Supplementary Information

Enhanced residual risk of abamectin induced by 6PPD: in water, soil, and vegetables

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Text S1: The corresponding locations of water samples are as follows: water-A (Tongzhou, Beijing, Chaobai River north section), water-B (Tongzhou, Beijing, Chaobai River south section), water-C (Changping, Beijing, lake in ming tombs), water-D (Wuhu, Anhui, Xingang Town field pond), water-E (Wuhu, Anhui, Xingang Town roadside pond), water-F (Maanshan, Anhui, Huanfeng Town roadside pond) and water-G (Yibin, Sichuan, Yangtze River). The corresponding locations of soil samples are as follows: soil-A (Tongzhou, Beijing, Chaobai riverside north section), soil-B (Tongzhou, Beijing, Chaobai riverside south section), soil-C (Changping, Beijing, ming tombs), soil-D (Wuhu, Anhui, Xingang Town field), soil-E (Wuhu, Anhui, Xingang Town roadside), soil-F (Maanshan, Anhui, Huanfeng Town roadside), soil-G (Yibin, Sichuan, Yangtze riverside), soil-H (Nanning, Guangxi University farm-1), soil-I (Nanning, Guangxi, Guangxi University farm-2), soil-J (Hefei, Anhui, Guanting Town filed), soil-K (Changsha, Hunan, Huanghua Town filed), soil-L (Yuxi, Yunnan, Xiushan Town field), soil-M (Haidian, Beijing, China Agricultural University gate roadside) and soil-N (Haidian, Beijing, China Agricultural University).

Text S2: Detailed steps of QuEChERS methods for abamectin analysis:

1.1 Abamectin in water: The samples from the degradation experiment of abamectin in water were directly subjected to HPLC-MS/MS detection after filtered through a 0.22 μm filter membrane.

1.2 Abamectin in soil: The soil is sandy red soil from Fujian, which was sieved through a 2mm mesh before use. 5g of soil was weighed into a 50 mL centrifuge tube

along with 5.0 g of NaCl, 5.0 mL of deionized water, and 5.0 mL of acetonitrile. The mixture was shaken for 5 min and then centrifuged at 3800 rpm for 5 min. Subsequently, 1 mL of acetonitrile was extracted and filtered through a 0.22 μm filter membrane before being transferred into an autosampler vial for HPLC-MS/MS analysis.

1.3 Abamectin in pak choi: 5.0 g of crushed pak choi was weighed into a 50 mL centrifuge tube, combined with 2.0 g of NaCl, 5.0 mL of deionized water, and 5.0 mL of acetonitrile. The mixture was shaken for 5 min and then centrifuged at 3800 rpm for 5 min. Subsequently, 1 mL of acetonitrile was extracted into an Eppendorf tube containing 50 mg of C18 and 100 mg of $MgSO_4$. The mixture was shaken for 1 min and then centrifuged at 10000 rpm for 1 min. Afterward, the sample was filtered through a 0.22 μm filter membrane before being transferred into an autosampler vial for HPLC-MS/MS analysis.

1.4 Abamectin in cabbage: 5.0 g of crushed cabbage was weighed into a 50 mL centrifuge tube, combined with 2.0 g of NaCl, 5.0 mL of deionized water, and 5.0 mL of acetonitrile. The mixture was shaken for 5 min and then centrifuged at 3800 rpm for 5 min. Subsequently, 1 mL of acetonitrile was extracted into an Eppendorf tube containing 30 mg of C18 and 100 mg of $MgSO_4$. The mixture was shaken for 1 min and then centrifuged at 10000 rpm for 1 min. Afterward, the sample was filtered through a 0.22 μm filter membrane before being transferred into an autosampler vial for HPLC-MS/MS analysis.

1.5 Abamectin in cabbage leaf: A circular slice cut from the cabbage was placed into

a 15 mL centrifuge tube, combined with 2.0 g of NaCl, 5.0 mL of deionized water, and 5.0 mL of acetonitrile. The mixture was shaken for 10 min and then centrifuged at 3800 rpm for 5 min. Then, 1 mL of acetonitrile was subjected to HPLC-MS/MS detection after filtered through a 0.22 μm filter membrane.

Table S1 Pretreatment methods for abamectin in various samples

Matrix	Extraction	Purification
Water	Subjected to HPLC-MS/MS detection after filtered	
Soil	5.0 g soil + 5.0 g NaCl + 5.0 mL H_2O + 5.0 mL acetonitrile	-
Pak choi	5.0 g pak choi + 2.0 g NaCl + 5.0 mL H_2O + 5.0 mL acetonitrile	50 mg C18 + 100 mg $MgSO_4$
Cabbage	5.0 g cabbage + 2.0 g NaCl + 5.0 mL H_2O + 5.0 mL acetonitrile	30 mg C18 + 100 mg $MgSO_4$
Cabbage leaf	A circular slice + 2.0 g NaCl + 5.0 mL H_2O + 5.0 mL acetonitrile	-

Table S2 The operating conditions of HPLC-MS/MS for abamectin and other macrolides

Analyte	Abamectin, Emamectin benzoate	Moxidectin, Ivermectin, Eprinomectin, Doramectin, Selamectin
Mobile phase	Acetonitrile: 0.1% formic acid	Acetonitrile: 0.1% formic acid
Flow rate	0.35 mL/min	0.50 mL/min
Injection volume	10 μL	10 μL
Column	25°C	25°C
Scanning	Multiple response monitoring	Multiple response monitoring
Ionization	Electrospray ionization (ESI) (+)	Electrospray ionization (ESI) (+)
Ion source	300 ℃	300 ℃
DL temperature	250 ℃	250 ℃
Heating block	400 ℃	400 ℃
Atomizing gas	3 L/min	3 L/min
Heating gas flow	10 L/min	10 L/min
Dry gas flow rate	10 L/min	10 L/min

