Supplementary Information (SI) for Green Chemistry.
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Bio-derived solvent-based automated dispersive liquid-liquid microextraction for pretreatment of diamide insecticides in environmental water samples

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Number of pages: 14

Number of tables: 9

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A Waters C_{18} column (2.1 × 100 mm, 1.7 μm) was used at 40 °C with a flow rate of 0.3 mL min^{-1} and an injection volume of 2 μL. The gradient elution conditions are detailed in Table S1. The ion source conditions included a source temperature of 550 °C and curtain gas, ion source gas 1, and ion source gas 2 delivered at 40, 55, and 55 psi, respectively. The optimized MS/MS parameters for chlorantraniliprole and flubendiamide under multiple reaction monitoring (MRM) conditions are presented in Table S2.

Table S1. The UHPLC-MS/MS gradient elution conditions.

Time (min)	Flow (mL min^{-1})	Mobile Phase A (%)	Mobile Phase B (%)
0	0.3	95	5
0.5	0.3	80	20
0.6	0.3	60	40
1.5	0.3	40	60
1.6	0.3	20	80
2.5	0.3	5	95
4.0	0.3	5	95
4.1	0.3	95	5

Mobile Phase A: 0.01% formic acid and 2 mmol L^{-1} ammonium formate mixed in water.

Mobile Phase B: Methanol.

Table S2. MS/MS optimized parameters with the multiple reaction monitoring conditions.

Diamide Insecticide	Polarity	Spray Valtage (V)	Settling Time (ms)	Pause Time (ms)	Precursor Ion (m/z)	Qualifier Ion (m/z)	Dwell Time (ms)	Declustering Potential (V)	Collision Energy (eV)
Chlorantraniliprole	Positive	5500	50	5	324	262 (Q) 242 (q)	30	63	28 37
Flubendiamide	Negative	4500	50	5	382	342 (Q) 314 (q)	30	92	30 37

Table S3. The Log P of the two diamide insecticides and four extractants.

Diamide Insecticide & Extractant	Log P
Chlorantraniliprole	2.9
Flubendiamide	4.1
Eucalyptol	3.4
Guaiacol	1.3
Methyl laurate	5.4
Methyl linoleate	7.6

Table S4. The toxicity information of γ-valerolactone.

		γ-valerolactone
1	Acute toxicity	LD_{50} = 8800mg kg^{-1} (rat)
2	Skin irritation or corrosion	Causes mild irritant effect
3	Eye irritation or corrosion	May cause irritation
4	Skin sensitization	No sensitizing effects known
5	Germ cell mutagenicity	No effects known
6	Carcinogenicity	No classification data on carcinogenic properties of this material is available from the EPA, IARC, NTP, OSHA or ACGIH
7	Developmental toxicity and reproductive toxicity	Developmental toxicity: NOAEL = 1000 mg kg^{-1} day^{-1} Reproductive toxicity: No NOAEL available. Exposure is below the TTC
8	Specific target organ toxicity -single exposure	No effects known
9	Specific target organ toxicity -repeated exposure	No effects known
10	Aspiration hazard	No effects known

Table S5. The toxicity information of eucalyptol.

		Eucalyptol
1	Acute toxicity	LD_{50} = 2480 mg kg^{-1} (rat)
2	Skin irritation or corrosion	Irritant to skin and mucous membranes
3	Eye irritation or corrosion	Irritating effect
4	Skin sensitization	No sensitizing effects known
5	Germ cell mutagenicity	No effects known
6	Carcinogenicity	No classification data on carcinogenic properties of this material is available from the EPA, IARC, NTP, OSHA or ACGIH
7	Developmental toxicity and reproductive toxicity	Developmental toxicity: NOAEL = 300 mg kg^{-1} day^{-1} Reproductive toxicity: Fertility NOAEL = 600 mg kg^{-1} day^{-1}
8	Specific target organ toxicity -single exposure	No effects known
9	Specific target organ toxicity -repeated exposure	No effects known
10	Aspiration hazard	No effects known

Table S6. Detailed indicators used to evaluate the environmental hazards of the QuEChERS.

