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Supplementary Material

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Characterisation of Neonicotinoid Insecticides in the Cocoa-producing Owena River Basin of Nigeria by a QuEChERS Method Coupled to Liquid Chromatography-Tandem Mass Spectrometry

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Table S1. Multiple reaction parameters for the developed LC/MS/MS method.

Neonic	Precursor ion masses	MS 1 Resolution (quadrupole)	Product ions masses	MS 2 Resolution (quadrupole)	Dwell time (10^{-3} s)	Fragmentor masses	Collision Energy (eV)	Cell Accelerator Voltage (V)	Polarity
IMI	256.1	Unit	209	Unit	100	96	14	7	+ ve
	256.1	Unit	175.1	Unit	100	96	18	7	+ ve
THA	253	Unit	126	Unit	100	103	22	7	+ ve
	253	Unit	90	Unit	100	103	42	7	+ ve
ACE	223.1	Unit	126	Unit	100	103	18	7	+ ve
	223.1	Unit	90.1	Unit	100	103	38	7	+ ve
THX	292	Unit	211.1	Unit	100	103	8	7	+ve
	292	Unit	131	Unit	100	104	20	7	+ve
3-CA	128	Unit	92.1	Unit	100	96	25	7	+ ve

(IMI = Imidacloprid; THA = Thiacloprid; ACE = Acetamiprid; THX = Thiamethoxam; 3-CA = 3-chloroaniline).
The tandem mass spectrometer works in positive polarity, *i.e.*, all ions produced are cations. "Unit resolution" means that one can separate each mass from the next integer mass, *i.e.*, it is possible to distinguish mass 50 from mass 51, or mass 1000 from mass 1001. This definition is commonly used when discussing resolution on quadrupole and ion trap mass spectrometers.

Table S2. Neonics standard solutions linear range, retention time, regression coefficient (r^2), Limit of detection (LOD), Limit of quantification (LOQ), Linear regression equation.

Neonics	Retention Time (minutes)	Regression coefficient (r^2)	LOD (µg/g)	LOQ (µg/g)	Linear regression equation $y = m(x) + c$
IMI	5.909	0.9992	0.002	0.005	y = 1E6(x) + 7317.3
THA	8.379	0.9995	0.0005	0.003	y = 392860(x) + 1683.2
ACE	6.859	0.9994	0.003	0.004	y = 2E6(x) + 8944.8
THX	5.149	0.9985	0.004	0.005	y = 246755(x) + 2024.8

Note that: 1E6 = 1 x10^6 and 2E6 = 2 x10^6.
(IMI = Imidacloprid; THA = Thiacloprid; ACE = Acetamiprid; THX= Thiamethoxam)

Table S3. Mean concentrations (µg/g) of neonicotinoid pesticide residues in cocoa-producing soil samples of owena river basin.

Sample code	Imidacloprid mean±sd	Thiacloprid mean±sd	Acetamiprid mean±sd	Thiamethoxam mean±sd
SI	ND	0.26±0.04	ND	0.60±0.03
S2	ND	ND	ND	ND
S3	ND	0.42±0.23	0.31±0.40	0.84±0.46
S4	ND	ND	0.69±0.34	1.07±0.12
S5	ND	1.06±0.58	ND	0.29±0.04
S6	ND	ND	0.78±0.44	0.43±0.22
S7	ND	ND	ND	ND
S8	ND	ND	ND	ND
S9	ND	0.48±0.15	ND	1.56±0.14
S10	ND	ND	ND	ND
∑NE	-	2.22	1.78	4.79
Range	-	0.26-1.06	O.31-0.78	0.29-1.56
Mean	-	0.56	0.59	0.80
SD	-	0.35	0.25	0.47
CV	-	62.5	42.37	58.75
ANOVA	-	P ≥ 0.05	P ≥ 0.05	P ≥ 0.05
Remarks	-	NS	NS	NS

∑NE = Total organochlorine pesticide residues; ND= Not detected, SD = Standard deviation; ANOVA=Analysis of variance; NS = No significant difference; S1-S10=Soil samples; CV = Coefficient of variation.

Table S4. Mean concentrations (µg/g) of neonicotinoid pesticide residues in sediment samples from owena river.

