SUPPLEMENTARY INFORMATION

Effect of ammonium on liquid- and gas-phase protonation and deprotonation in electrospray ionization mass spectrometry

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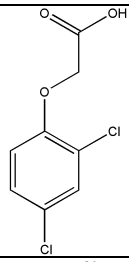
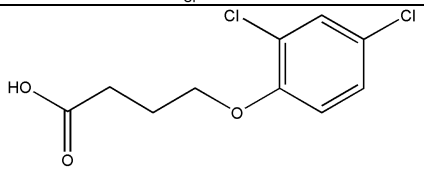
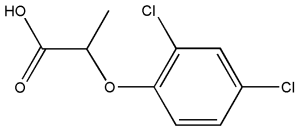
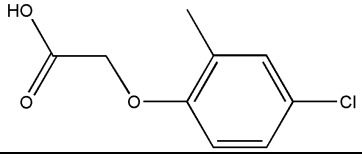
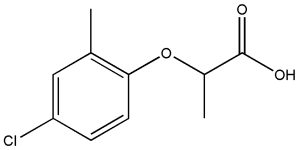
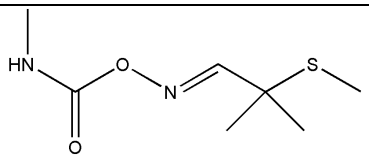
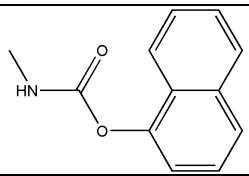
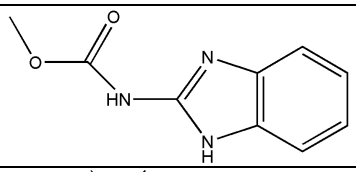
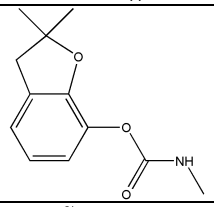
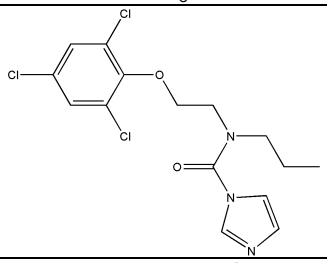
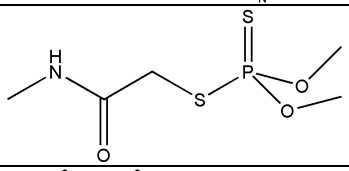
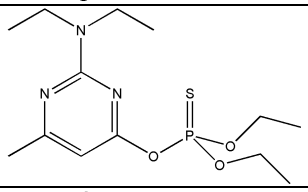
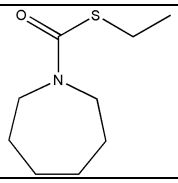
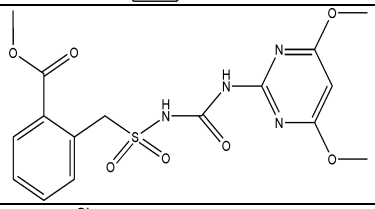
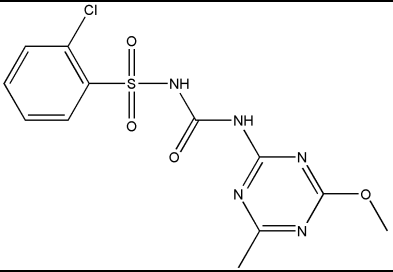