		QuEChERS
1	Acidification	N_2 (LC-MS/MS)
2	Persistent organics	No
3	Bio-accumulation	No
4	Ecotoxicity	Acetonitrile: Fish LC_{50} = 1640 mg L^{-1} Methanol: *Pimephales promelas* LC_{50} > 10000 mg L^{-1} Acetic acid: *Oncorhynchus mykiss* LC_{50}> 1000 mg L^{-1} Ammonium hydroxide: *Daphnia magna* LC_{50} = 25.4 mg L^{-1}
5	Energy usage/ Global warming	A small amount of energy consumption (vortex for 4min, and centrifugation for 15min) No powerful greenhouse gases
6	Eutrophication	Nitrogen element in acetonitrile, PSA, and ammonium hydroxide
7	Flammability	Acetonitrile, methanol, and acetic acid
8	Human toxicity	Acetonitrile: LD_{50} = 2730 mg kg^{-1} (rat) Methanol: LD_{50} = 5628 mg kg^{-1} (rat) Acetic acid: LD_{50} = 4960 mg kg^{-1} (rat) Ammonium hydroxide: LD_{50} = 350 mg kg^{-1} (rat)
9	Human carcinogenicity	Acetonitrile, methanol, and ammonium hydroxide
10	Ozone depletion	Regents without chlorine, bromine, and fluorine
11	Resource depletion	No relevant reagents used
12	Smog formation	No organic gas emissions
13	Mass of waste	Sample: 10 mL Acetonitrile: 15 mL Acetic acid: 0.1 mL Ammonium hydroxide: 0.1 mL $MgSO_4$: 5.2 g NaCl: 1 g PSA: 0.4 g C_{18}: 0.4g Mobile phase: 5.25 mL Total: 37.45 mL
14	water consumption	Sample: 10 mL Mobile phase: ≈ 2.6 mL Total: 12.6 mL

Table S7. Detailed indicators used to evaluate the environmental hazards of the MSPE.

		MSPE
1	Acidification	No
2	Persistent organics	No
3	Bio-accumulation	No
4	Ecotoxicity	Acetonitrile: Fish LC_{50} = 1640 mg L^{-1}
5	Energy usage/ Global warming	A small amount of energy consumption (vortex for 15 min) No powerful greenhouse gases
6	Eutrophication	Nitrogen element in acetonitrile
7	Flammability	Acetonitrile
8	Human toxicity	Acetonitrile: LD_{50} = 2730 mg kg^{-1} (rat)
9	Human carcinogenicity	Acetonitrile
10	Ozone depletion	Regents without chlorine, bromine, and fluorine
11	Resource depletion	No relevant reagents used
12	Smog formation	No organic gas emissions
13	Mass of waste	Sample: 7 mL Acetonitrile: 1 mL IL-MMIPs: 0.005 g Mobile phase: 7 mL Total: 15.005 mL
14	water consumption	Sample: 7 mL Mobile phase: 1.75 mL Total: 8.75 mL

Table S8. Detailed indicators used to evaluate the environmental hazards of the dSPE.

		dSPE
1	Acidification	N_2 (LC-MS/MS)
2	Persistent organics	No
3	Bio-accumulation	No
4	Ecotoxicity	Acetonitrile: Fish LC_{50} = 1640 mg L^{-1}
5	Energy usage/ Global warming	A medium amount of energy consumption (ultrasonic, centrifuge, vacuum evaporator) No powerful greenhouse gases
6	Eutrophication	Nitrogen element in acetonitrile
7	Flammability	Acetonitrile
8	Human toxicity	Acetonitrile: LD_{50} = 2730 mg kg^{-1} (rat)
9	Human carcinogenicity	Acetonitrile
10	Ozone depletion	Regents without chlorine, bromine, and fluorine
11	Resource depletion	No relevant reagents used
12	Smog formation	Evaporation of 0.2 mL acetonitrile
13	Mass of waste	Acetonitrile: 0.2 mL Sample: 1 mL MOF: 0.002 g Mobile phase: 1.6 mL Total: 2.802 mL
14	Water consumption	Sample: 1 mL Mobile phase: 0.534 mL Total: 1.534 mL

Table S9. Detailed indicators used to evaluate the environmental hazards of the SPE.