Sample code	Imidacloprid mean±sd	Thiacloprid mean±sd	Acetamiprid mean±sd	Thiamethoxam mean±sd
SdI	ND	0.04±0.13	0.06±0.08	0.16±0.06
Sd2	ND	0.07±0.09	ND	0.20±0.10
Sd3	ND	ND	ND	ND
Sd4	ND	ND	ND	ND
Sd5	ND	0.05±0.02	0.04±0.01	0.08±0.02
Sd6	ND	ND	ND	ND
Sd7	ND	0.09±0.04	0.12±0.03	0.12±0.03
Sd8	ND	ND	ND	ND
Sd9	ND	ND	ND	ND
Sd10	ND	ND	ND	ND
∑NEONICS	-	0.25	0.22	0.56
Range	-	0.06-0.09	0.04-0.12	0.08-0.20
Mean	-	0.06	0.07	0.14
SD	-	0.02	0.04	0.05
CV	-	33.33	57.14	35.71
ANOVA	P ≥ 0.05	P ≥ 0.05	P ≥ 0.05	P ≥ 0.05
Remarks	- NS	NS	NS	NS

∑NE = Total organochlorine pesticide residues; ND= Not detected, SD = Standard deviation; ANOVA=Analysis of variance; NS = No significant difference; S1-S10=Soil samples; CV = Coefficient of variation.

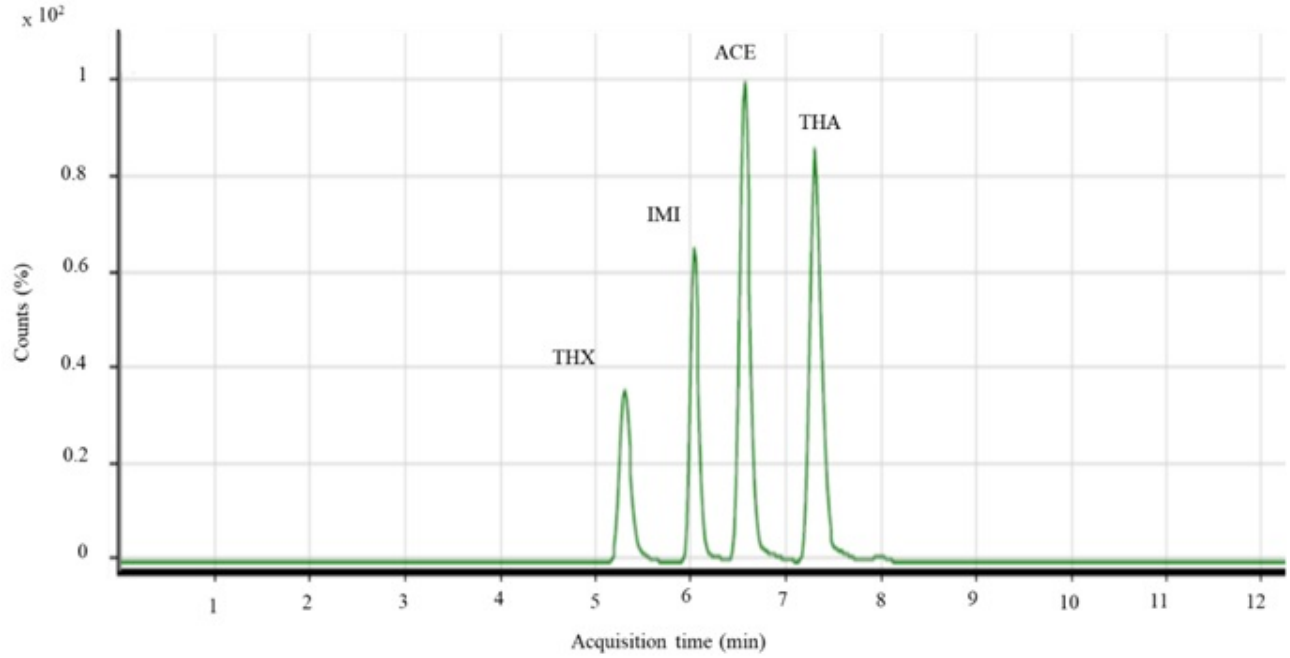

Fig. S1(a). Ion chromatogram of thiamethoxam (THX); imidacloprid (IMI); acetamiprid (ACE) and thiacloprid (THA) analyzed with LC-MS/MS at 1ppm.

