



Supplementary Material

Simultaneous Analysis and Dietary Exposure risk Assessment of Fomesafen, Clomazone, Clethodim and its Two Metabolites in Soybean Ecosystem

Kyongjin Pang and Jiye Hu*

School of Chemistry and Biological Engineering, University of Science Technology Beijing, Beijing, 100083, PR China

Address: Lab of Pesticide Residues and Environmental Toxicology, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, China

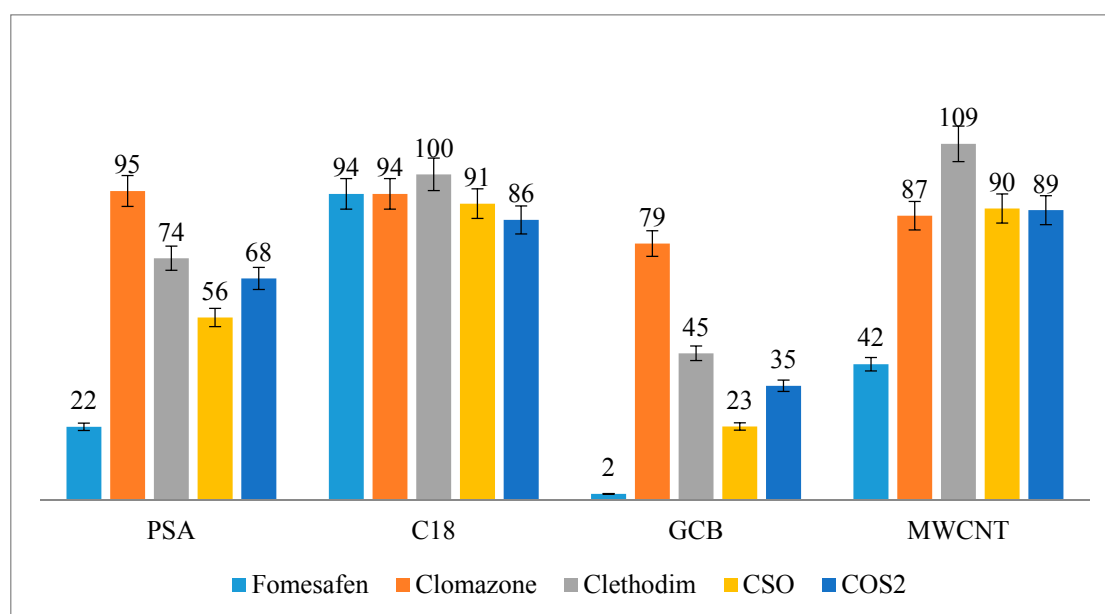


Figure 1. Recoveries (%) of fomesafen, clomazone, clethodim, CSO and CSO₂ in soybean matrix using various d-SPE.

* Corresponding author. Tel: +86 82376002 Fax: +86 1082376002

E-mail address: jyhu@ustb.edu.cn (Jiye Hu) , banggyongjin@163.com (Kyongjin Pang)