72 Table S3 The MRM parameters of abamectin and other macrolides

Analyte	Precursor ion (*m/z*)	Product ion (*m/z*)	Dwell Time (msec)	Q1 Pre Bias(V)	CE	Q3 Pre Bias(V)
Abamectin	895.60	449.40	100	-32	-64	-32
		751.40*	100	-32	-64	-22
Moxidectin	640.83	623.15*	100	-40	-15	-22
		529.15	100	-40	-12	-38
Ivermectin	897.50	240.00*	100	-34	-55	-25
		449.40	100	-34	-55	-10
Eprinomectin	936.60	352.00	100	-26	-60	-13
		490.00*	100	-26	-55	-15
Doramectin	921.55	353.2	100	-34	-58	-23
		449*	100	-34	-53	-30
Selamectin	770.96	627.20*	100	-20	-17	-22
		609.20	100	-20	-19	-30
Emamectin benzoate	886.60	158.10*	100	-34	-55	-25
		126.30	100	-34	-55	-10

73

74 Table S4 The recovery and RSD of the proposed methods for the analyzing abamectin
75 in soil and on leaf at three fortification levels

Analytes	0.04 mg/kg		0.4 mg/kg		4 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Abamectin in soil	108.16	3.40	100.33	3.20	90.32	2.60
Abamectin on leaf	105.36	2.79	94.58	3.17	96.53	5.92

76

77 Table S5 The recovery and RSD of the proposed methods for the analyzing abamectin
78 in pak choi and cabbage at three fortification levels

Analytes	0.05 mg/Kg	0.5 mg/Kg	5 mg/Kg

	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Abamectin in pak choi	102.44	3.50	100.27	4.40	85.68	1.70
Abamectin in cabbage	111.73	7.57	104.10	5.93	99.26	9.24

Table S6 The operating conditions of HPLC-MS/MS for 6PPD

	6PPD
Mobile phase	MeOH: Deionized water/90: 10
Flow rate	0.3 mL/min
Column temperature	25°C
Injection volume	5 μL
Scanning	Multiple response monitoring (MRM)
Ionization	Electrospray ionization (ESI) (+)
Nebulizer	35 PSI
Gas flow	10.0 L/min
Gas temperature	350 ℃

Table S7 The MRM parameters of 6PPD

Analyte	Precursor ion (*m/z*)	Product ion (*m/z*)	Cell energy (CE) (eV)	Fragmentor (V)
6PPD	269.3	184.1*	20	110
		211.0	20	110

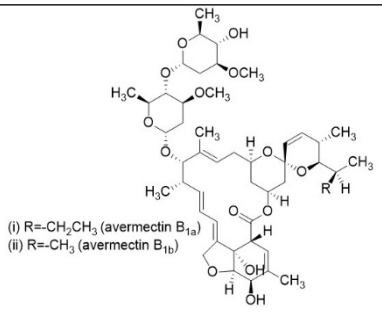
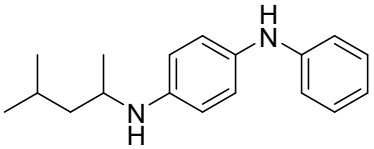
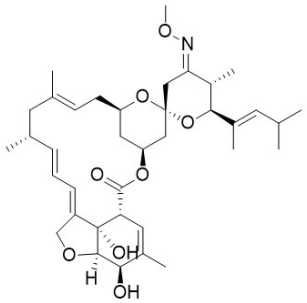
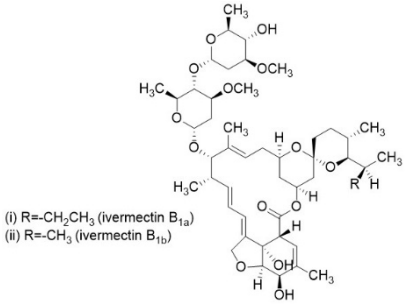
Table S8 Pretreatment methods for abamectin in various samples

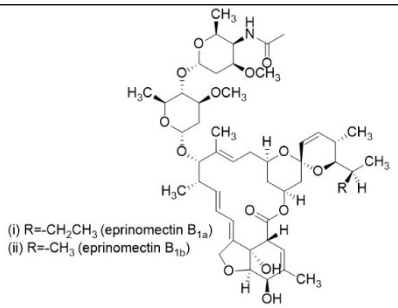
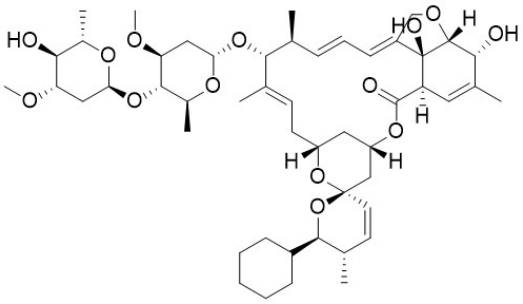
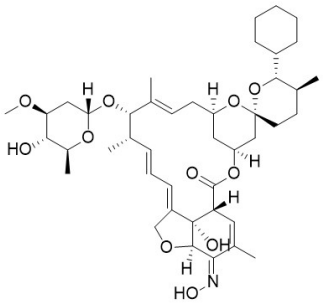
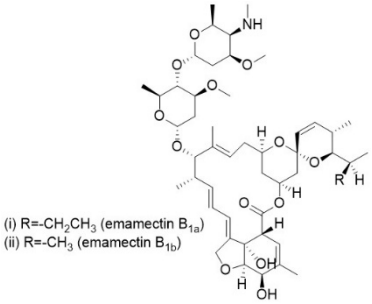
Matrix	Extraction	Purification
Water	5.0 mL water + 2.0 g NaCl + 5.0 mL acetonitrile	100 mg $MgSO_4$
Soil	5.0 g soil + 2.0 g NaCl + 5.0 mL H_2O + 5.0 mL acetonitrile	100 mg $MgSO_4$

