Asian Journal of Chemistry; Vol. 28, No. 7 (2016), 1493-1497

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19730

Persistence of Clodinafop Propargyl and its Metabolite in Soil and Wheat Crop under North Western Himalayan Region

N. SHARMA[1,*], E. SHARMA[1], N. THAKUR[1], A. GULATI[2], R. JOSHI[2] and V. SHARMA[1]

[1]Department of Agronomy, Forages and Grassland Management, College of Agriculture, Chaudhary Sarwan Kumar Himachal Pradesh Krishi Vishvavidyalaya, Palampur-176 062, India
[2]CSIR-Institute of Himalayan Bioresources and Technology, Palampur-176 062, India

*Corresponding author: E-mail: sharma_neelam29@rediffmail.com

Received: 16 November 2015; *Accepted*: 11 January 2016; *Published online*: 31 March 2016; AJC-17835

A field investigation was carried out to study persistence and accumulation of clodinafop-propargyl residues in wheat. Soil samples and wheat plant samples from field experiment were collected at 0 (2 h), 1, 3, 5, 7, 10, 15 and 30 days after herbicide application and at the crop harvest. In soil and plant both, the parent ester rapidly degraded to its major metabolite *i.e.* clodinafop acid. Clodinafop-propargyl @ 30 and 60 g/ha persisted in soil up to zero day after herbicide application, whereas at higher dose *i.e.* 120 g/ha clodinafop ester in soil persisted up to 3 days. In case of plant samples, clodinafop ester residues were detected only at zero day after herbicide application at two rates of clodinafop *i.e.* 60 and 120 g/ha. In all clodinafop applied treatments, more than 90 % of major metabolite clodinafop acid in soil dissipated within 10 days after herbicide application. The dissipation of clodinafop acid at all the levels of application in soil followed first order kinetics with half life varying from 1.89-3.01 days. Clodinafop acid in plant persisted up to 1 day after herbicide application at lower dose *i.e.* 30 g/ha whereas, at 60 g/ha persisted up to 3 days and at 120 g/ha persisted up to 5 days only. The wheat straw and wheat grain samples were free from residues of clodinafop ester and acid both.

Keywords: Persistence, Clodinafop propagryl, Clodinafop acid, Wheat, Soil.

INTRODUCTION

Clodinafop propargyl (Topik 15 % WP) effectively controls isoproturon resistant little seed canary grass biotypes (*Phalaris minor* Retz.) along with other weeds of wheat. Clodinafop-propargyl is a post emergence recommended herbicide for control of annual grasses in cereals, including *Phalaris, Avena, Lolium and Setaria sp*. [1]. This herbicide belongs to aryloxy-phenoxy propionate chemical family and is being used largely to control weeds in wheat [2,3]. It can be used at very low rates (30-80 g a.i. ha) to control a wide range of grassy weeds species at a wide range of growth stages. Clodinafop-propargyl inhibits the acetyl co-enzyme A carboxylase (ACCase), which is essential for production of lipids (fatty acids) needed for plant growth. This is rapidly translocated to the growing point of leaves and stems and accumulates in the meristematic tissues. This herbicide is rapidly converted to the acid form clodinafop, which is taken up *via* leaves and hinders the de novo synthesis of fatty acids by inhibition of the enzyme AcetylCoA carboxylase. It interferes with the production of fatty acids needed for plant growth in susceptible grassy weeds. Depending on the species, growing condition and crop competition, leaves and growing points turn yellow within 2 to 3 weeks after application. Thereafter, colour changes and loss of vigour followed by a browning and complete control 3 to 5 weeks after application [4]. The chemical analysis of this herbicide for ascertaining its environmental fate is of utmost importance. In environment, clodinafop-propargyl rapidly degraded to the acid derivative of clodinafop as major metabolite. Clodinafop-propargyl has a toxicity class of World Health Organization III, whereas it was classified as "Likely to be Carcinogenic to Humans" by the U.S. Environmental Protection Agency [5]. Clodinafop-propargyl is highly toxic to aquatic species. To ensure the safety of food for consumers, many countries and organizations have established maximum residue limits (MRLs) for clodinafop-propargyl (including its metabolite clodinafop) in commodities. A few studies have focused on terminal residue of clodinafop-propargyl in wheat crop and soil [6,7]. In this study, analysis of clodinafop-propargyl and clodinofop acid in wheat grain, wheat plant, wheat straw and soil was carried out using high performance liquid chromatography.