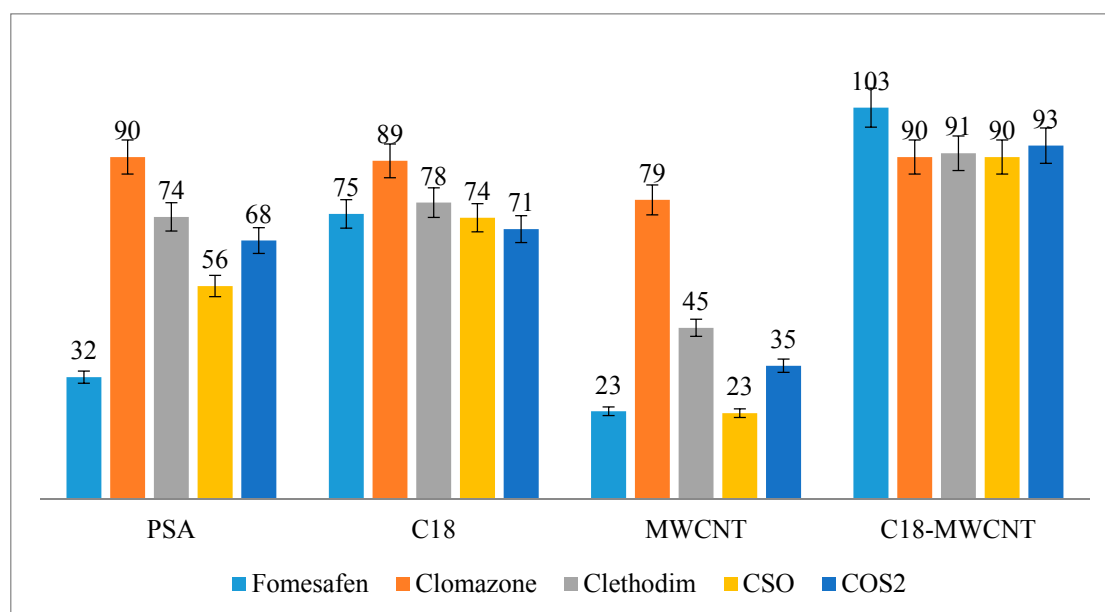


Figure 2. Recoveries (%) of fomesafen, clomazone, clethodim, CSO and COS₂ in green soybean matrix using various d-SPE.

Table 1. Properties of soil and climate conditions in different field trial sites.

Sites	pH value of soils	Organic matter content of soils (%)	Average temperature (°C)	Rainfalls (mm)	East longitude, Northern latitude
Heilongjiang	6.90	3.2	22.4	152	128°45' E, 45°05' N
Liaoning	7.10	3.4	26.3	500	123°25' E, 41°48' N
Inner Mongolia	7.20	2.7	23.7	550	113°07' E, 40°59' N
Shanxi	7.20	1.9	24.0	300	110°15' E, 35°49' N
Anhui	7.4	1.2	28.1	1270	116°93' E, 34°19' N
Guangxi	7.1	1.4	25.2	2208	108°21' E, 22°49' N

Table 2. LODs linear relationships, and repeatabilities ($n = 6$) for determination of three herbicides in different matrices.

compound	matrix	Matrix matched calibration	correlation coefficient (R^2)	Matrix effect (%)
Fomesafen	Soybean	$y = 8057.9x + 117.33$	0.9904	13
	Green	$y = 3154.6x - 10.634$	0.9996	-1.2
	Soybean	$y = 4306.8x + 1.3098$	0.9997	0.9
	Straw			
Clomazone	Soybean	$y = 74881x - 43.316$	0.9996	-6.2
	Green	$y = 45304x - 33.917$	0.9998	-5.8
	Soybean	$y = 64759x - 222.85$	0.9995	-11
	Straw			
Clethodim	Soybean	$y = 42386x + 1410.3$	0.9932	10
	Green	$y = 20250x + 248.78$	0.9998	9
	Soybean	$y = 37915x - 30.726$	0.9994	-3.1
	Straw			
CSO	Soybean	$y = 216191x + 2060.3$	0.9966	10
	Green	$y = 54838x + 282.88$	0.9999	13
	Soybean	$y = 113576x + 230.81$	1	11
	Straw			
CSO ₂	Soybean	$y = 50382x + 131.49$	0.9996	8
	Green	$y = 22006x + 100.57$	0.9999	14
	Soybean	$y = 39572x + 123.32$	0.9999	11
	Straw			

Table 3. Terminal residues of fomesafen in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of Application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	105	<0.01	<0.01	<0.01
Shanxi	721.5	1	98	<0.01	<0.01	<0.01
Liaoning	721.5	1	120	<0.01	<0.01	<0.01
Guangxi	721.5	1	109	<0.01	<0.01	<0.01
Anhui	721.5	1	50	<0.01	<0.01	<0.01

Table 4. Terminal residues of Clomazone in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of Application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	105	<0.01	<0.01	<0.01
Shanxi	721.5	1	98	<0.01	<0.01	<0.01
Liaoning	721.5	1	120	<0.01	<0.01	<0.01
Guangxi	721.5	1	109	<0.01	<0.01	<0.01
Anhui	721.5	1	50	<0.01	<0.01	<0.01