		SPE
1	Acidification	N_2 (UHPLC-MS/MS and gas used for drying)
2	Persistent organics	No
3	Bio-accumulation	No
4	Ecotoxicity	Methanol: *Pimephales promelas* $LC_{50} > 10000$ mg L^{-1}
5	Energy usage/ Global warming	A high amount of energy consumption (dried under vacuum for 20 min, 40 °C water bath with a gentle stream of N_2) No powerful greenhouse gases
6	Eutrophication	Nitrogen element in N_2 and the Oasis HLB
7	Flammability	Methanol
8	Human toxicity	Methanol: $LD_{50} = 5628$ mg kg^{-1} (rat) Oasis HLB: Divinylbenzene: $LD_{50} = 4040$ mg kg^{-1} (rat)
9	Human carcinogenicity	Divinylbenzene and methanol
10	Ozone depletion	Regents without chlorine, bromine, and fluorine
11	Resource depletion	No relevant reagents used
12	Smog formation	Evaporation of 4 mL methanol
13	Mass of waste	Sample: 60 mL Methanol: 9.3 mL Ultrapure water: 68.3 mL Oasis HLB: 0.06 g Mobile phase: 10 mL Total: 147.66 mL
14	Water consumption	Sample: 60 mL Ultrapure water: 68.3 mL Mobile phase: 4.42 mL Total: 132.72 mL

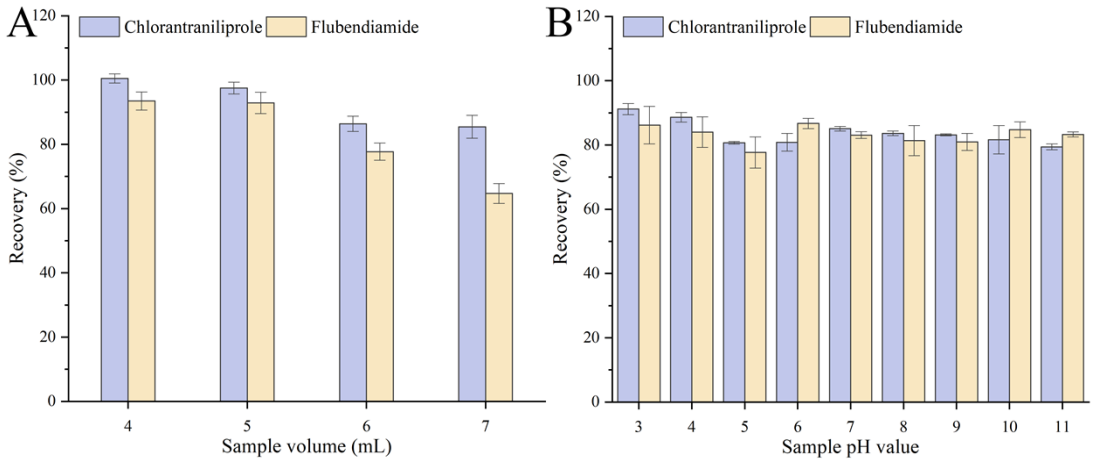

Fig. S1. Optimization of BDS-ADLLME Parameters. The figure presents the optimization of two key BDS-ADLLME parameters: (A) sample volume and (B) sample pH value. All other experimental conditions were held constant as follows: eucalyptol was used as the extractant; the extractant and dispersant volume ratio was 1:6; the total volume of extractant and dispersant was 1000 μL; 5 mixing cycles were employed; mixing speed was set at 430 μL s^{-1}; sample volume was varied (A) or set at 5 mL (B); and no salt or pH buffer was added.