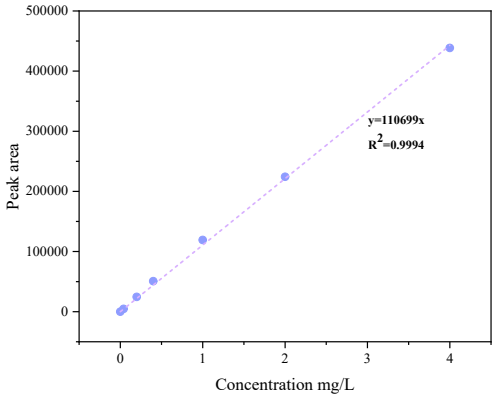
Table S9 The recovery and RSD of the proposed methods for the analyzing 6PPD in water and soil at three fortification levels

Analytes	0.05 mg/kg		0.5 mg/kg		5 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
6PPD in water	88.95	6.54	95.32	5.22	98.27	4.24
6PPD in soil	100.32	5.13	82.26	8.36	79.04	8.98

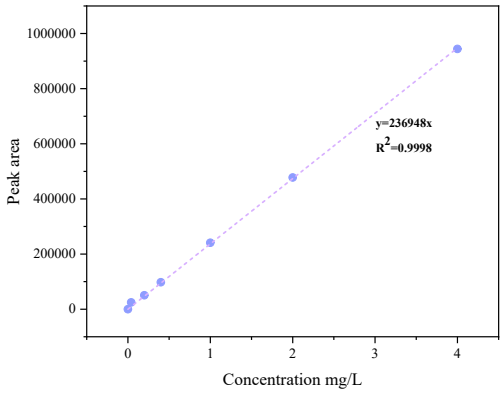
Table S10 The structure of 6PPD and macrolides

Analyte	Structure
Abamectin	
6PPD	
Moxidectin	
Ivermectin	

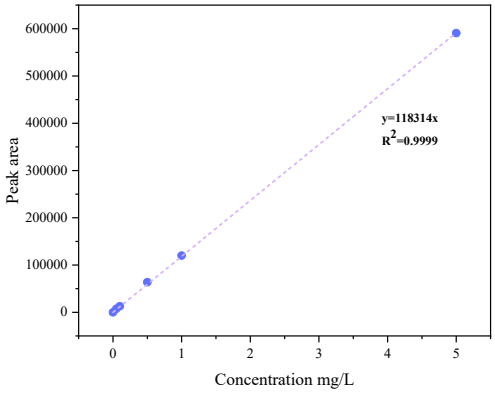
Eprinomectin	
Doramectin	
Selamectin	
Emamectin benzoate	


y=110699x
R2=0.9994
Peak area
Concentration mg/L

a


y=236948x
R2=0.9998
Peak area
Concentration mg/L

b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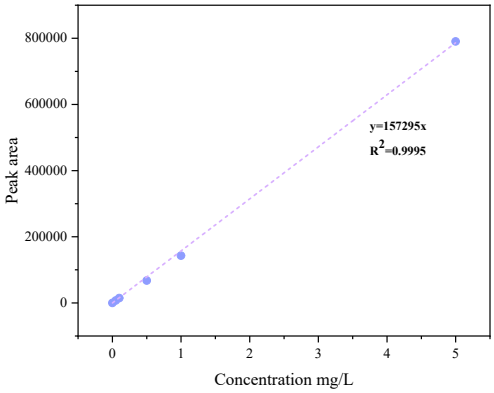
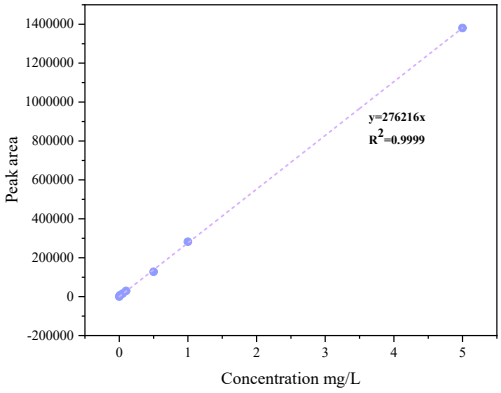
Peak area
Concentration mg/L