EXPERIMENTAL

Design of field experiment: Field experiment consisting of four treatments *viz*., clodinafop-propargyl 30 g/ha, clodinafop-

propargyl 60 g/ha, clodinafop-propargyl 120 g/ha along with control was laid out in randomized block design at the Research Farm of Department of Agronomy, CSKHPKV, Palampur during *rabi* 2012-13 and 2013-14. The experimental site was located at 32°3' N latitude, 76°3' E longitude and at an altitude of 1290.8 m above mean sea level and falls in sub temperate mid hill zone of Himachal Pradesh, India. For each treatment, plots of 4.1 m × 2 m were selected with wheat variety HPW155 sown in 22.5 cm row spacing. Physico-chemical properties of soil were carried out prior to spray of the chemical in the field. The soil of experiment field with silty clay loam in texture (25 % sand, 41 % silt and 33 % clay) with acidic pH 5.17 [8] and organic carbon 1.22 % [9]. The fertility status of experiment field was medium in available N (205.1 kg ha^{-1}) [10], higher in available P (25.0 kg/ha) [11] and available K (230.9 kg/ha) [8].

Climatic conditions: The climate parameters for Season I (*rabi* 2013) were: temperature mean minimum 9.8 °C and mean maximum 25.3 °C; total rainfall 508.6 mm; average relative humidity range 37 to 70 % and for Season II (*rabi* 2014) were: temperature mean minimum 8.9 °C and mean maximum 20.9 °C and total rainfall 485 mm; and average relative humidity range 30 to 70 %.

Application of herbicide: Topik (WP) containing 15 % active ingredient was obtained from local dealer in Palampur. Spray application of clodinafop-propargyl was given at 30, 60 and 120 kg/ha along with control for both years by using a volume spray of 750 L water/ha with the help of Knapsack sprayer with flat fan nozzle. Herbicide was sprayed in the month of January during both the years.

All solvents used in study were of analytical grade and purchased from Merck India Pvt. Ltd. Clodinafop-propargyl (99.5 % pure) reference material was procured from Sigma Aldrich, India. The authentic sample of clodinafop acid required for the study was prepared by alkaline hydrolysis of clodinafop-propargyl technical grade (96.4 %) procured from Pioneer Pesticides Pvt. limited by adopting the slightly modified method given by Roy and Singh [12]. The prepared compound *i.e.* acid having m.p. 210 °C gave a single spot on TLC and single sharp peak in HPLC at λ_{max} 240 nm. The clodinafop ester and acid solutions were scanned at different wavelengths to work out λ_{max}. The maximum absorbance for ester and acid was found at wavelength 270 and 240 nm, respectively. In present study, to analyze both compounds simultaneously the optimum λ_{max} selected was 240 nm.

Sample collection: Periodic analysis of soil and wheat plant samples was carried out at 0 (2 h), 1, 3,5,7,10,15 and 30 days after herbicide application and at harvest for the residue analysis. On each sampling day, soil and wheat plant samples from all the plots were collected and brought to the laboratory. Soil samples from all the treatments were air dried, passed through 2 mm sieve. 50 g representative sample was taken by quartering. Fresh plants from sampling rows were collected at different intervals of time *i.e.* 0, 1, 3, 5, 7, 10, 15 and 30 days after herbicide spray. Wheat straw and grain samples were collected at maturity of crop. The representative 20 g of wheat straw and 50 g of wheat grain samples, respectively were taken for quantitative determination of clodinafop-propargyl residues.

Extraction and cleanup for residue analysis

Soil: A representative soil sample (50 g) was taken and 1-2 drops of ammonia (NH_4OH) was added. 80 mL of ethyl acetate (solvent) was added after smell of ammonia disappeared and shaken on horizontal shaker for 0.5 h. The contents were filtered through buchner funnel. Extraction was done twice with same solvent (50 mL each) and combined filtrate was dried on a rotary vacuum evaporator at 30-40 °C to dryness. Clean up was not required in this case and the residue was dissolved in 5 mL of HPLC methanol for HPLC analysis.

