Supplementary Information

A novel extraction method for simultaneous determination of neonicotinoid insecticides and their metabolites in human urine

(***In entire manuscript, the red font represents the modification)***

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Submission to: Analytical Method

Materials and Methods

Sample Preparation of QuEChERS Method

Urine sample (3 mL) was transferred into a pp tube and 1 ng of mixed internal standard solution was spiked. Then 3 mL of 1% acetic acid in acetonitrile was added, and the mixture was shaken vigorously for 2 min. After the tube was centrifuged at 5000 g for 5 min, the 1.5 mL of supernatant was transferred to a 2 mL of tube and mixed with 20 mg of purifying agents (PSA, C18, or GCB). The tube was shaken vigorously for 1 min and centrifuged at 5000 g for 5 min. Finally, the supernatant was placed into an LC vial to carry out analysis.

Table S1 MRM transitions and other LC-MS/MS conditions.

Pesticide	t_R (min)[b]	Ion transition	Fragmentor (V)	Collision energy (eV)
ACE	6.4	223→56	140	13
		223→126[a]	140	17
IMI	6.1	256→175	80	18
		256→209[a]	80	10
CLO	5.9	250→132	80	6
		250→169[a]	80	12
THD	6.9	253→186	140	10
		253→126[a]	140	16
THM	5.6	292→181	80	22
		292→211[a]	80	6
DIN	4.8	203→87	80	14
		203→129[a]	80	8
DN	8.9	158→102	80	15
		158→57[a]	80	20
UF	0.8	159→67	80	16
		159→85[a]	80	14
5-OH-IMI	6.2	272→191	70	16
		272→225[a]	70	10
N-dm-ACE	1.6	209→90	70	12
		209→126[a]	70	26
ACE-d_3	6.4	226→59	80	16
		226→126[a]	80	18
IMI-d_4	6.1	260→179	120	14
		260→213[a]	120	10
CLO-d_3	5.9	253→172	80	10
		253→132[a]	80	10
THD-d_4	6.9	257→190	80	14
		257→126[a]	80	19
THM-d_3	5.6	295→184	80	20
		295→214[a]	80	10

[a] Transitions used for quantification ion; [b] Retention time

35

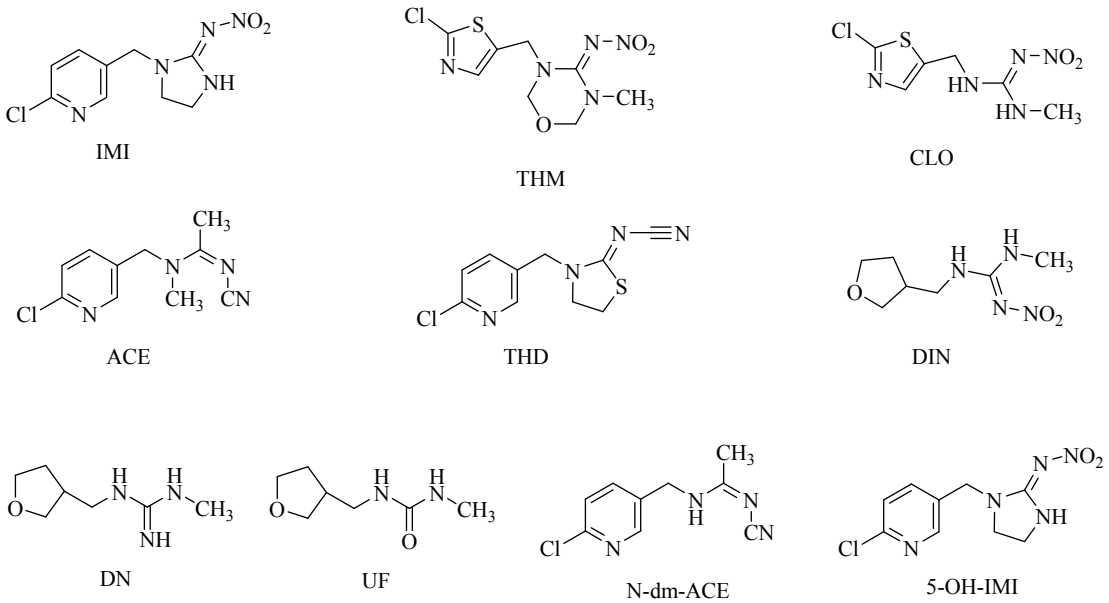

Figure S1 Chemical structure of NEOs and their metabolites.

