fufenozide, and (VI) sediment blank.

Table 2. Recoveries of fufenozide in water, soil, and sediment samples.

Matrix	LOD (µg/L or µg/kg)	Fortification level (µg/L or µg/kg)	Recovery (%)	RSD (%)
Water	0.1	0.1	89.5	5.3
		10.0	94.2	4
Soil	3.3	3.3	98.5	6.3
		333	85.6	7.8
Sediment	2.5	2.5	99.3	6.0
		500	95.5	1.2

acceptable ranges of 85.6% to 99.3% in the three matrixes, with the associated relative standard deviations (RSDs) of 1.2% to 7.8%. The present study provided a high sensitivity and recovery approach to meet the requirements of fufenozide residue investigation in aquatic systems. The results represented a similar recovery of fufenozide in soil analysis compared with previous reports [16-18]; however, the volume of organic solvent used in the present method for soil sample extraction is 35 mL, which is much less than the published methods which used no less than 120 mL [16-18], which indicates the present approach has great advantages in the areas of cost savings and environmental safety.

Fufenozide Exposure in Semi-Field Test

The concentrations of fufenozide exposure in the dryland aquatic ecosystem are shown in Table 3. Fufenozide

can be carried by runoff into surface water. After the artificial rainfall, the rainwater carried the pesticide into the bodies of water, and the exposure levels of fufenozide were determined to be 5.2 µg/kg in ditch sediment, 4.5 µg/kg in pond sediment, 0.9 µg/L in ditch water, and 0.3 µg/L in pond water. The present study revealed that fufenozide could cause exposure to aquatic systems after application in dryland fields. Particularly when heavy rainfall occurred immediately after application, runoff could be induced which may cause fufenozide exposure to the ditch and pond; otherwise, when rainfall took place later there was a lower risk of fufenozide exposure to aquatic systems from agricultural fields than in the former case. 4 days after rainfall, the exposure levels of fufenozide became lower than 2.5 µg/kg for sediment and less than 0.1 µg/L for water in both the ditch and pond. The result indicates that fufenozide dissipated rapidly in the aquatic ecosystems.

Photolysis and biotransformation by microorganisms were related to fufenozide degradation in surface water based on previous laboratory studies [32, 33]. Additionally, in the present study fufenozide dissipated quickly in soil, which was consistent with the published half-life (5.7-6.4 d) [18] in Southern China.

Acute TERst

The exposure levels in the ditch and in the pond were all below 1 µg/L when fufenozide was carried through the ditch into the pond by rainfall, 1 day after application. TERst was higher than 48,000, based on the LC_{50} (Zebra fish, 96 h) of fufenozide, which was 48 mg/L [10], indicating no risk to fish. Owing to its toxicity toward arthropods, however, fufenozide may pose a risk to aquatic invertebrates, although no information on its toxicology to shrimp, crab, and the like
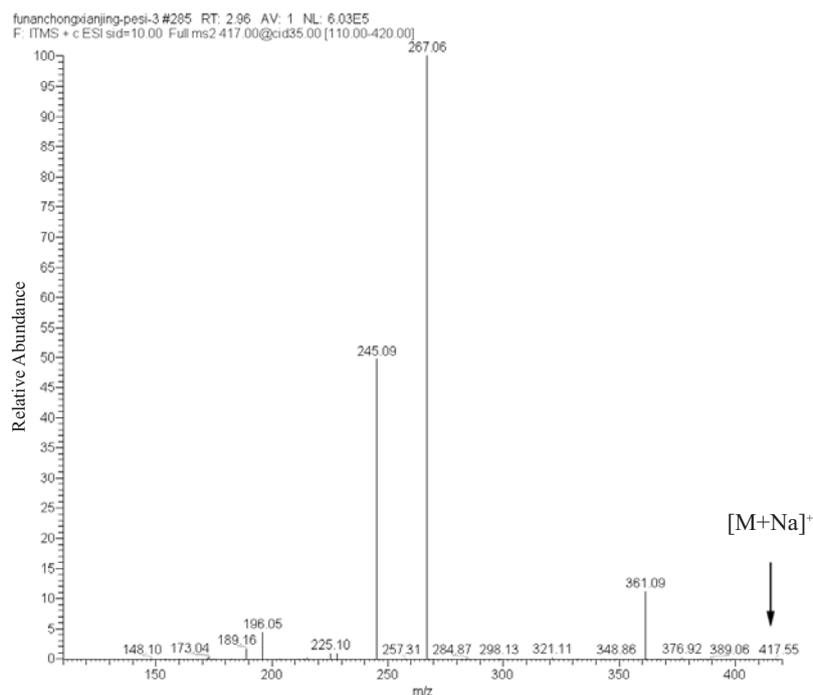

Fig. 4. Fufenozide spectrum.

Table 3. Fufenozide residue concentrations based on the semi-field test.