After extraction of the ester with ethyl acetate, the solvent was evaporated to dryness. The residue was dissolved in 50 mL of 0.1 N KOH (aqueous) and the contents of the flask were heated at 60 °C on a water bath for 0.5 h. The aqueous solution was partitioned with ethyl acetate (3 × 50 mL). The organic layer was collected over anhydrous Na_2SO_4 and solvent was evaporated to dryness on rotary evaporator. Clean up was not required in this case and the residue was dissolved in 5 mL of HPLC methanol for HPLC analysis.

Wheat plant: Plant samples were analyzed for both clodinafop ester and clodinafop acid content. The chopped plant sample (20 g) was crushed with 20 mL acetone and filtered on suction through Buchner funnel. Extraction was repeated twice with 10 mL acetone each time. The combined extract was evaporated and residue kept for further clean up. For clean up, neutral alumina (4 g) was packed in the glass column (2 cm i.d. 30 cm long) sandwiched between anhydrous Na_2SO_4 (2 g) on both the sides. The concentrated plant extract in 2 mL acetone was added at the top after pre washing of column with *n*-hexane. It was then eluted with *n*-hexane, *n*-hexane:benzene (1:1) and *n*-hexane:acetone (9:1). For ester quantification, *n*-hexane:benzene (1:1) fraction was collected. For acid quantification, *n*-hexane: acetone (9:1) fraction was collected. The collected fractions were evaporated on water bath and residue was dissolved in HPLC Methanol for HPLC analysis.

Wheat straw and grain: Wheat straw and grain samples were analyzed for both clodinafop ester and clodinafop acid content. The chopped straw (20 g) or powdered grain sample 50 g was taken in a filter paper thimble and extracted with 250 mL of ethyl acetate using Soxhlet apparatus for 6 h. No clean up was required in the case of wheat straw and grain samples. The contents were concentrated to dryness on a rotary vacuum evaporator and residue was finally dissolved in methanol for HPLC analysis.

Detection method: The residues of clodinafop ester and acid were quantified using Shimadzu HPLC equipped with UV detector and C-18_e (25 cm × 4.6 mm, 5 µm) column. Estimation was done at 240 nm wavelength using mobile phase-methanol: water (80:20) with flow rate at 1 mL/min. Injection volume was 20 µL.

Recovery experiments: Recovery experiments were conducted to determine the efficacy of the analytical procedure. As clodinafop propargyl rapidly converts to clodinafop acid in plant and soil environment, a method was standardized for the simultaneous analysis of ester and acid from different matrices. The recoveries of clodinafop ester from soil, plant, wheat straw and grain samples fortified at 0.25 and 0.50 µg/g

of herbicide and clodinafop acid from soil, plant, wheat straw and grain samples fortified at 0.50, 1.00 and 5.00 µg/g of herbicide.

RESULTS AND DISCUSSION

Clodinafop ester: The recoveries of clodinafop ester from soil, plant, wheat straw and grain samples fortified at 0.25 and 0.50 µg/g of herbicide are given in Table-1. From spiked samples of soil, plant, wheat straw and wheat grain, clodinafop ester per cent recoveries were 80.4 and 78.4 %, 79.2 and 84.6 %, 86.0 and 84.2 %, 81.6 and 83.0 %, respectively. The average per cent recoveries of clodinafop ester in different substrates *i.e.* soil, plant, wheat straw and grain were above 78 %. The above values of per cent recoveries are well within acceptable limits and are in direct conformity with findings of several other workers [13-15].

The data on persistence and per cent dissipation of clodinafop-propargyl in soil at different doses have been presented in Table-2. Initial residues of clodinafop-propargyl applied at 30, 60 and 120 g/ha were 0.32, 0.58 and 1.50 µg/g, respectively in first year and 0.30, 0.44 and 1.49 µg/g in second year, respectively. After 24 h of herbicides application *i.e.* on first day, the residues of clodinafop-propargyl reached below detectable level at lower doses of ester *i.e.* 30 and 60 g/ha. Whereas, higher dose *i.e.* 120 g/ha resulted into 0.45 and 0.54 µg/g clodinafop ester residues in first and second year, respectively. The corresponding per cent losses of applied clodinafop ester were 100, 100 and 63.8 %, respectively at one day after herbicide application. The amount of clodinafop-propargyl in first and second season at 3 days after herbicide application @ 120 g/ha was found to be 0.12 and 0.16 µg/g, respectively. The results of field experiment conducted to study clodinafop ester residues in soil revealed that during both the seasons clodinafop ester persisted in soil up to 0 days after herbicide application at30 and 60 g/ha whereas, at higher dose 120 g/ha clodinafop ester persisted up to 3 days. The parent ester rapidly converts to clodinafop acid in soil, which is also responsible for herbicide activity. The above findings are in conformity with results reported by Roy *et al.* [14].