Table 5. Mean concentrations (µg/L) of neonicotinoid pesticide residues in owena river surface water samples.

Sample code	Imidacloprid mean±sd	Thiacloprid mean±sd	Acetamiprid mean±sd	Thiamethoxam mean±sd
RI	ND	ND	ND	ND
R2	ND	ND	ND	ND
R3	ND	0.03±0.01	0.06±0.04	0.16±0.15
R4	ND	0.06±0.02	0.08±0.03	0.07±0.03
R5	ND	ND	ND	ND
R6	ND	ND	ND	ND
R7	ND	0.08±0.09	0.09±0.01	0.05±0.03
R8	ND	ND	ND	ND
R9	ND	ND	ND	ND
R10	ND	ND	ND	ND
S10	ND	ND	ND	ND
∑NEONICS	-	0.17	0.23	0.28
Range	-	0.03-0.08	0.06-0.09	0.05-0.16
Mean	-	0.06	0.08	0.09
SD	-	0.03	0.02	0.06
CV	-	50.00	25.00	66.67
ANOVA	-	$P \geq 0.05$	$P \geq 0.05$	$P \geq 0.05$
Remarks	--	NS	NS	NS

∑NE = Total organochlorine pesticide residues; ND= Not detected, SD = Standard deviation; ANOVA=Analysis of variance; NS = No significant difference; S1-S10=Soil samples; CV = Coefficient of variation.