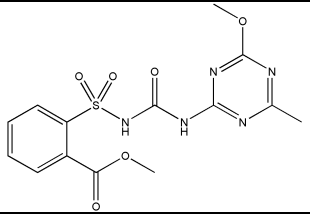
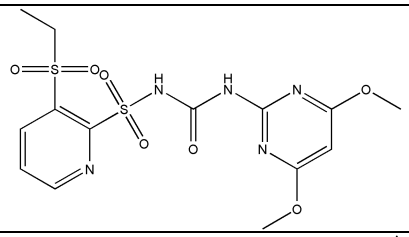
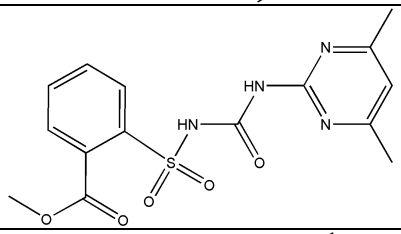
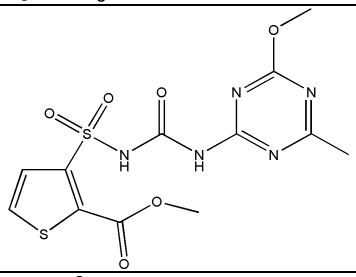
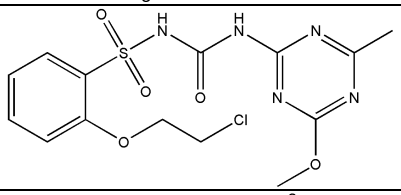
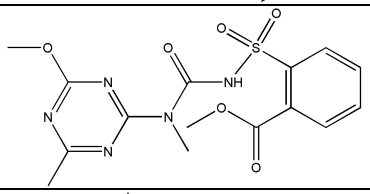
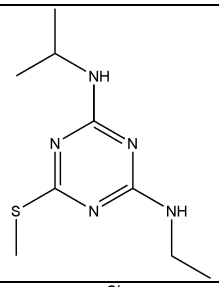
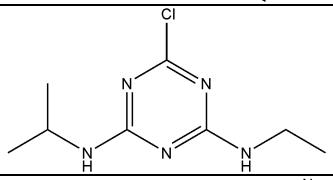
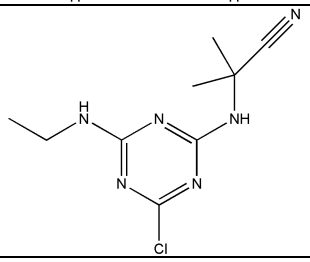
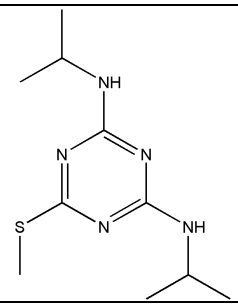
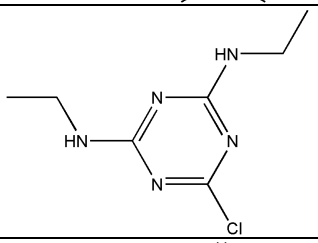
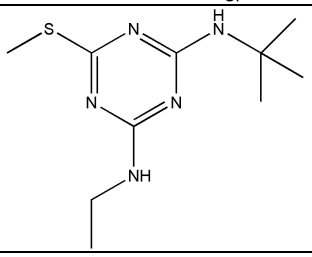
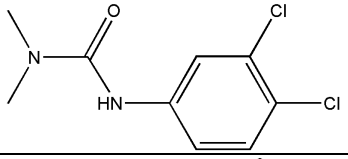
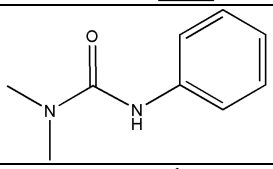
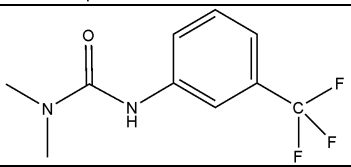
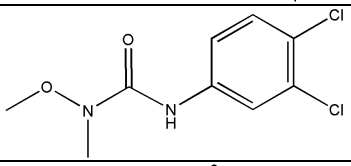
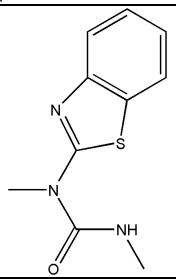
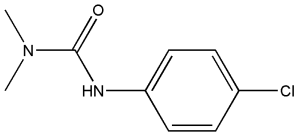
Table S1. Molecular formula, structure and CAS number of compounds investigated