In wheat plant, initial residues of clodinafop-propargyl applied at 30 g/ha were below detectable level. Clodinafop-propargyl @ 60 and 120 g/ha were 0.090 and 0.132 µg/g in first year and 0.082 and 0.126 µg/g second year, respectively

TABLE-1
PER CENT RECOVERIES OF CLODINAFOP ESTER AND CLODINAFOP ACID FROM DIFFERENT MATRICES WITH KNOWN AMOUNT OF HERBICIDE

Herbicide	Clodinafop ester			Clodinafop acid		
	Amount added (µg/g)	*Average amount recovered (µg/g)	Average recovery (%)	Amount added (µg/g)	*Average amount recovered (µg/g)	Average recovery (%)
Soil	0.25	0.201 ± 0.021	80.4	0.50	0.415 ± 0.021	83.0
	0.50	0.392 ± 0.017	78.4	1.00	0.774 ± 0.013	77.4
				5.00	4.050 ± 0.007	81.0
Plant	0.25	0.198 ± 0.075	79.2	0.50	0.393 ± 0.022	78.6
	0.50	0.423 ± 0.102	84.6	1.00	0.829 ± 0.019	82.9
				5.00	4.110 ± 0.011	82.2
Wheat straw	0.25	0.215 ± 0.054	86.0	0.50	0.408 ± 0.012	81.6
	0.50	0.422 ± 0.128	84.2	1.00	0.789 ± 0.008	78.9
				5.00	3.982 ± 0.014	79.6
Wheat grain	0.25	0.204 ± 0.019	81.6	0.50	0.395 ± 0.004	79. 0
	0.50	0.415 ± 0.022	83.0	1.00	0.759 ± 0.024	75.9
				5.00	4.020 ± 0.009	80.4

*Values are mean of five determinations with standard deviation (±)

TABLE-2
RESIDUES OF CLODINAFOP-PROPARGYL IN SOIL AND PLANT SAMPLE TREATED AT DIFFERENT DOSES

Herbicide	Days after herbicide application	Residues (µg/g) Rates of clodinafop-propargyl application (g/ha)					
		30 g/ha		60 g/ha		120 g/ha	
		2013	2014	2013	2014	2013	2014
Soil	0	0.32 ± 0.028	0.30 ± 0.014	0.58 ± 0.028	0.44 ± 0.028	1.50 ± 0.014	1.49 ± 0.04
	1	BDL	BDL	BDL	BDL	0.45 ± 0.0014 (70.0)	0.54 ± 0.014 (63.8)
	3	BDL	BDL	BDL	BDL	0.12 ± 0.028 (92.0)	0.16 ± 0.014 (89.3)
	5	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL
	10	BDL	BDL	BDL	BDL	BDL	BDL
	15	BDL	BDL	BDL	BDL	BDL	BDL
Plant	0	BDL	BDL	0.090 ± 0.0014	0.082 ± 0.0028	0.132 ± 0.0028	0.126 ± 0.0014
	1	BDL	BDL	BDL	BDL	BDL	BDL
	3	BDL	BDL	BDL	BDL	BDL	BDL

*Values are mean of five determinations with standard deviation (±)
Below detectable limit (BDL ≤ 0.05µg/g); Values given in parentheses are per cent dissipation.

which after 1 day of herbicide application reached to below detectable limit at all the three applications (Table-2). Clodinafop ester in plant might have metabolized within one day of application. These findings are in direct conformity with results reported by several workers [13,14,16].