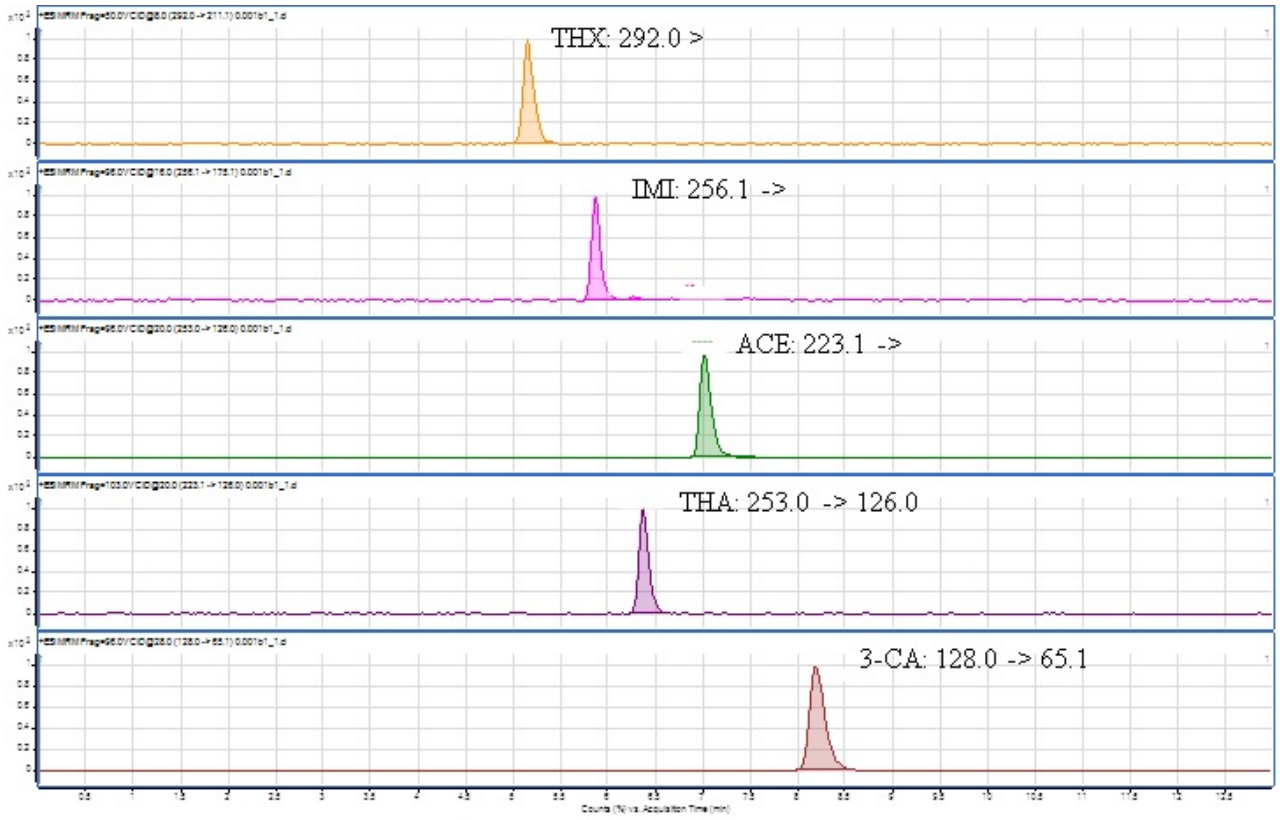

Fig. S1(b). Ion chromatogram of four standards and Internal Standards of 3-chloroaniline and their most abundant ions for confirmation.

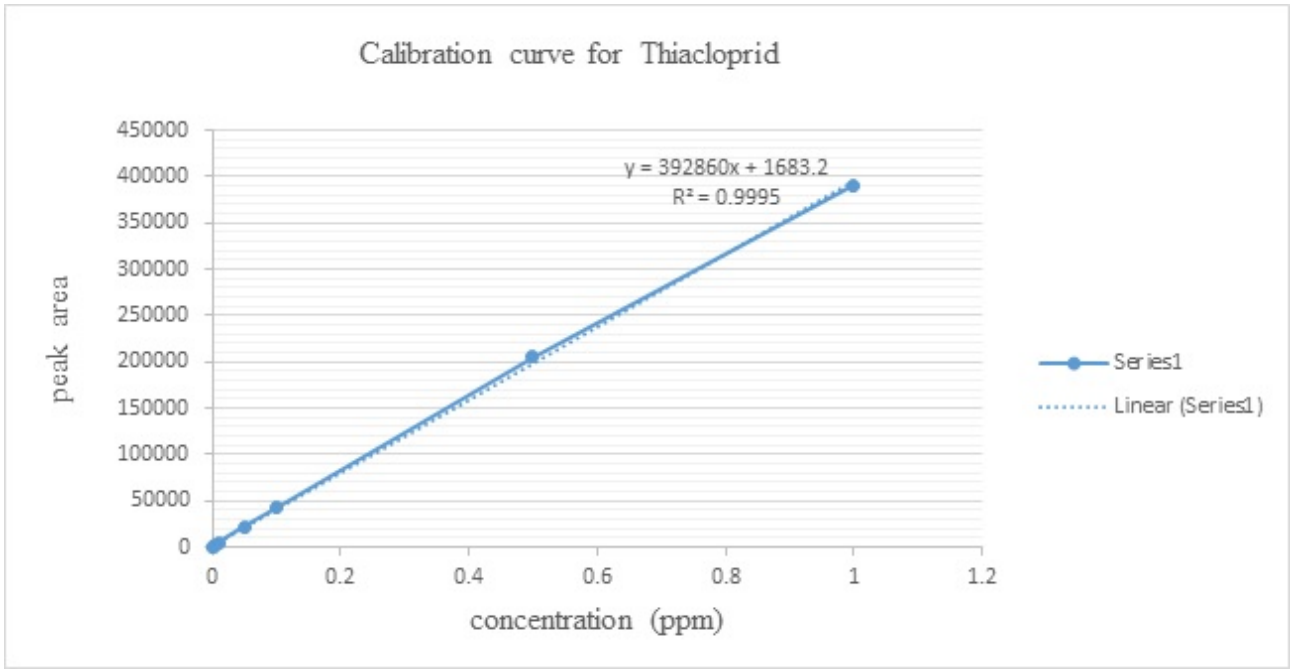

Fig. S2. Calibration curve for thiocloprid.