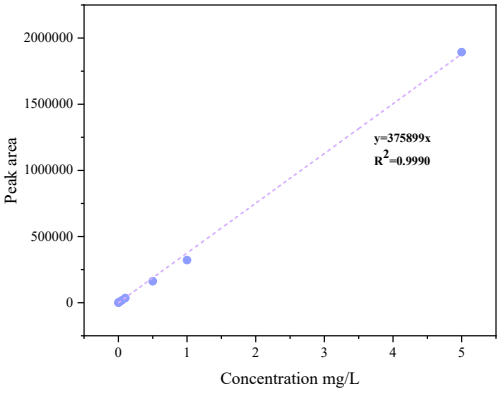
c


y=157295x
R2=0.9995
Peak area
Concentration mg/L

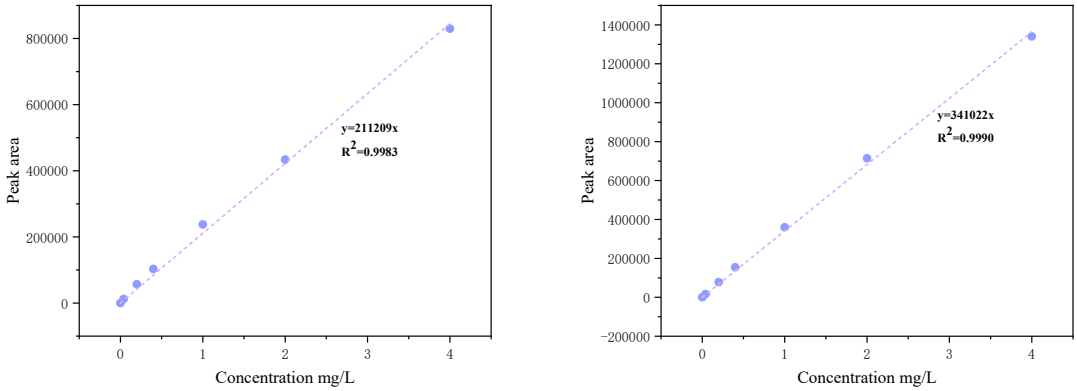
d


y=276216x
R2=0.9999
Peak area
Concentration mg/L

e


y=375899x
R2=0.9990
Peak area
Concentration mg/L

f



g h

Figure S1 The calibration curves of abamectin in soil (a) and solvent (b), in pak choi (c) and solvent (d), in cabbage (e) and solvent (f), on cabbage leaf (g) and solvent (h).

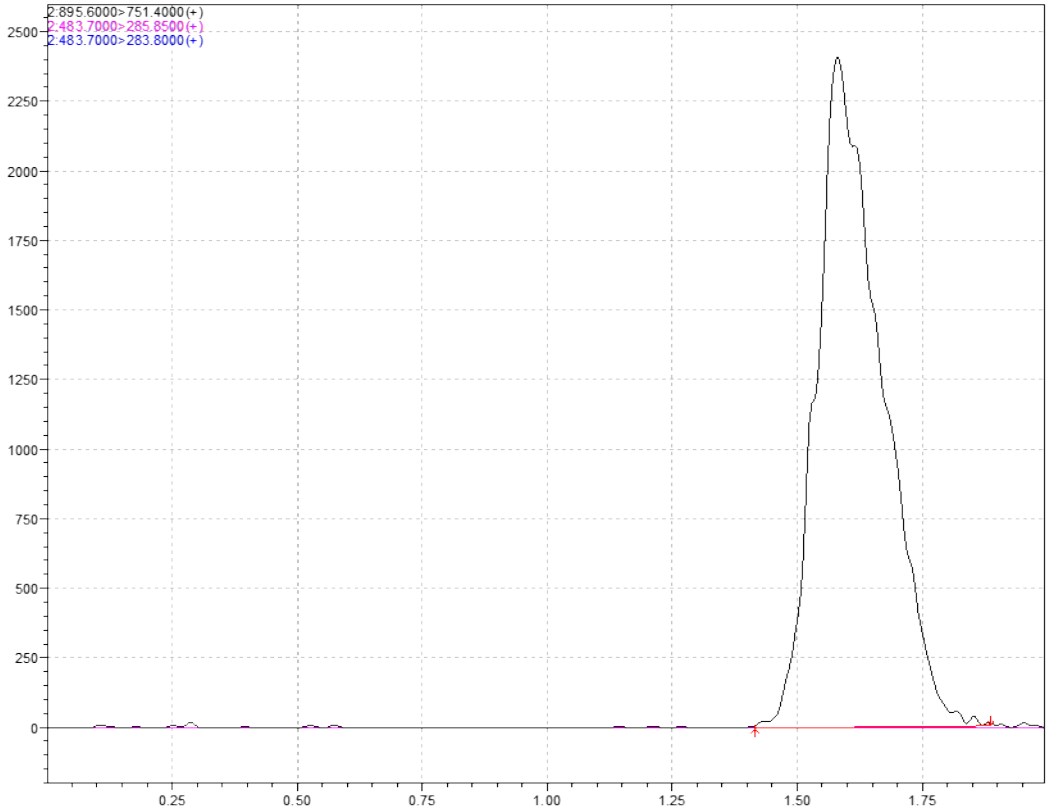
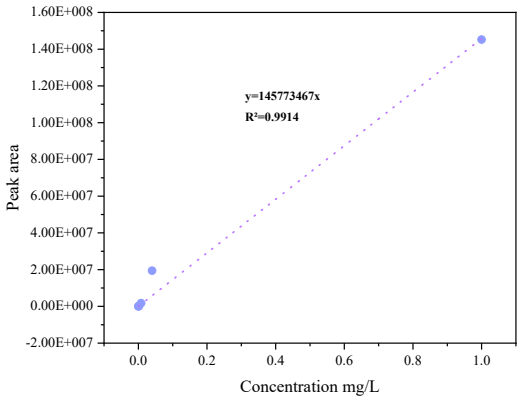
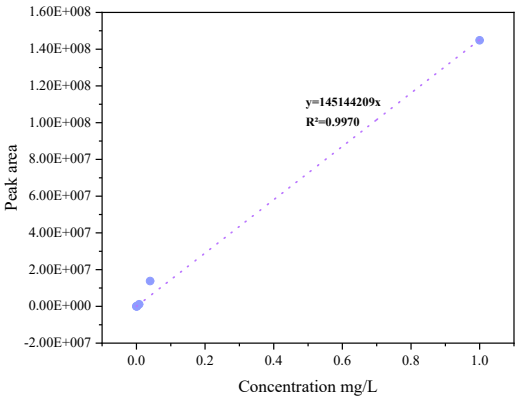