Category of compounds	Compound name Molecular formula Molecular weight pK_a CAS number	Molecular structure
Phenoxy acids	2,4-D $C_8H_6Cl_2O_3$ 221.04 2.64 94-75-7	
	DB, 2, 4-DB $C_{10}H_{10}Cl_2O_3$ 249.09 4.8 94-82-6	
	Dichlorprop $C_9H_8Cl_2O_3$ 235.07 3.00 120-36-5	
	MCPA $C_9H_9ClO_3$ 200.62 3.07 94-74-6	
	Mecoprop $C_{10}H_{11}ClO_3$ 214.65 3.78 7085-19-0	
Carbamates	Aldicarb $C_7H_{14}N_2O_2S$ 190.26 -NA 116-06-3	
	Carbaryl $C_{12}H_{11}NO_2$ 201.22 - NA 63-25-2	

	Carbendazim $C_9H_9N_3O_2$ 191.19 4.2 10605-21-7	
	Carbofuran $C_{12}H_{15}NO_3$ 221.26 - NA 1563-66-2	
Imidazole	Prochloraz $C_{15}H_{16}Cl_3N_3O_2$ 376.67 3.8 67747-09-5	
Organophosphate	Dimethoate $C_5H_{12}NO_3PS_2$ 229.25 2.0 (20^{o}C) 60-51-5	
	Pirimiphos-ethyl $C_{13}H_{24}N_3O_3PS$ 333.38 4.30 23505-41-1	
Thicarbamate	Molinate (Liquid) $C_9H_{17}NOS$ 187.30 -NA 2212-67-1	
Sulfonylurea	Bensulfuron methyl $C_{16}H_{18}N_4O_7S$ 410.40 5.2 83055-99-6	
	Chlorsulfuron $C_{12}H_{12}ClN_5O_4S$ 357.77 3.60 64902-72-3	
	Metsulfuron methyl $C_{14}H_{15}N_5O_6S$ 381.36 3.33 74223-64-6	

	Rimsulfuron $C_{14}H_{17}N_5O_7S_2$ 431.44 4 122931-48-0	
	Sulfometuron methyl $C_{15}H_{16}N_4O_5S$ 364.38 5.2 74222-97-2	
	Thifensulfuron-methyl (Pinnacle) $C_{12}H_{13}N_5O_6S_2$ 387.40 4 (25°C) 79277-27-3	
	Triasulfuron $C_{14}H_{16}ClN_5O_5S$ 401.82 4.64 (20°C) 82097-50-5	
	Tribenuron-methyl $C_{15}H_{17}N_5O_6S$ 395.39 4.7 101200-48-0	
Triazines	Ametryn $C_9H_{17}N_5S$ 227.33 4.1(20°C) 834-12-8	
	Atrazine $C_8H_{14}ClN_5$ 215.69 1.7 1912-24-9	
	Cyanazine $C_9H_{13}ClN_6$ 240.69 0.63 21725-46-2	

	Prometryn $C_{10}H_{19}N_5S$ 241.40 4.1 7287-19-6	
	Simazine $C_7H_{12}ClN_5$ 201.70 1.62 (20°C) 122-34-9	
	Terbutryn $C_{10}H_{19}N_5S$ 241.40 4.3 886-50-0	
Substituted urea	Diuron $C_9H_{10}Cl_2N_2O$ 233.10 -NA 330-54-1	
	Fenuron $C_9H_{12}N_2O$ 164.21 -NA 101-42-8	
	Fluometuron $C_{10}H_{11}F_3N_2O$ 232.20 -NA 2164-17-2	
	Linuron $C_9H_{10}Cl_2N_2O_2$ 249.10 -NA 330-55-2	
	Methabenzthiazuron $C_{10}H_{11}N_3OS$ 221.28 -NA 18691-97-9	
	Monuron $C_9H_{11}ClN_2O$ 198.65 -NA 150-68-5	

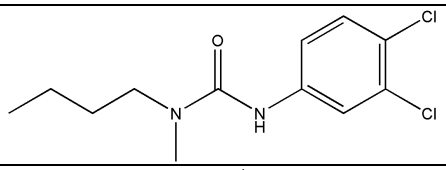
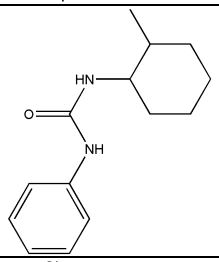
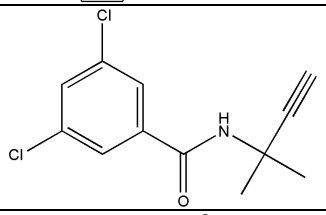
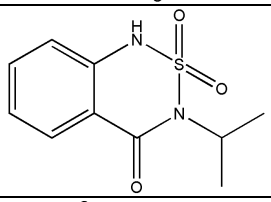
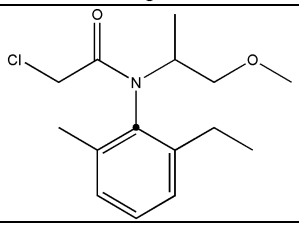
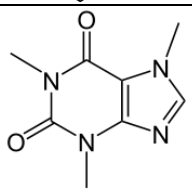
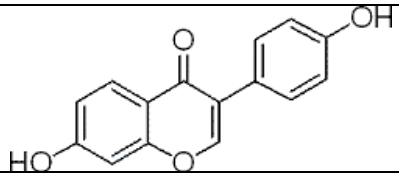
	Neburon $C_{12}H_{16}Cl_2N_2O$ 275.18 -NA 555-37-3	
	Siduron $C_{14}H_{20}N_2O$ 232.32 -NA 1982-49-6	
Substitued amide	Propyzamide $C_{12}H_{11}Cl_2NO$ 256.13 -NA 23950-58-5	
Benzothiadiazole	Bentazone $C_{10}H_{12}N_2O_3S$ 240.28 3.3 (24^{o}C) 25057-89-0	
Chloroacetanilide	Metolachlor $C_{15}H_{22}ClNO_2$ 283.80 -NA 51218-45-2	
Caffeine	Caffeine $C_8H_{10}N_4O_2$ 194.19 10.4 （40 °C） 58-08-2	
Isoflavones	Daidzein $C_{15}H_{10}O_4$ 254.24 pK_{a1} 7.77, pK_{a2} 9.74 486-66-8	