Table 5. Terminal residues of Clethodim in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of Application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	105	<0.01	<0.01	<0.01
Shanxi	721.5	1	98	<0.01	<0.01	<0.01
Liaoning	721.5	1	120	<0.01	<0.01	<0.01
Guangxi	721.5	1	109	<0.01	<0.01	<0.01
Anhui	721.5	1	50	<0.01	<0.01	<0.01

Table 6. Terminal residues of CSO in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of Application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	105	<0.01	<0.01	<0.01
Shanxi	721.5	1	98	<0.01	<0.01	<0.01
Liaoning	721.5	1	120	<0.01	<0.01	<0.01
Guangxi	721.5	1	109	<0.01	<0.01	<0.01
Anhui	721.5	1	50	<0.01	<0.01	<0.01

Table 7. Terminal residues of CSO₂ in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of Application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	105	<0.01	<0.01	<0.01
Shanxi	721.5	1	98	<0.01	<0.01	<0.01
Liaoning	721.5	1	120	<0.01	<0.01	<0.01
Guangxi	721.5	1	109	<0.01	<0.01	<0.01
Anhui	721.5	1	50	<0.01	<0.01	<0.01

Table 8. Terminal residues of fomesafen in green soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	89	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	76	<0.01	<0.01	<0.01
Shanxi	721.5	1	73	<0.01	<0.01	<0.01
Liaoning	721.5	1	87	<0.01	<0.01	<0.01
Guangxi	721.5	1	82	<0.01	<0.01	<0.01
Anhui	721.5	1	22	<0.01	<0.01	<0.01

Table 9. Terminal residues of Clomazone in green soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	89	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	76	<0.01	<0.01	<0.01
Shanxi	721.5	1	73	<0.01	<0.01	<0.01
Liaoning	721.5	1	87	<0.01	<0.01	<0.01
Guangxi	721.5	1	82	<0.01	<0.01	<0.01
Anhui	721.5	1	22	<0.01	<0.01	<0.01

Table 10. Terminal residues of Clethodim in green soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	89	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	76	<0.01	<0.01	<0.01
Shanxi	721.5	1	73	<0.01	<0.01	<0.01
Liaoning	721.5	1	87	<0.01	<0.01	<0.01
Guangxi	721.5	1	82	<0.01	<0.01	<0.01
Anhui	721.5	1	22	<0.01	<0.01	<0.01

Table 11. Terminal residues of CSO in green soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	89	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	76	<0.01	<0.01	<0.01
Shanxi	721.5	1	73	<0.01	<0.01	<0.01
Liaoning	721.5	1	87	<0.01	<0.01	<0.01
Guangxi	721.5	1	82	<0.01	<0.01	<0.01
Anhui	721.5	1	22	<0.01	<0.01	<0.01

Table 12. Terminal residues of CSO₂ in green soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	89	<0.01	<0.01	<0.01
Inner Molgolia	721.5	1	76	<0.01	<0.01	<0.01
Shanxi	721.5	1	73	<0.01	<0.01	<0.01
Liaoning	721.5	1	87	<0.01	<0.01	<0.01
Guangxi	721.5	1	82	<0.01	<0.01	<0.01
Anhui	721.5	1	22	0.015	0.014	0.015

Table 13. Terminal residues of fomesafen in soybean straw.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.02	<0.02	<0.02
Inner Molgolia	721.5	1	105	<0.02	<0.02	<0.02
Shanxi	721.5	1	98	<0.02	<0.02	<0.02
Liaoning	721.5	1	120	<0.02	<0.02	<0.02
Guangxi	721.5	1	109	<0.02	<0.02	<0.02
Anhui	721.5	1	50	<0.02	<0.02	<0.02

Table 14. Terminal residues of Clomazone in soybean straw.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.02	<0.02	<0.02
Inner Molgolia	721.5	1	105	<0.02	<0.02	<0.02
Shanxi	721.5	1	98	<0.02	<0.02	<0.02
Liaoning	721.5	1	120	<0.02	<0.02	<0.02
Guangxi	721.5	1	109	<0.02	<0.02	<0.02
Anhui	721.5	1	50	<0.02	<0.02	<0.02

Table 15. Terminal residues of Clethodim in soybean straw.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.02	<0.02	<0.02
Inner Molgolia	721.5	1	105	<0.02	<0.02	<0.02
Shanxi	721.5	1	98	<0.02	<0.02	<0.02
Liaoning	721.5	1	120	<0.02	<0.02	<0.02
Guangxi	721.5	1	109	<0.02	<0.02	<0.02
Anhui	721.5	1	50	<0.02	<0.02	<0.02