Clodinafop acid: The data on per cent recoveries of clodinafop acid from different matrices *i.e.* soil, plant, wheat straw and grain are given in Table-1. The clodinafop acid recoveries in soil spiked @ 0.50, 1.00 and 5.00 µg/g ranged from 77.4 to 83.2 %, respectively. Wheat plant, straw and grain were fortified with clodinafop acid at three levels *i.e.* 0.50, 1.00 and 5.00 µg/g and their per cent recovery values ranged from 78.6 to 82.9, 78.9 to 81.6 and 75.9 to 80.4, respectively. The average per cent recoveries of clodinafop acid in soil, wheat plant wheat grain and wheat straw were above 75 %. The above values of per cent recoveries are well within acceptable limits and are in direct conformity with findings of several other workers [12,14].

In soil, clodinafop-propargyl rapidly degrades to the acid derivative-clodinafop as major metabolite. The data on persistence and per cent dissipation of clodinafop acid in soil at different doses have been presented in Table-3. Initial residues of clodinafop acid in first and second season at application of clodinafop propagryl @ 30, 60 and 120 g/ha were 0.102, 0.209 and 0.305 µg/g, respectively and 0.195, 0.266 and 0.368 µg/g, respectively. During both the seasons at 5 days after herbicide application, average 30 % of clodinafop acid remained in soil. In all three clodinafop acid treatments, approximately 80 % of applied herbicide in soil dissipated within 7 days after herbicide application.

The logarithmic plots of herbicides residues application *vs*. time indicated that the dissipation of clodinafop acid at all three levels of application 30, 60 and 120 g/ha fitted first order kinetics decay curves. The correlation coefficient for all three applied doses *i.e.* 30, 60 and 120 g/ha were 0.90, 0.96 and 0.97, respectively indicating perfect fit. Clodinafop propagryl when applied @ 30, 60 and 120 g/ha resulted into 0.49, 1.48 and 2.08 µg/g, respectively of clodinafop acid residues in wheat plant in first year and 0.52, 1.56 and 2.30 µg/g, respectively in second year. The data on per cent dissipation as given in Table-3 revealed that about 70 % of all clodinafop acid *i.e.* major metabolite of clodinafop-propargyl dissipated within three days after herbicide application at three levels of herbicide application *i.e.* 30, 60 and 120 g/ha in both the years.

The results of field experiment conducted revealed that during both the seasons clodinafop acid residues persisted in soil up to 5 days after herbicide application at lower dose *i.e.* 30 g/ha whereas at higher doses *i.e.* 60 g/ha and 120 g/ha clodinafop acid persisted up to 7 days and 10 day, respectively. Similar results on persistence of clodinafop acid in soil were reported by other workers [12,14].

The time *vs*. log residue plot is linear, dissipation followed first order kinetic reaction. These findings are in direct conformity with Roy & Singh [13] and Guan *et al.* [16]. The half-life values of clodinafop 30, 60 and 120 g/ha in soil were 1.89, 2.76 and 3.01 days, respectively. The lower values of half-life during present investigation in soil may be due to combined effect of soil physico-chemical properties and weather conditions likewise high relative humidity and moderate temperature. Guan *et al*. [16] noticed the half-life of clodinafop acid were 7.04 -11.22 days in soil.

Terminal residues of clodinafop-propargyl and its major metabolite clodinafop acid in wheat straw and wheat grain were below detectable level in both straw and grain samples