Table S2 Comparison of intensity of Na adduct $[M+Na]^+$ and protonated ions ($[M+H]^+$) in methanol mobile phases containing additives (A) 1 mM formic acid-0.4 mM ammonia (pH 3.7) and (B) 1 mM formic acid (pH 3.5). For experimental condition, see Experimental Section of the text.

Ion mode	Compound	pK_a	Retention time (min)		$\frac{[M+Na]^+_{(A)}}{[M+H]^+_{(A)}}$	$\frac{[M+Na]^+_{(B)}}{[M+H]^+_{(B)}}$	$\frac{[M+Na]^+_{(A)}}{[M+Na]^+_{(B)}}$	$\frac{[M+H]^+_{(A)}}{[M+H]^+_{(B)}}$
			(A) pH3.7	(B) pH3.5				
ESI+	Dimethoate	2.00	15.74	15.68	0.36	11.9	0.2	5.05
	Aldicarb		20.92	20.92	0.23	2.2	0.2	1.94
	Cyanazine		24.36	24.24	0.21	0.3	0.8	1.25
	Monuron		25.02	24.96	0.04	0.9	0.2	3.47
	Thifensulfuron	4.00	25.51	26.17	0.79	2.2	1.1	3.20
	Sulfometuron methyl	5.20	27.38	27.38	0.41	3.3	0.6	4.65
	Chlorsulfuron	3.60	28.22	29.73	0.49	3.4	0.5	3.45
	Fluometuron		31.11	30.99	0.03	0.9	0.1	3.12
	Diuron		34.61	34.55	0.03	0.6	0.2	4.45
	Bensulfuron methyl	5.20	36.84	36.78	0.09	1.4	0.3	5.20
	Siduron		37.87	37.75	0.17	1.2	0.3	2.32
	Metolachlor		42.81	42.75	0.16	2.4	0.2	2.43
	Neburon		45.35	45.22	0.06	1.1	0.3	4.99
	Prochloraz		47.94	46.91	0.41	0.4	1.1	0.97
	Pirimiphos-ethyl		52.22	51.62	0.01	0.0	0.3	0.85
	Carbaryl		29.18	29.12	0.02	0.8	0.1	4.49
	Fenuron		13.99	13.93	0.04	0.9	0.1	2.20
	Rimsulfuron	4.00	20.50	20.44	1.09	5.3	0.9	4.59
	Triazines							
	Ametryn	4.10	35.58	32.02	No	No	No	1.03
	Atrazine	1.70	31.72	31.60	No	No	No	0.99
	Cyanazine	0.63	24.36	24.24	No	No	No	1.25
	Prometryn	4.10	40.52	37.14	No	No	No	0.95
	Simazine	1.62	25.57	25.51	No	No	No	0.90
	Terbutryn	4.30	41.37	37.87	No	No	No	1.05
ESI-								$\frac{[M-H]^-_{(A)}}{[M-H]^-_{(B)}}$
	2, 4-D	2.64	29.70	33.38	NA	NA	NA	0.40
	2, 4-DB	4.80	43.14	43.26	NA	NA	NA	0.74
	Dichlorprop	3.00	35.55	38.92	NA	NA	NA	0.42
	MCPA	3.07	31.81	35.18	NA	NA	NA	0.44
	Mecoprop	3.78	37.05	39.77	NA	NA	NA	0.44
	Bentazone	3.30	19.99	25.11	NA	NA	NA	0.87
	Fluometuron		31.08	31.02	NA	NA	NA	0.63
	Diuron		34.58	34.52	NA	NA	NA	0.92
	Neburon		45.32	45.25	NA	NA	NA	0.89
	Siduron		37.84	37.72	NA	NA	NA	0.96

No - No sodium adduct ions were observed. NA - Not applicable.