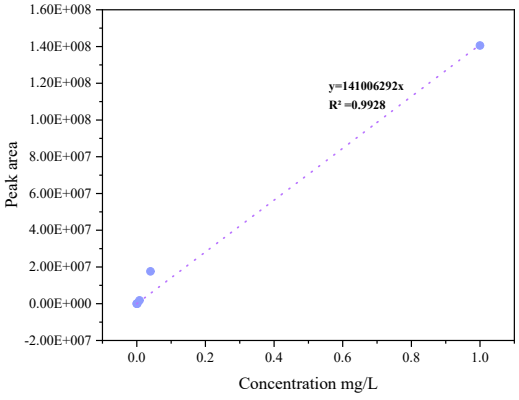
Figure S2 The chromatogram of abamectin in acetonitrile at a concentration of 0.05 mg/L



a

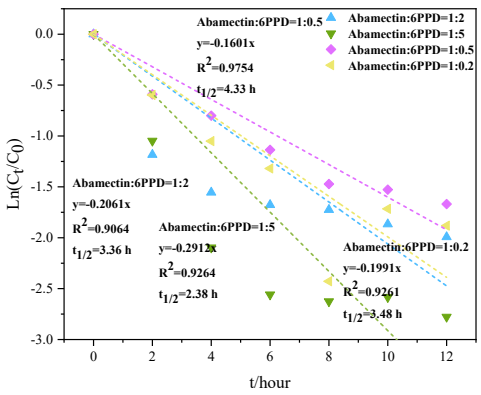


b

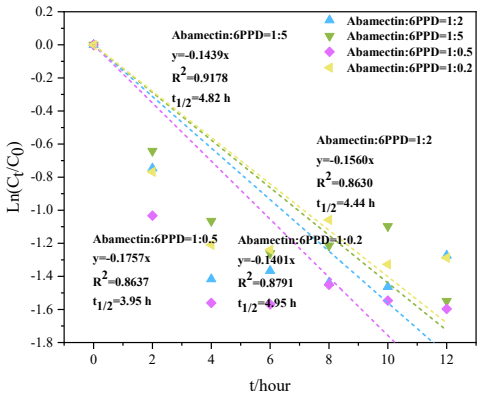


c

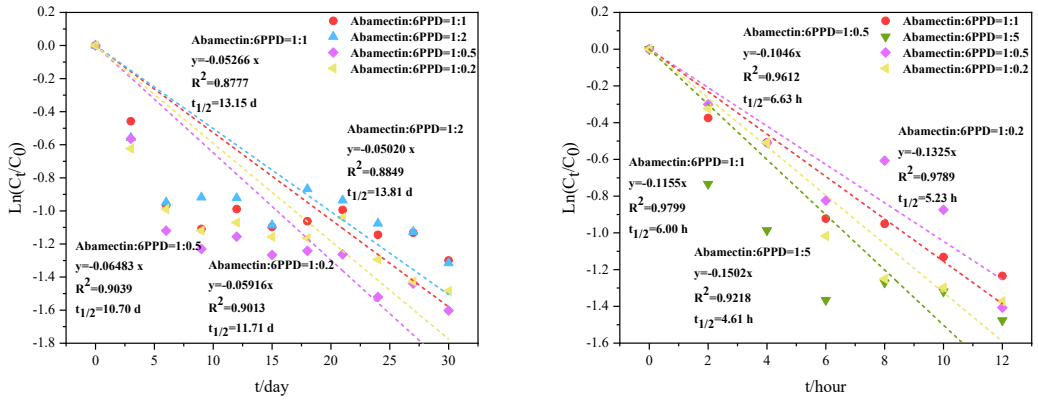
100 Figure S3 The calibration curves of 6PPD in water (a), soil (b) and solvent (c).