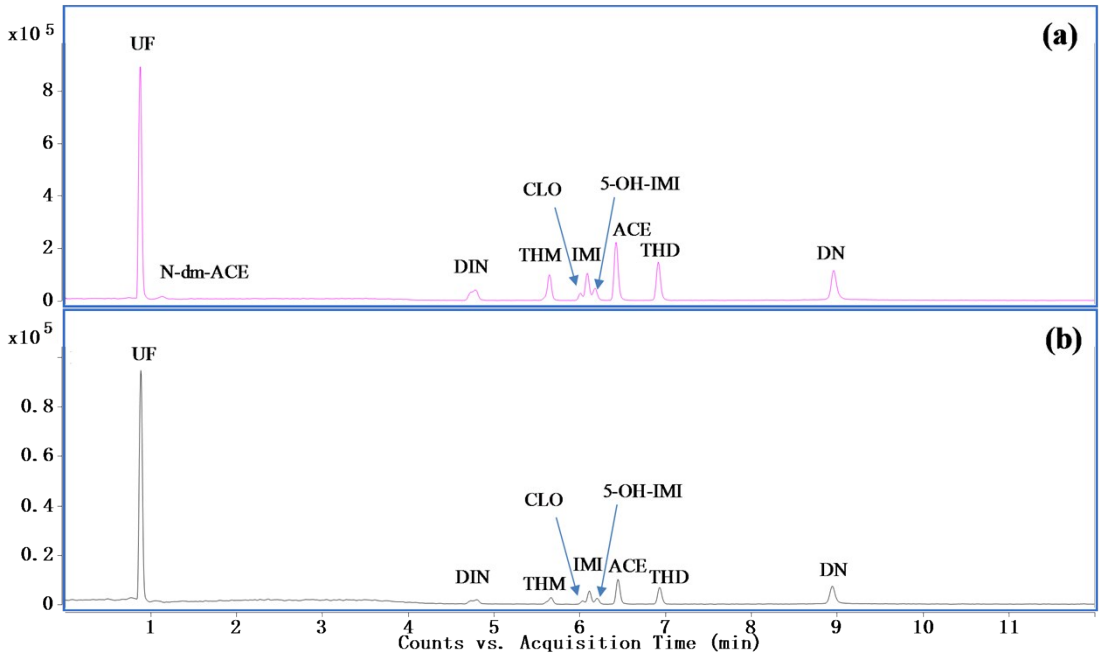

Figure S2 LC-MS/MS chromatography in MRM acquisition mode of NEOs and their metabolites (100 ng/mL) testing difference mobile phase: ultrapure water/acetonitrile (a) and ultrapure water/methanol (b)

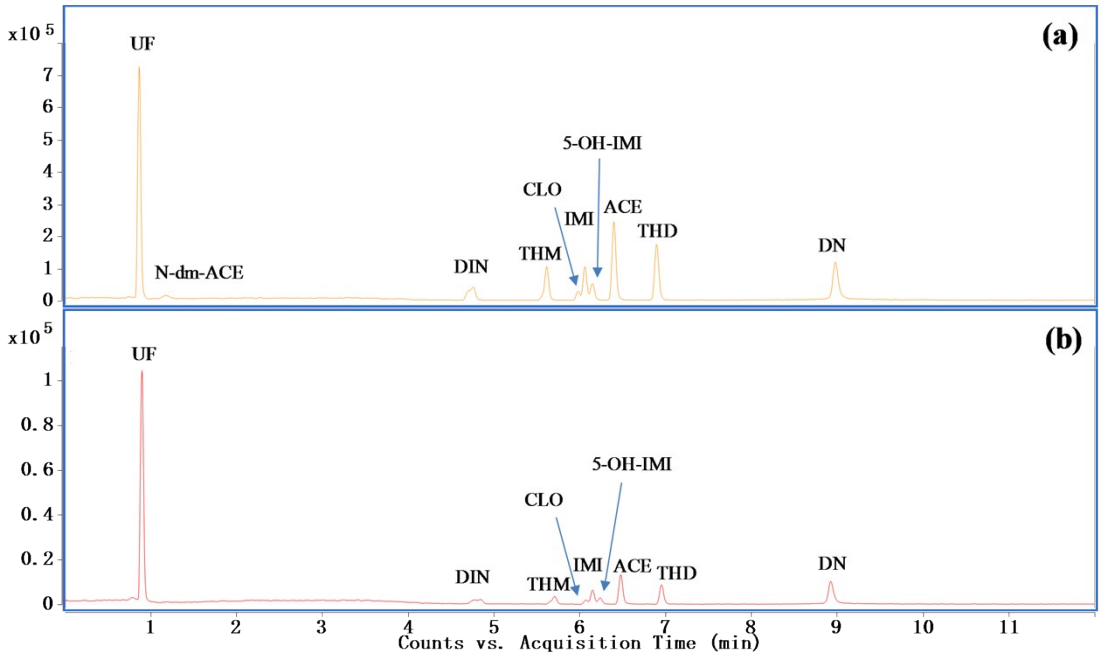

Figure S3 LC-MS/MS chromatography in MRM acquisition mode of NEOs and their metabolites (100 ng/mL) testing difference mobile phase: 0.1% formic acid in ultrapure water/acetonitrile (a) and 5 mM ammonium acetate in ultrapure water /methanol (b).