Note: Other compounds that are listed in Table S1 but not shown above have similar trends with those from dimethoate to rimsulfuron. Ammonium does not have significant influences on ion signal of protonated daidzein (refer to Fig. 2A).

Table S3. Physical properties of aprotic solvents (methanol, acetonitrile, water and ammonia)

Solvent	Gas-phase basicity (kJ/mol)	Proton affinity (kJ/mol)	Volatility (Torr)	Surface tension (dyn/cm)	Viscosity (cp)	Autodissociation constant pKs	Dielectric constant
CH_3CN	756	788	88.8 (25 °C)	19.10 (20 °C)	0.38 (15 °C)	28.5	37.5 (20 °C)
CH_3OH	728	761	125 (25 °C)	22.55 (20 °C)	0.55 (20 °C)	16.7	32.7 (25 °C)
H_2O	660	697		73 (20 °C)	1.002 (20 °C)		78.5 (25 °C)
NH_3	819	854					

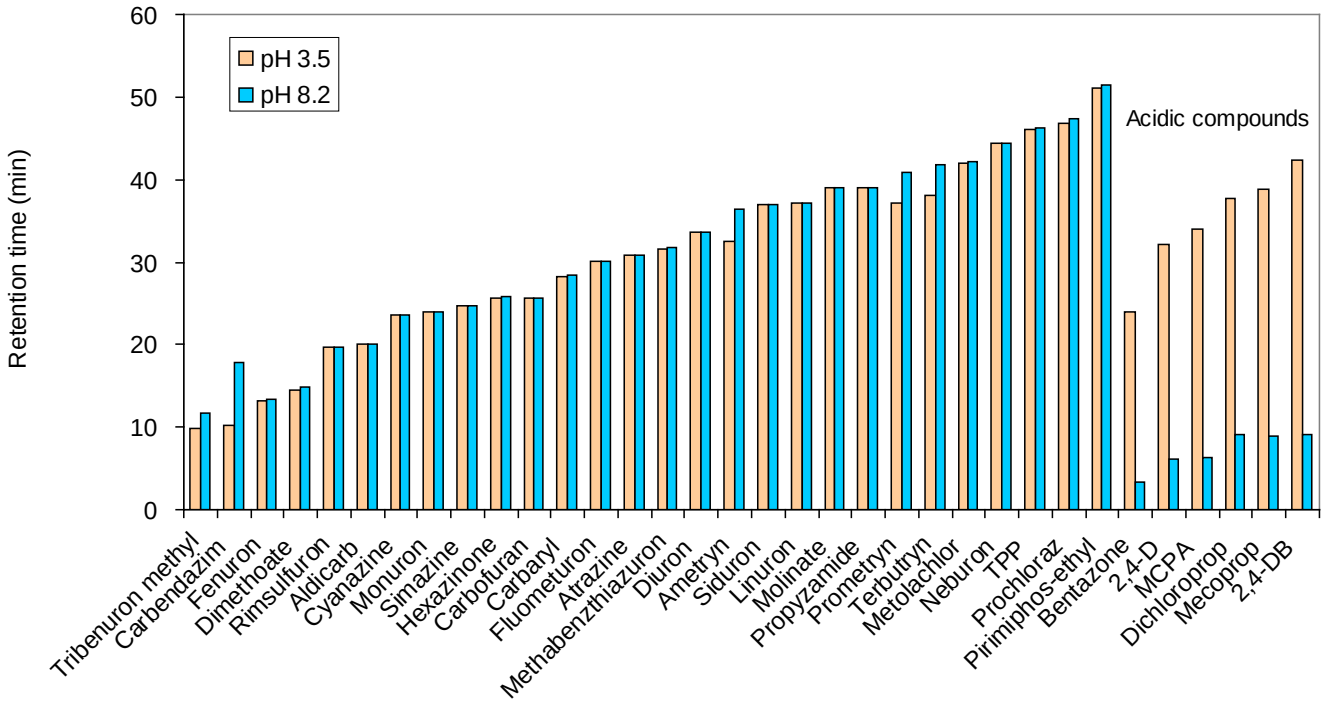


Fig. S1 Comparison of retention time between formic acid-methanol mobile phase (pH 3.5) and ammonia doped methanol phase (pH 8.2).