Sampling schedule	Soil (µg/kg)	Sediment (µg/kg)			Surface water (µg/L)		
	A	B	C	D	B	C	D
Before application	ND	ND	ND	ND	ND	ND	ND
1 hr after application	195.7±3.4	ND	ND	ND	ND	ND	ND
26 hr after application	38.8±1.5	5.2±0.1	4.5±0.1	ND	0.9±0.01	0.30±0.006	ND
5 days after application	23.5±0.4	ND	ND	ND	ND	ND	ND
7 days after application	7.1±0.5	ND	ND	ND	ND	ND	ND

Soil, Sediment – Soil and sediment samples were analyzed based on dry weight, fufenozide residues are denoted as the means±standard deviation (for n=3)

A, B, C, D – Sampling site A, B, C and D (refer to Fig.2), A: soil samples in testing field; B: water or sediment samples in ditch; C, D: water or sediment samples in pond

ND – Not detected

is available. When fufenozide is sprayed, its entry into surface water, such as ponds or rivers, must be prevented. In addition, the dryland agricultural fields are situated significantly closer to the ditches and ponds in southern China than those in northern China. Hence, the aquatic systems in southern China are more vulnerable and more likely to experience fufenozide exposure from the agricultural area than those in the North. In the present study, we performed the aquatic environmental risk assessment of fufenozide by semi-field test. Although the precipitation was mimicked artificially in order to induce a conservative runoff, we kept the rest of the test field as nature, which may reflect the natural risk of fufenozide. However, because semi-field tests cannot represent 100% real nature conditions, the risk assessment results in the present study would be a pilot analysis. The field test is an alternative to validate the risk of fufenozide to the aquatic ecosystem in the future.

Conclusions

The risk of fufenozide entry into ditches and ponds was investigated in a dryland aquatic system comprising an agriculture field, a ditch, and a pond to assess environmental risks based on the TER method [34]. A fast HPLC-MS/MS approach was developed to determine the fufenozide concentrations in the soil, water, and sediments. The detection limits were 3.3 µg/kg, 2.5 µg/kg, and 0.1 µg/L for the soil, sediment, and water samples, respectively. The results show that fufenozide can be flushed into ditches and ponds by heavy rainfall. This pesticide then dissipates rapidly in the soil and water-sediment systems and is safe for the fish in the adjacent aquatic system. However, given the paucity of eco-toxicological data for other aquatic organisms, the risks of fufenozide need to be re-evaluated in the future.

Acknowledgements

References

1. GOLFINOPOULOS S. K., NIKOLAOU A. D., KOSTOPOULOU M. N., XILOURGIDIS N. K., VAGI M. C., LEKKAS D. T. Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere **50**, (4), 507, **2003**.
2. LÓPEZ F. J., PITARCH E., EGEA S., BELTRAN J., HERNÁNDEZ F. Gas chromatographic determination of organochlorine and organophosphorus pesticides in human fluids using solid phase microextraction. Anal. Chim. Acta **433**, (2), 217, **2001**.
3. GEYIKÇI F., BÜYÜKGÜNGÖR H. Monitoring of organochlorine pesticides in the surface waters from Mid-Black Sea Region, Turkey. Environ. Monit. Assess. **173**, 127, **2010**.
4. VIŇAS P., CAMPILLO N., LÓPEZ-GARCÍA I., AGUINAGA N.HERNÁNDEZ-CÓRDOBA M. Determination of pesticides in waters by capillary gas chromatography with atomic emission detection. J. Chromatogr. A **978**, (1-2), 249, **2002**.
5. HAITH D. A. Ecological risk assessment of pesticide runoff from grass surfaces. Environ. Sci. Technol. **44**, (16), 6496, **2010**.
6. KODAKA R., SUGANO T., KATAGI T. Degradation of esfenvalerate in illuminated water-sediment system. J. Pestic. Sci. **34**, (1), 27, **2009**.
7. PETTY D. G., SKOGERBOE J. G., GETSINGER K. D., FOSTER D. R., HOUTMAN B. A., FAIRCHILD J. F., ANDERSON L. W. The aquatic fate of triclopyr in whole-pond treatments. Pest Manag. Sci. **57**, (9), 764, **2001**.
8. SUN J. Y., LIANG P., GAO X. W. Inheritance of resistance to a new non-steroidal ecdysone agonist, fufenozide, in the diamondback moth, *Plutella xylostella* (Lepidoptera: Plutellidae). Pest Manag. Sci. **66**, (4), 406, **2010**.
9. NI J. P. Fufenozide, an excellent insecticide. World Pestic. **29**, 62, **2007** [In Chinese].
10. ZHANG X. N. New IGRs JS118. World Pestic. **27**, (4), 48, **2005** [In Chinese].
11. LI Y. F., ZHU L. M., NI Y. P., HUANG C. X., ZHANG X. N. The action mode of JS118 on several important agrictural insects. Mod. Agrochem. **2**, (4), 12-13, 46, **2003** [In Chinese].
12. ZHANG X. N., LI Y. F., NI Y. P., ZHU L. M., HU J. B., JIANG M. G. Study of synthesis and bioactivity of new diacylhydrazines IGRs JS118. Pestic. **42**, (12), 18, **2003** [In Chinese].