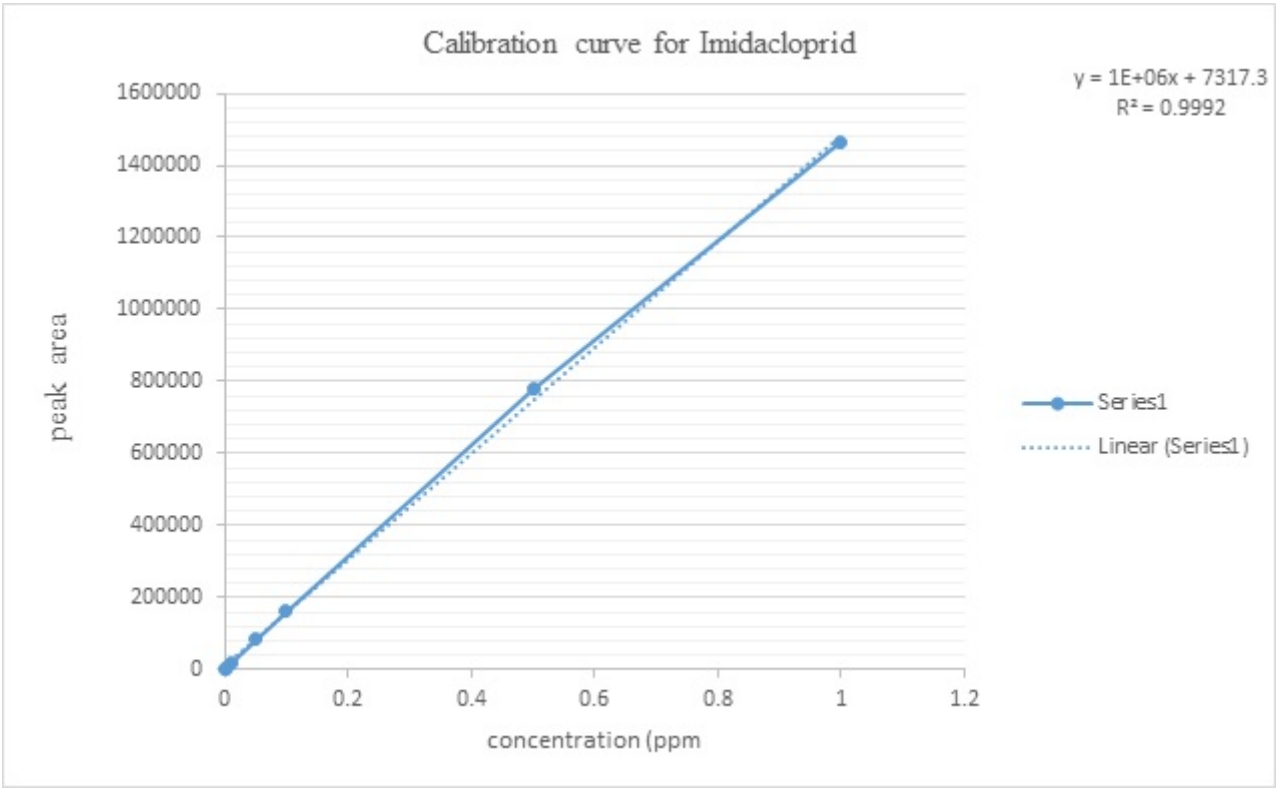

Fig. S3. Calibration curve for Imidacloprid.