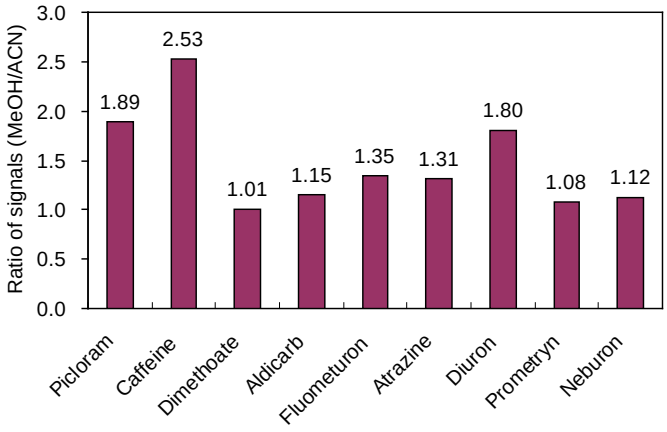


Fig. S2 The signal ratio of protonated analytes in methanol and acetonitrile solutions. Additive: 1 mM formic acid and 0.4 mM ammonia (pH 3.7)

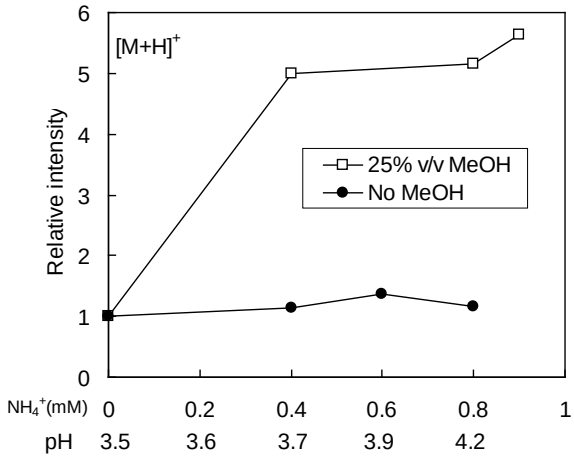


Fig. S3 Effect of ammonium concentration in formic acid (1 mM)-methanol (25% v/v) solution on the intensity of protonated ion for dimethoate.