a

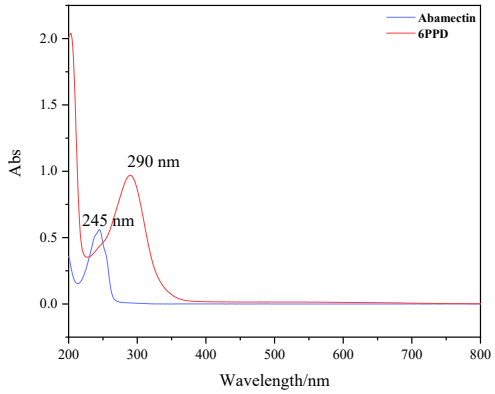


b



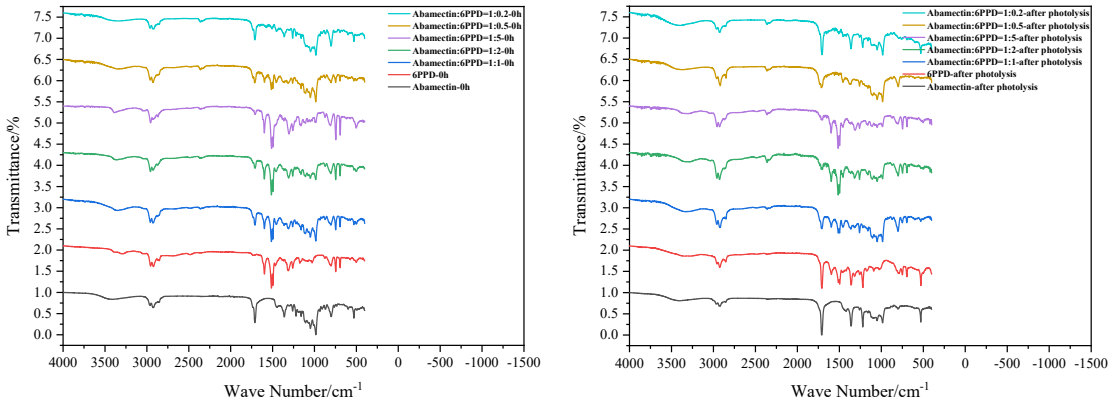
c d

101 Figure S4 The other treatment groups on prolongation of abamectin half-life in water
102 (a), soil (b), soil under darkness (c), and on cabbage leaf (d).
103