Table 16. Terminal residues of CSO in soybean straw.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.02	<0.02	<0.02
Inner Molgolia	721.5	1	105	<0.02	<0.02	<0.02
Shanxi	721.5	1	98	<0.02	<0.02	<0.02
Liaoning	721.5	1	120	<0.02	<0.02	<0.02
Guangxi	721.5	1	109	<0.02	<0.02	<0.02
Anhui	721.5	1	50	<0.02	<0.02	<0.02

Table 17. Terminal residues of CSO₂ in soybean.

Site of field trial	Sprayed dosage (g a.i. /ha)	Number of application	Interval of application (d)	Terminal residues (mg/kg)		
				1	2	Average
Heilongjiang	721.5	1	118	<0.02	<0.02	<0.02
Inner Molgolia	721.5	1	105	<0.02	<0.02	<0.02
Shanxi	721.5	1	98	<0.02	<0.02	<0.02
Liaoning	721.5	1	120	<0.02	<0.02	<0.02
Guangxi	721.5	1	109	0.030	0.028	0.029
Anhui	721.5	1	50	<0.02	<0.02	<0.02

Table 18. Recoveries, RSDs and LOQs of five substances (fomesafen, clomazone, clethodim, CSO and CSO₂) in several matrices by previous study.

Compounds	Matrix	Recovery (%)	RSDs (%)	LOQs (mg/kg)	LODs (µg/kg)	Equipement	pretreatment
Fomesafen	Tomato [1]	99-102	4.2	0.001	0.0015	LC-MS/MS	QuEChERS
	Soil [2]	83-102	≤4.02	0.05		HPLC-DAD	Liquid-liquid
	Plant [2]	85-99	3.51	0.05		HPLC-DAD	Liquid-liquid
	Earthworm [2]	84-91	3.29	0.05		HPLC-DAD	Liquid-liquid
	Juice [6]	96-98	3.7	0.297 mg/L	0.089 mg/L	Cyclic Voltammetry	Liquid-liquid
	Leek [10]	76.3-88.4	18	0.01	10	LC-MS/MS	QuEChERS
Clomazone	River water [11]	87.3-104	≤4.07	0.1 µg/L		HPLC-DAD	Liquid-liquid
	Soil [9]	87-92	8.78	0.01	0.25	LC-MS/MS	QuEChERS
	Soybean [3]	96-97	4.9	0.01		LC-MS/MS	Liquid-liquid
	Soybean [4]	94-106	6	0.01		LC-MS/MS	QuEChERS
	Green soybean [4]	89-109	11	0.01		LC-MS/MS	QuEChERS
	Soybean straw [4]	91-106	3	0.01		LC-MS/MS	QuEChERS
	Leek [10]	95-95	8.1	0.01	1	LC-MS/MS	QuEChERS
Clethodim	radish, tomato, onion, sweet	91-118	≤10	0.05	10	LC-MS/MS	Liquid-liquid

	potato, kidney bean, carrot, cabbage, lettuce [7]						
	Rape plant [5]	85-90.1	≤6.9	0.01	4	LC-MS/MS	QuEChERS
	Rape seed [5]	84.6-96.7	≤5.4	0.05	10	LC-MS/MS	QuEChERS
	green tobacco leaf [8]	78.3-88.1	7.0	0.08	0.024	LC-MS/MS	QuEChERS
	cured tobacco leaf [8]	93.9-94.6	6.8	0.2	0.06	LC-MS/MS	QuEChERS
CSO	Rape plant [5]	80.3-84.9	≤5.4	0.01	3	LC-MS/MS	QuEChERS
	Rape seed [5]	78.7-101.6	≤7.6	0.05	10	LC-MS/MS	QuEChERS
	green tobacco leaf [8]	74.8– 104.4	≤3.4	0.08	0.024	LC-MS/MS	QuEChERS
	cured tobacco leaf [8]	87.6-105.5	≤5.7	0.2	0.06	LC-MS/MS	QuEChERS
CSO ₂	Rape plant [5]	83.6-84.8	≤3.9	0.01	3	LC-MS/MS	QuEChERS
	Rape seed [5]	91.6-102.8	≤7.7	0.05	10	LC-MS/MS	QuEChERS
	green tobacco leaf [8]	89.2-96.7	≤6.2	0.08	0.024	LC-MS/MS	QuEChERS
	cured tobacco leaf [8]	89.3-102.0	≤5.0	0.2	0.06	LC-MS/MS	QuEChERS