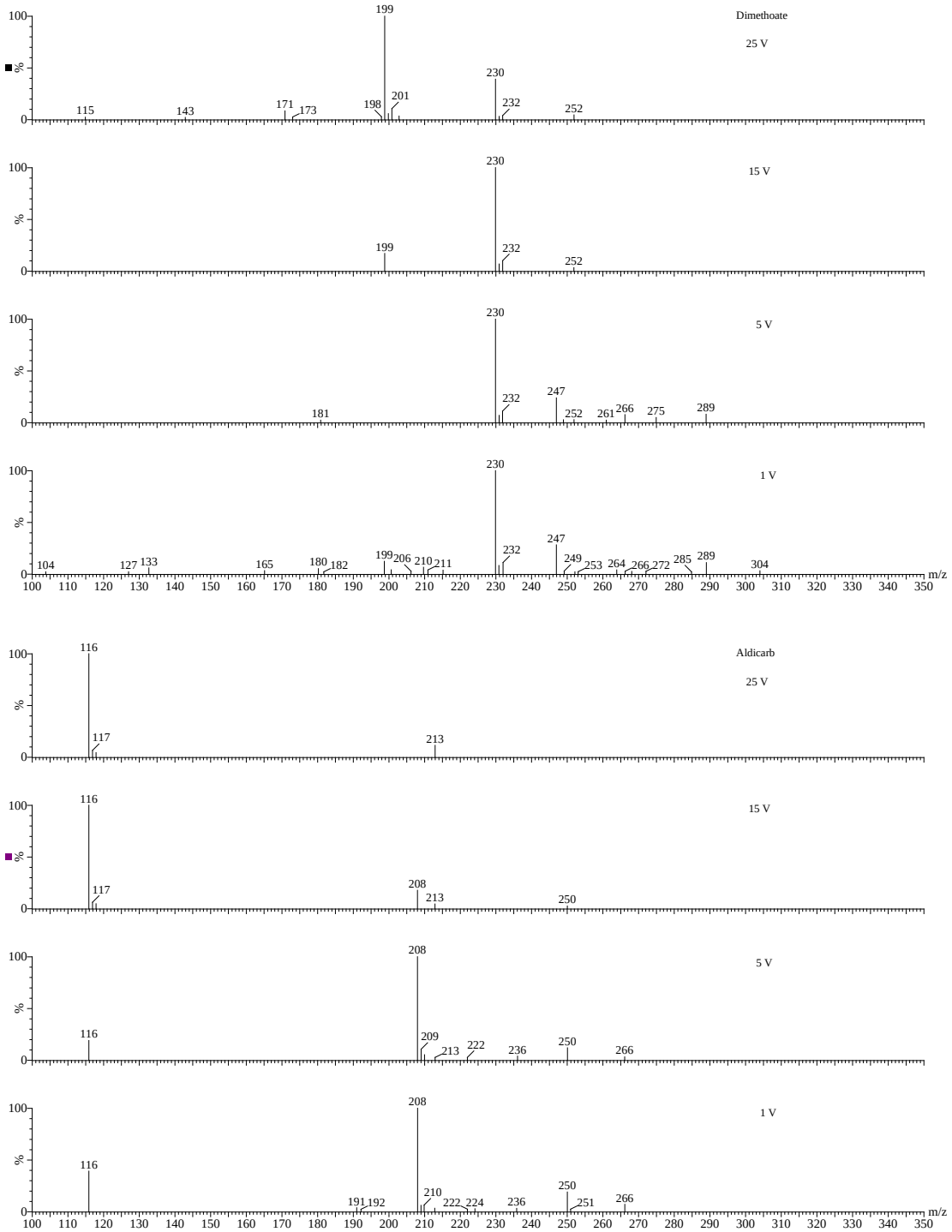


Fig. S4 Mass spectra of dimethoate and aldicarb under different cone voltages. m/z 247 and 208 are $[M+NH_4]^+$ for dimetnoate and aldicarb, respectively; m/z 252 and 213 are $[M+Na]^+$ for dimetnoate and aldicarb, respectively; m/z 230 is $[M+H]^+$ for dimethoate; m/z 199 is a fragmented species of dimethoate; m/z 116 is a fragmented species of aldicarb. Mobile phase additive: 1 mM formic acid + 0.4 mM ammonia (pH 3.7).

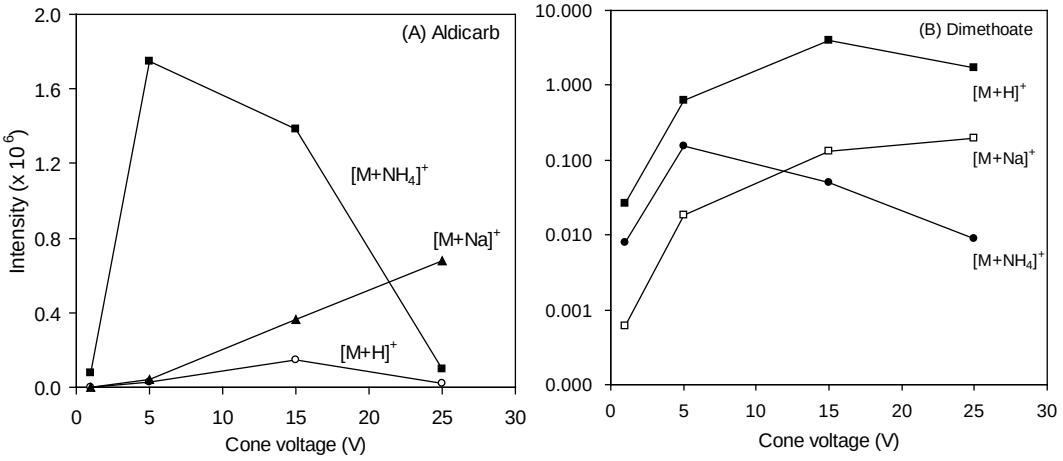


Fig. S5 Effect of cone voltages on the intensity of ammoniated, sodiated and protonated molecules for (A) aldicarb and (B) dimethoate.