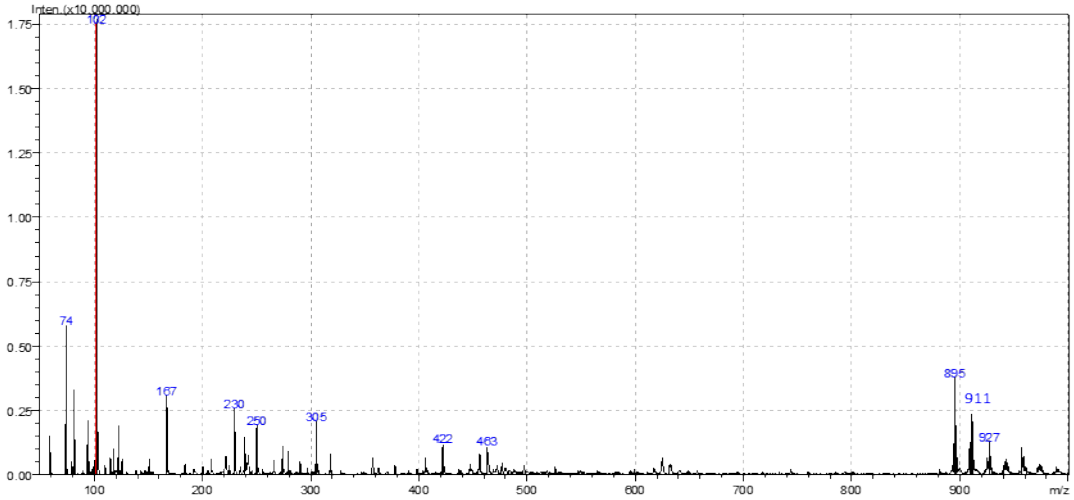
104

105 Figure S5 The absorption spectra of abamectin and 6PPD in acetonitrile.

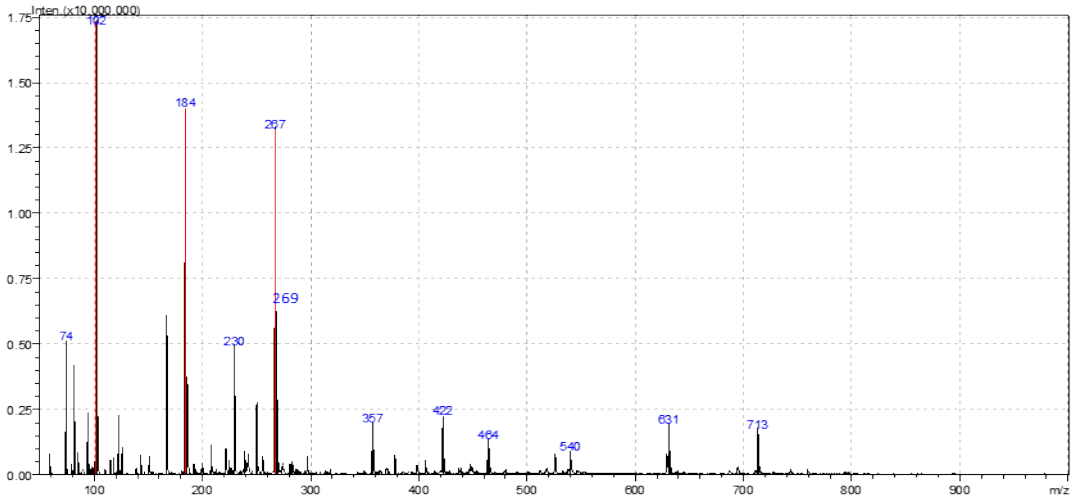


a b

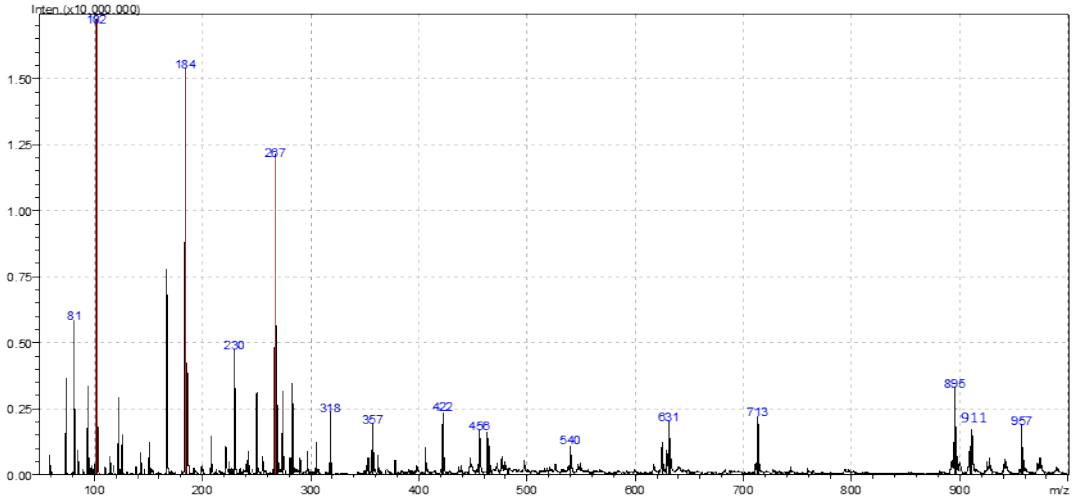
106 Figure S6 The FTIR spectrogram of abamectin, 6PPD, abamectin:6PPD=1:1,
107 abamectin:6PPD=1:2, abamectin:6PPD=1:5, abamectin:6PPD=1:0.5 and
108 abamectin:6PPD=1:0.2 before photolysis (a) and after photolysis (b).


Inten.(x10,000,000)
102
74
167
230
250
305
422
463
895
911
927
m/z

a


Inten.(x10,000,000)
102
184
267
269
74
230
357
422
464
540
631
713
m/z

b


Inten.(x10,000,000)
102
184
267
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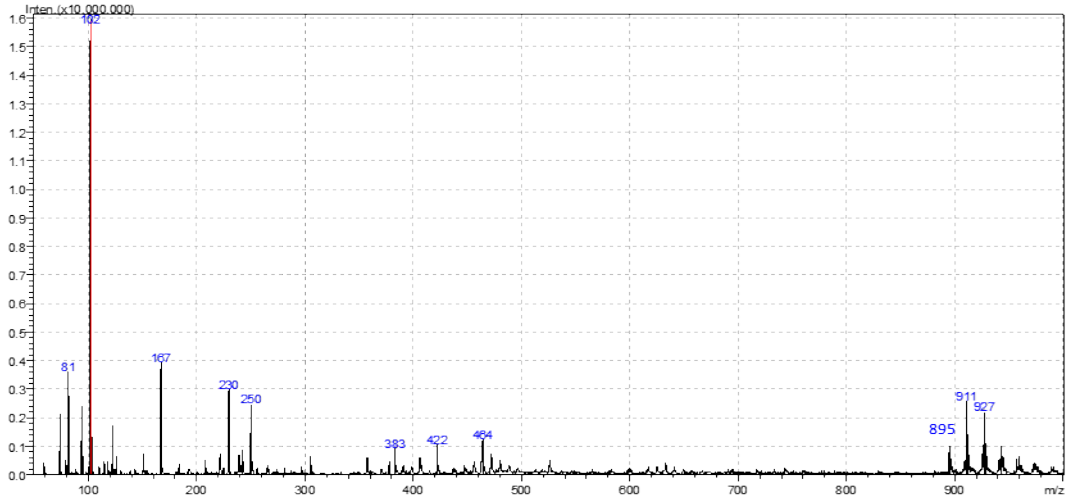
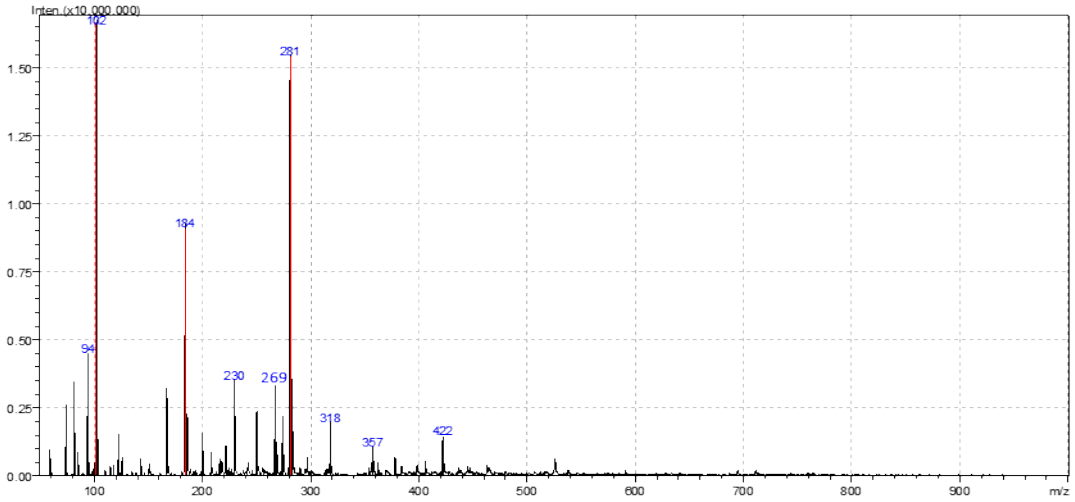
957
m/z