References

- [1] Li, Z.; Di Gioia, F.; Hwang, J.; Hong, J.; Ozores-Hampton, M.; Zhao, X.; Pisani, C.; Rosskopf, E.; Wilson, P.C. Dissipation of fomesafen in fumigated, anaerobic soil disinfestation-treated, and organic-amended soil in Florida tomato production systems, *Pest. Manag. Sci.* **2019**. <https://doi.org/10.1002/ps.5558>.
- [2] Khorram, M.S.; Zheng, Y.; Lin, D.; Zhang, Q.; Fang, H.; Yu, Y. Dissipation of fomesafen in biochar-amended soil and its availability to corn (*Zea mays* L.) and earthworm (*Eisenia fetida*), *J Soil. Sedimet.* **2016**, *16*, 2439-2448.
- [3] Hu, J.Y.; Cao, D.; Deng, Z.B. Determination of clomazone residues in soybean and soil by high performance liquid chromatography with DAD detection, *B. Environ. Contam. Tox.* **2011**, *86*, 444-448.
- [4] Hussan, H.N.M.; He, H.R.; Du, P.Q.; Wu, X.H.; Liu, X.G.; Xu, J.; Dong, F.S.; Zheng, Y.Q. Determination of clomazone and acetochlor residues in soybean (*Glycine max* (L.) Merr.), *Int. J. Environ. An. Ch.* **2020**, DOI: 10.1080/03067319.2019.1694668.
- [5] You, X.; Liang, L.; Liu, F. Dissipation and residues of clethodim and its oxidation metabolites in a rape-field ecosystem using QuEChERS and liquid chromatography/tandem mass spectrometry, *Food. Chem.* **2014**, *43*, 170-174.
- [6] Demir, E.; Inam, R. Square Wave Voltammetric Determination of Fomesafen Herbicide Using Modified Nanostructure Carbon Paste Electrode as a Sensor and Application to Food Samples, *Food. Anal. Method.* **2017**, *10*, 74-82.
- [7] Ishimitsu, S.; Kaihara, A.; Yoshii, K.; Tsumura, Y.; Nakamura, Y.; Tonogai, Y. Determination of clethodim and its oxidation metabolites in crops by liquid chromatography with confirmation by LC/MS, *J. Aoac. Int.* **2001**, *84*, 1172-1178.
- [8] Wang, F.; Yang, G.Q.; Xu, J.; Yu, W.W.; Shi, L.H.; Zeng, S.; Chen, L.Z.; Hu, D.Y.; Zhang, K.K. Simultaneous determination and method validation of clethodim and its

- metabolites clethodim sulfoxide and clethodim sulfone in tobacco by LC-MS/MS, *Biomed. Chromatogr.* **2018**, *32*, e4148.
- [9] Du, P.Q., Wu, X.H., Xu, J., Dong, F.S., Liu, X.G., Zhang, Y., Zheng, Y.Q. Clomazone influence soil microbial community and soil nitrogen cycling, *Sci. Total. Environ.* **2018**, *644*, 475–485.
- [10] Zou, N., Han, Y.T., Li, Y.J., Qin, Y.H., Gu, K.J., Zhang, J.R., Pan, C.P., Li, X.S. Multiresidue Method for Determination of 183 Pesticide Residues in Leeks by Rapid Multiplug Filtration Purification and Gas Chromatography-Tandem Mass Spectrometry, *J. Agr. Food. Chem.*, **2015**, *64*, 6061–6070.
- [11] Zanella, R., Primel, E.G., Machado, S.L.O., Gonçalves, F.F., Marchezan, E. Monitoring of the herbicide clomazone in environmental water samples by solidphase extraction and high-performance liquid chromatography with ultraviolet detection. *Chromatographia.* **2002**, *55*, 573–577.