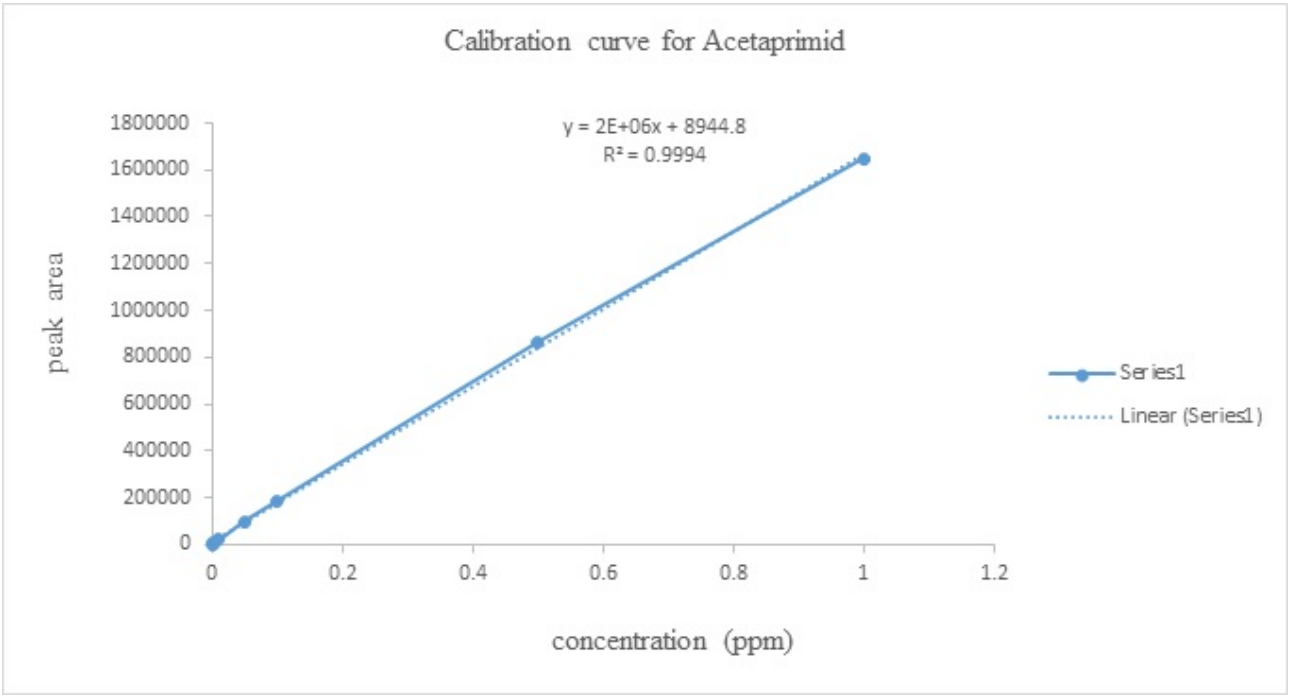

Fig. S4. Calibration curve for Acetamiprid.