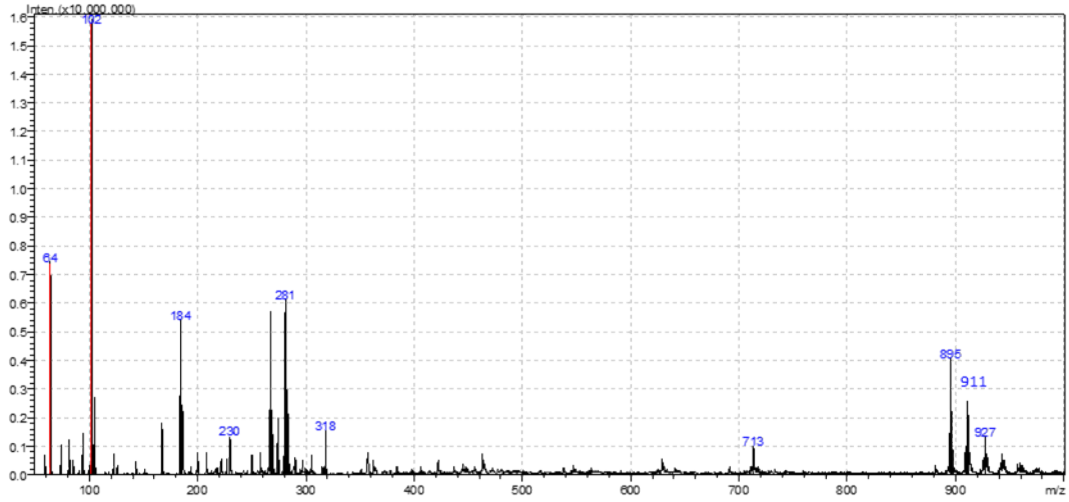
c



d

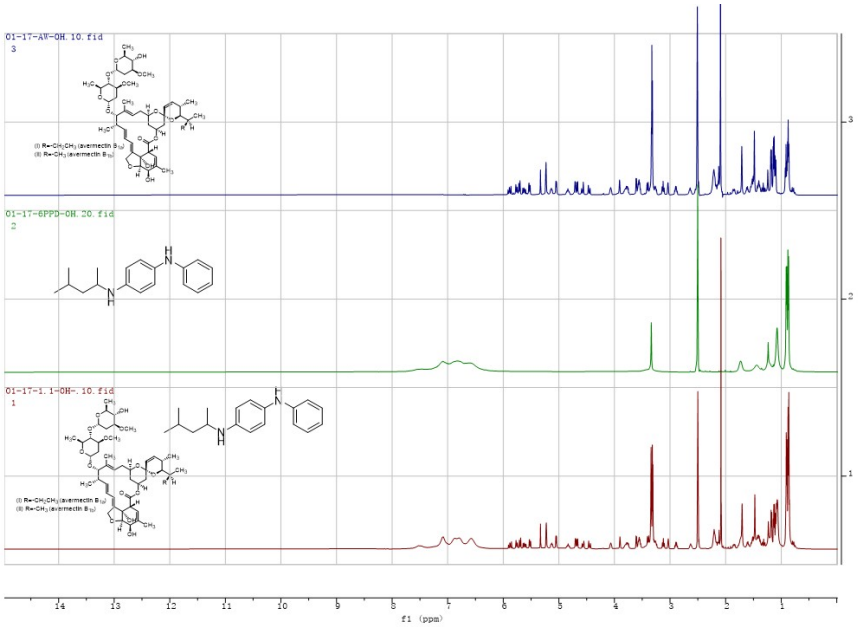


e

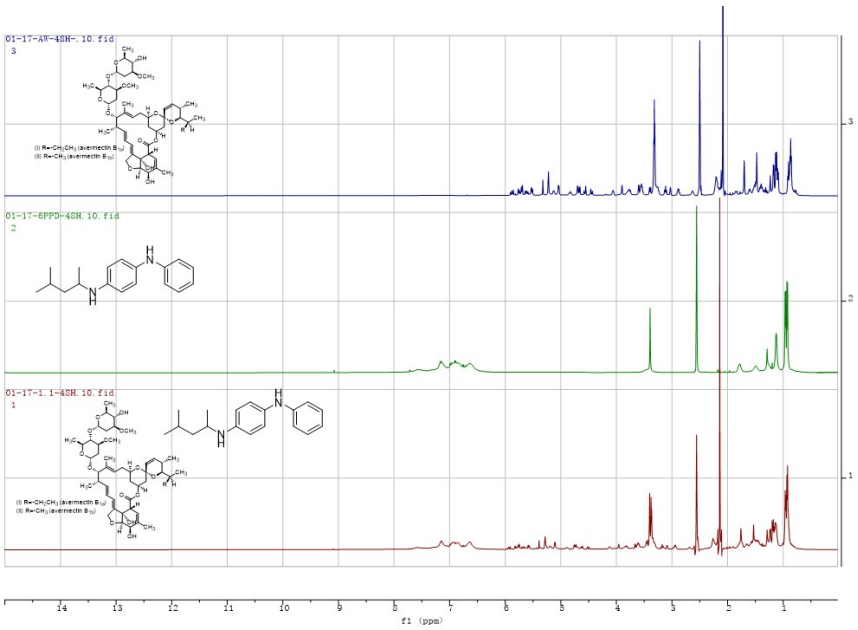


f

Figure S7 The total ion chromatograms of abamectin (a: before photolysis, d: after photolysis), 6PPD (b: before photolysis, e: after photolysis) and abamectin: 6PPD=1:1 (c: before photolysis, f: after photolysis).



a



b

Figure S8 The ^{1}H NMR spectra of abamectin, 6PPD and abamectin:6PPD=1:1 before photolysis (a) and after photolysis (b).