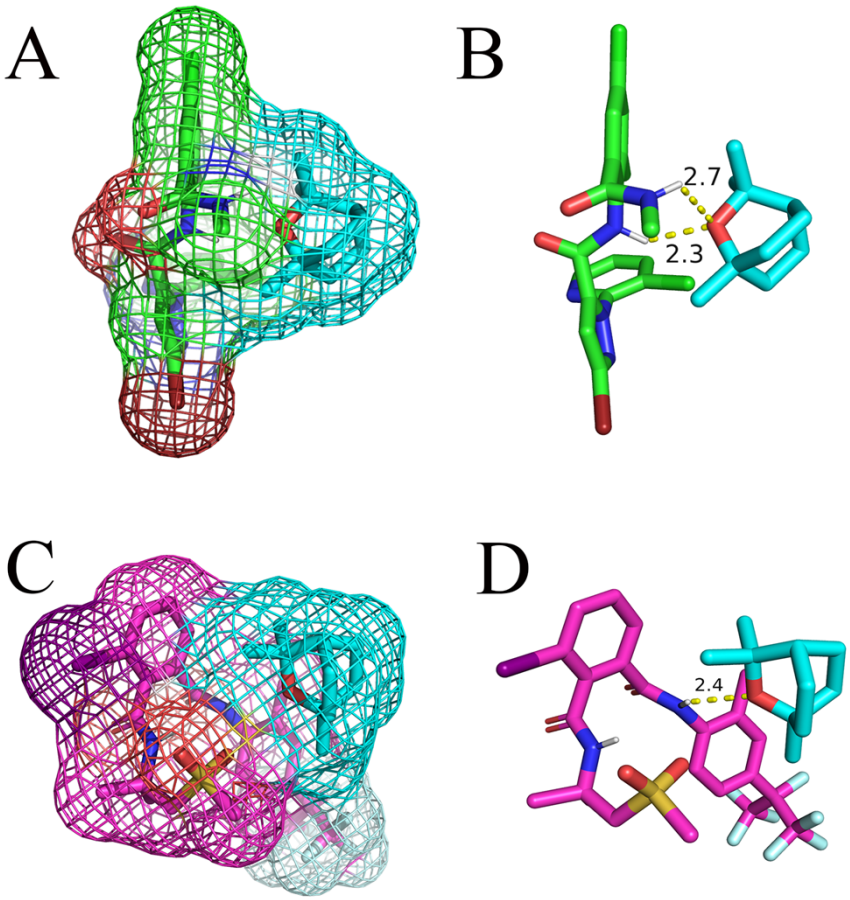

Fig. S2. Molecular docking results of eucalyptol with chlorantraniliprole and flubendiamide. (A) electron density distribution, and (B) binding mode of eucalyptol with chlorantraniliprole, (C) electron density distribution, and (D) binding mode of eucalyptol with flubendiamide.

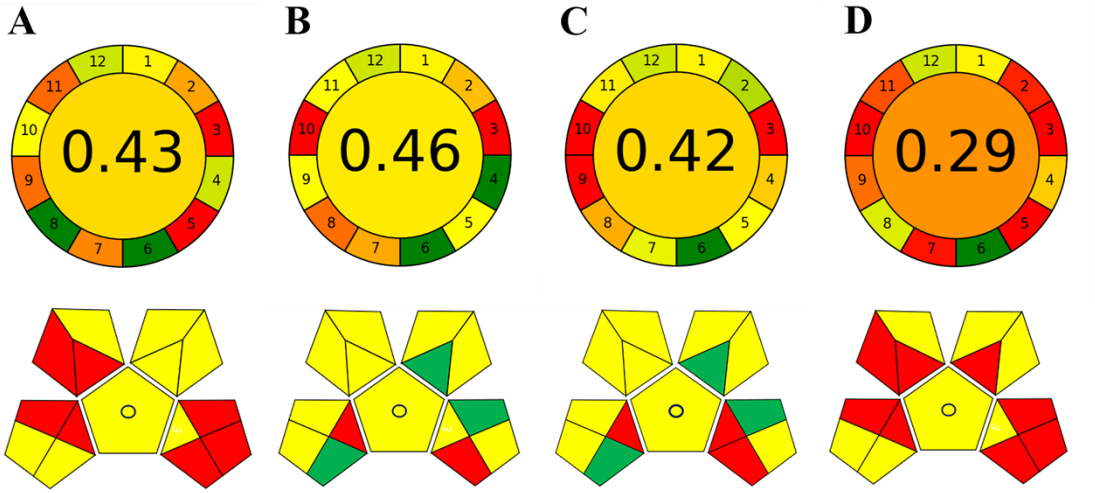

Fig. S3. Green assessment of the method mentioned in method comparison by using AGREE and GAPI. (A) the QuEChERS method. (B) the MSPE method. (C) the dSPE method. (D) the SPE method.