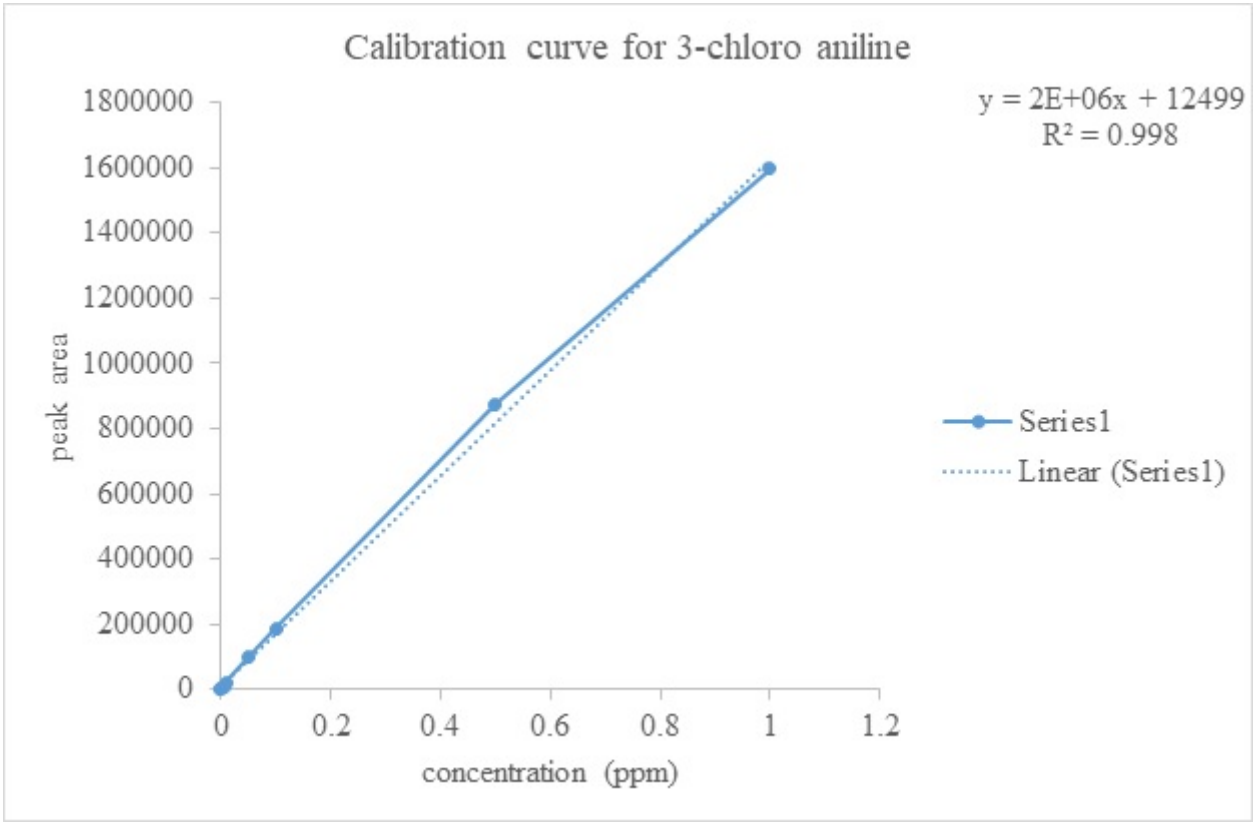

Fig. S5. Calibration curve for 3- chloro aniline (Internal standard).

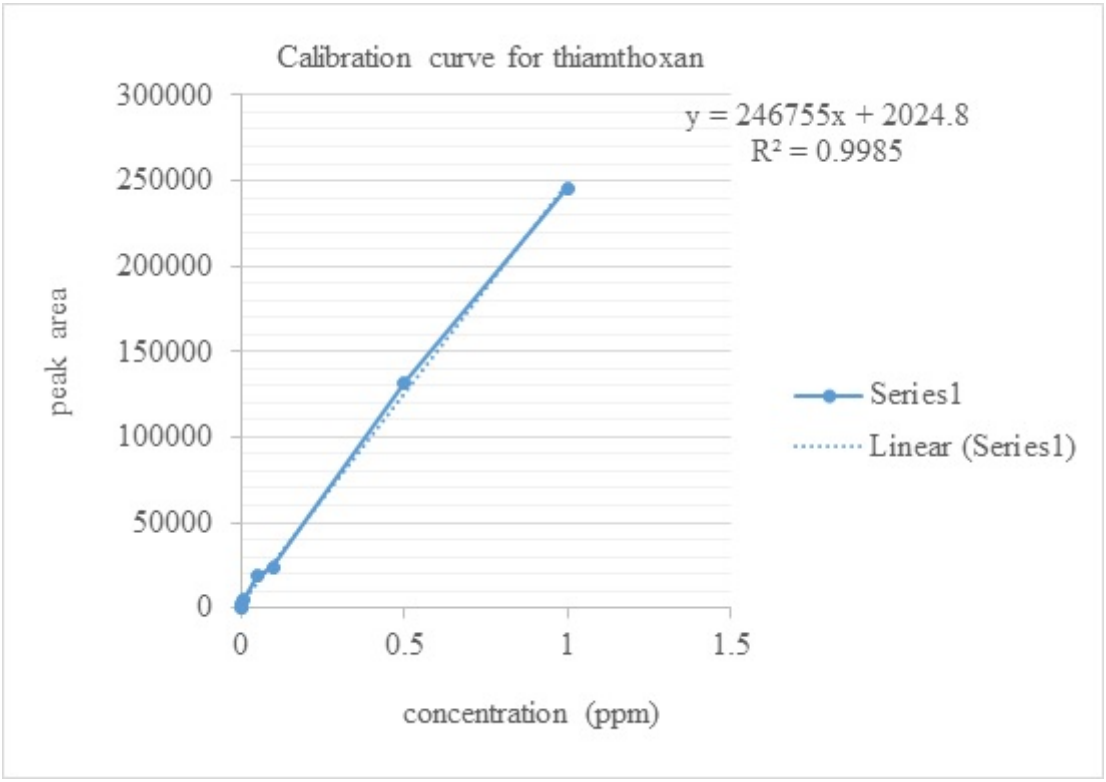

Fig. S6. Calibration curve for Thiamthoxan.