13. ZHU L. M., NI Y. P., LI Y. F., ZHANG X. N., TANG M. J., XIAO Q. Interior biological activity of JS118 on tea geometrid. Mod. Agrochem. **1**, (5), 15, **2002** [In Chinese].

14. ZHENG Z. X., HU J. Y. Damaging effects of pesticide JS-118 on DNA of mice cells measured by the single cell gel electrophoresis assay. Asian J. Ecotox. **5**, (4), 569, **2010** [In Chinese].

15. FENG S. L., KONG Z. M., WANG X. M., ZHAO L. R.PENG P. A. Acute toxicity and genotoxicity of two novel pesticides on amphibian, Rana N. Hallowell. Chemosphere **56**, (5), 457, **2004**.

16. CAO B., YU C. Z., XU J. Analytical method for determination of furan tebufenozide residue by HPLC. Pestic. Sci. Admin. **31**, (4), 29, **2010** [In Chinese].

17. HU J. Y., DENG Z. B., QIN D. M. Determination of diacylhydrazines-type insect growth regulator JS-118 residues in cabbage and soil by high performance liquid chromatography with DAD detection. B. Environ. Contam. Tox. **83**, (6), 803, **2009**.

18. ZENG Q., LIN Y., HUANG Q. H., ZOU H. J., LÜ Z. M., LIU X. JS118 degradation and final residue in cauliflower plants and soil. Fujian J. Agr. Sci. **22**, (1), 19, **2007** [In Chinese].

19. NIE G., WU C. X., GAO M. L., WANG G. C., CHEN B. K., ZHANG Z. M. Determination of pestiside fufenozide by HPLC. J. Southwest China Normal U. **34**, (6), 151, **2009** [In Chinese].

20. ZHANG H., WU L. Q., XIE L., HE H. M., ZHU J. H. The determination of tebufenozide, methoxyfenozide and fuxian residues in cabbage, pakchoi and tomato by high performance liquid chromatography. Mod. Sci. Instrum. **3**, 55, **2006** [In Chinese].

21. ZHOU H., WANG J. W., YANG W. Y., QIAN M. R. Degradation dynamics of tebufenozide and fufenozide in Beijing onions. Journal of Zhejiang Agricultural Sciences **6**, 1349, **2010** [In Chinese].

22. SOLER C., MAÑES J., PICÓ Y. The role of the liquid chromatography-mass spectrometry in pesticide residue determination in food. Crit. Rev. Anal. Chem. **38**, (2), 93, **2008**.

23. PETROVIC M., FARRÉ M., de ALDA M. L., PEREZ S., POSTIGO C., KÖCK M., RADJENOVIC J., GROS M., BARCELO D. Recent trends in the liquid chromatography-mass spectrometry analysis of organic contaminants in environmental samples. J. Chromatogr. A **1217**, (25), 4004, **2010**.

24. MALIK A. K., BLASCO C., PICÓ Y. Liquid chromatography-mass spectrometry in food safety. J. Chromatogr. A **1217**, (25), 4018, **2010**.

25. JI F. Y. Water and waste water monitoring. 60-66, **2006** [In Chinese].

26. WU J. Soil monitoring. pp. 260-266, **2006** [In Chinese].

27. US FDA Guidance for Industry: Mass Spectrometry for Confirmation of the Identity of Animal Drug Residues. 2-8, **2003**.

28. European Commission Council Directive of 15 July 1991 concerning the placing of plant protection products on the market (91/414/EEC). **1991**.

29. FOCUS FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, EC document reference SANCO/4802/2001-rev.2. 245 pp. **2001**.

30. European Commission Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009, concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. **2009**.

31. Di MUCCIO A., FIDENTE P., BARBINI D. A., DOMMARCO R., SECCIA S., MORRICA P. Application of solid-phase extraction and liquid chromatography-mass spectrometry to the determination of neonicotinoid pesticide residues in fruit and vegetables. J. Chromatogr. A **1108** (1), 1-6, **2006**.

32. HU J. Y., LIU C., ZHANG Y. C., ZHENG Z. X. Hydrolysis and photolysis of diacylhydrazines-type insect growth regulator JS-118 in aqueous solutions under abiotic conditions. B. Environ. Contam. Tox. **82**, (5), 610, **2009**.

33. GUO C., LI D. H., CHEN J. H., GUO B. Y., WANG H. L., LI J. Z. Degradation of furan tebufenozide in laboratory and field trials. Sci. China Chem. **53**, (8), 1818, **2010**.

34. AUTERI D., MANGIAROTTI M. Pesticide risk assessment to protect aquatic systems. Management of Intentional and Accidental Water Pollution pp. 75-84, **2006**.