TABLE-3
RESIDUES OF CLODINAFOP ACID IN SOIL AND PLANT SAMPLE TREATED AT DIFFERENT DOSES

Herbicide	Days after herbicide application	Residues (µg/g) Rates of clodinafop-propargyl acid application (g/ha)					
		30 g/ha		60 g/ha		120 g/ha	
		2013	2014	2013	2014	2013	2014
Soil	0	0.102 ± 0.012	0.195 ± 0.003	0.209 ± 0.012	0.266 ± 0.07	0.305 ± 0.016	0.368 ± 0.05
	1	0.069 ± 0.004 (32.4)	0.122 ± 0.002 (37.4)	0.078 ± 0.012 (37.3)	0.170 ± 0.02 (36.0)	0.220 ± 0.06 (27.9)	0.230 ± 0.06 (37.5)
	3	0.041 ± 0.005 (59.8)	0.084 ± 0.007 (56.9)	0.092 ± 0.005 (56.0)	0.113 ± 0.03 (55.2)	0.182 ± 0.014 (40.3)	0.144 ± 0.02 (60.9)
	5	0.033 ± 0.0014 (67.6)	0.055 ± 0.001 (71.8)	0.055 ± 0.0028 (73.6)	0.085 ± 0.05 (68.0)	0.116 ± 0.008 (61.9)	0.110 ± 0.04 (70.1)
	7	0.023 ± 0.002 (77.4)	BDL	0.035 ± 0.007 (83.2)	0.038 ± 0.02 (85.7)	0.064 ± 0.0014 (79.0)	0.054 ± 0.02 (85.3)
	10	BDL	BDL	0.018 ± 0.007 (91.3)	BDL	0.029 ± 0.004 (90.4)	0.035 ± 0.05 (90.5)
	15	BDL	BDL	BDL	BDL	0.010 ± 0.005 (96.7)	BDL
Plant	0	0.49 ± 0.06	0.52 ± 0.014	1.48 ± 0.014	1.56 ± 0.014	2.08 ± 0.06	2.30 ± 0.14
	1	0.12 ± 0.014 (75.5)	0.13 ± 0.014 (75)	0.36 ± 0.028 (75.7)	0.41 ± 0.05 (70.5)	0.84 ± 0.014 (59.6)	0.78 ± 0.028 (66.1)
	3	BDL	BDL	0.26 ± 0.014 (82.4)	0.3 ± 0.14 (80.7)	0.52 ± 0.014 (75.0)	0.66 ± 0.028 (71.3)
	5	BDL	BDL	BDL	BDL	0.21 ± 0.014 (89.9)	0.25 ± 0.014 (89.0)
	7	BDL	BDL	BDL	BDL	BDL	BDL

*Values are mean of five determinations with standard deviation (±)
Below detectable limit (BDL ≤ 0.03 µg/g); Values given in parentheses are per cent dissipation.

at harvest. The above findings are in conformity with results given by several workers [7,15,16].

Conclusion

The low persistence of clodinafop ester and its major metabolite clodinafop acid and no adverse effect on wheat plant and grain quality even at double of the recommended dose (120 g ha^{-1}) revealed that the compound is not toxic in nature and may provide the solution as safe effective alternative herbicide for use in wheat both in terms of quality and food safety.

REFERENCES

1. C.D.S. Tomloin, The Pesticide Manual, vol. 14 BCPC UK (2006).
2. J. Gherekhloo, M.D. Osuna and R. De Prado, *Weed Res.*, **52**, 367 (2012).
3. M.A. Baghestani, E. Zand, S. Soufizadeh, M. Mirvakili and N. Jaafarzadeh, *Weed Biol. Manage.*, **7**, 209 (2007).
4. Anonymous www.agf.gov.bc.ca/pesticides//infosheets/clodinafop.pdf. [November 2013] (2004).
5. W.J. Gui, Q.X. Dong, S.L. Zhou, X.X. Wang, S.Y. Liu and G.N. Zhu, *Environ. Toxicol. Chem.*, **30**, 1576 (2011).
6. R. Kumar and B. Kumari, *Environ. Ecol.*, **26**, 2149 (2008).
7. S. Sondhia and J.S. Mishra, *Indian J. Weed Sci.*, **37**, 296 (2005).
8. M.H. Jackson, Soil Chemical Analysis, Prentice Hall of India Pvt. Ltd., New Delhi (1967).
9. C.S. Piper, Soil and Plant Analysis, Hans Publisher Co., Bombay, pp 59-63 (1966).
10. B.V. Subbiah and G.L. Asiza, *Curr. Sci.*, **25**, 259 (1956).
11. S.R. Olsen, C.V. Cole, F.S. Watanable and L.A. Dean, Estimation of Available Phosphorus by Extraction with Sodium Bicarbonate, US Department of Agricultural Circulation, vol. 93, p. 19 (1954).
12. S. Roy and S.B. Singh, *J. Environ. Sci. Health B*, **40**, 525 (2005).
13. S. Roy and S.B. Singh, *Bull. Environ. Contam. Toxicol.*, **77**, 260 (2006).
14. S. Roy, T.K. Das and S.B. Singh, *Pesticide Res. J.*, **18**, 87 (2006).
15. A. Chandi, S.K. Randhawa and S.P. Mehra, *J. Res. Punjab Agric. Univ.*, **44**, 23 (2007).
16. W. Guan, Y. Ma and H. Zhang, *Bull. Environ. Contam. Toxicol.*, **90**, 750 (2013).