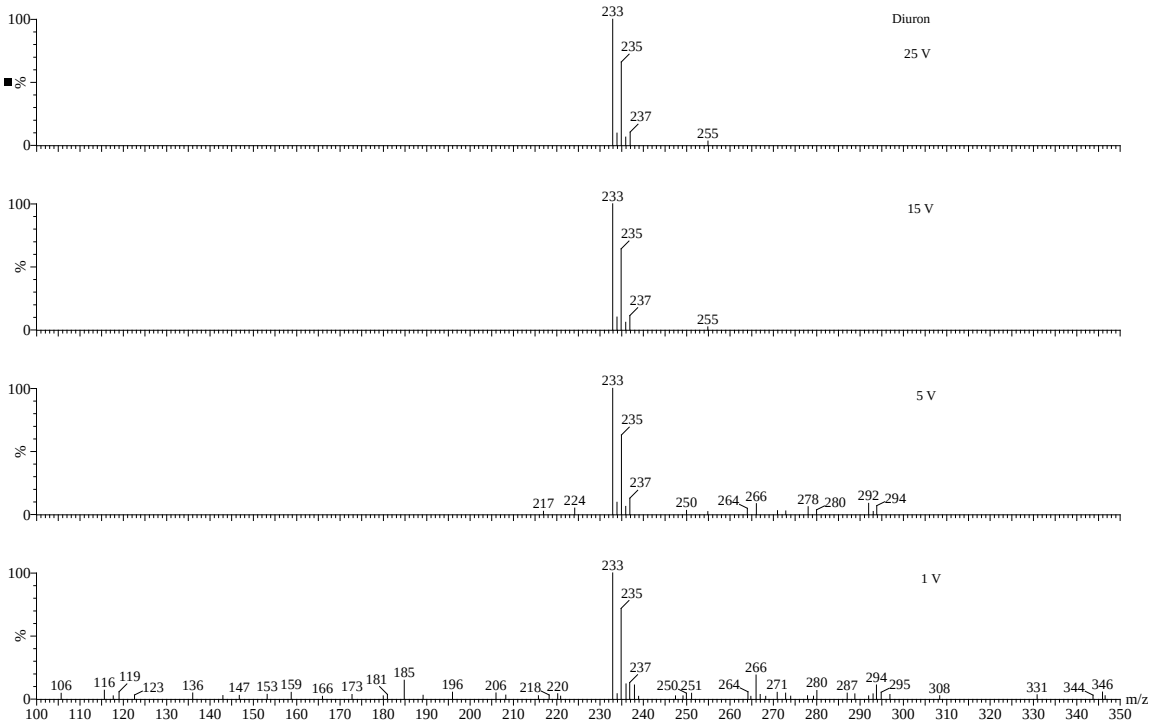


Fig. S6 Mass spectra of diuron under different cone voltages with 1 mM formic acid-0.4 mM ammonia (pH 3.7) as mobile phase additives. m/z 250 is $[M+NH_4]^+$ and m/z 255 is $[M+Na]^+$.

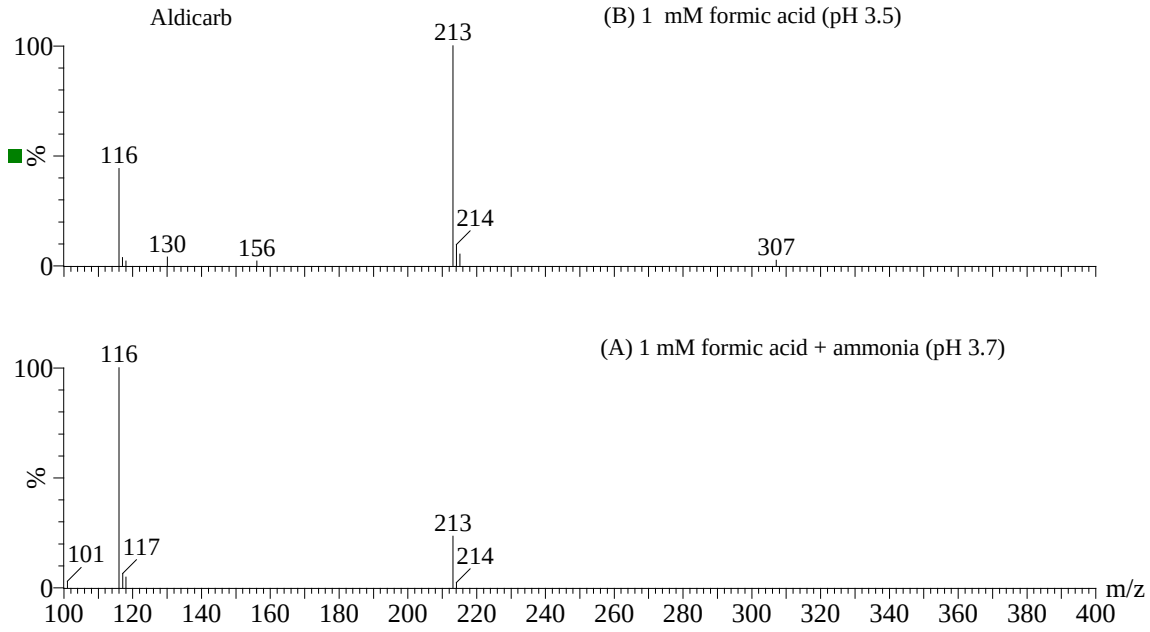


Fig. S7 Comparison of mass spectra of aldicarb from 1 mM formic acid-methanol solution (pH 3.5) and 1 mM formic acid-0.4 mM ammonia methanol solution (pH 3.7). m/z 213 is Na adduct ion and m/z 116 is a fragmented species of the molecule.