



# A simple analytical method for simultaneous determination of currently used pesticide (CUP) residue in river water using LC-MS/MS <sup>☆</sup>



Ananya Bhuiya<sup>a,b</sup>, Sabina Yasmin<sup>a</sup>, M. Golam Mustafa<sup>b</sup>, Tajnin Jahan<sup>a</sup>,  
Md. Atikur Rahman<sup>a</sup>, Sarker Kamruzzaman<sup>a</sup>, Mohammad Moniruzzaman<sup>c</sup>,  
Md Humayun Kabir<sup>a,c,\*</sup>

<sup>a</sup> Institute of National Analytical Research and Service (INARS), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dr. Qudrat-i-Khuda Road, Dhanmondi, Dhaka, 1205, Bangladesh

<sup>b</sup> Department of Oceanography, Noakhali Science and Technology University, Noakhali, 3814, Bangladesh

<sup>c</sup> Central Analytical and Research Facilities (CARF), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dr. Qudrat-i-Khuda Road, Dhanmondi, Dhaka, 1205, Bangladesh

## ARTICLE INFO

### Method name:

Modified Salting-out assisted liquid-liquid microextraction (SALLME)

### Keywords:

Pesticide residue analysis  
Salting-out assisted liquid-liquid microextraction  
Environmental sample

## ABSTRACT

Pesticide residue monitoring in river water is obligatory for their negative ecotoxicological consequences. The current-use pesticides (CUPs) include a diverse range of synthetic pesticides registered by regulatory bodies worldwide as an alternative to the banned organochlorine pesticides (OCPs). Nowadays, CUPs are preferred for agricultural and non-agricultural purposes due to their low persistence and moderate toxicity. This work aimed to optimize a rapid, sensitive salting-out assisted liquid-liquid microextraction (SALLME) method for the simultaneous determination of seven multi-class CUPs. An optimized dose of C18, GCB, and PSA was employed to facilitate an effective and commercially viable clean-up for routine analysis of pesticide residues, followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The optimized SALLME method showed good repeatability and reproducibility, along with low LOD and LOQ values, according to the SANTE/11,312/2021 guidelines. The method validation parameters confirmed the applicability of the optimized SALLME method for trace-level residue analysis in river water. The core advantages of the validated method are:

- The method follows simple steps and is cost-effective for the routine analysis of multi-class pesticide residues in river water.
- The analytical method is simple and highly sensitive; this could be extended to detect and quantify other pesticides depending on their physicochemical properties.

<sup>☆</sup> **Related research article:** Bhuiya, A., Yasmin, S., Mustafa, M.G., Shaikh, M. A. A., Saima, J., Moniruzzaman, M., Kabir, M. H. (2024). Spatiotemporal distribution, ecological risk assessment, and human health implications of currently used pesticide (CUP) residues in the surface water of Feni River, Bangladesh. *Science of The Total Environment*, 173857, ISSN 0048–9697, <https://doi.org/10.1016/j.scitotenv.2024.173857>

\* Corresponding author.

E-mail address: [humayunkabir@bcsir.gov.bd](mailto:humayunkabir@bcsir.gov.bd) (M.H. Kabir).

<https://doi.org/10.1016/j.mex.2024.103065>

Received 19 June 2024; Accepted 17 November 2024

Available online 19 November 2024

2215-0161/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC license

(<http://creativecommons.org/licenses/by-nc/4.0/>)

## Specifications table

Subject area:	Environmental Science
More specific subject area:	Environmental Analytical Chemistry, Sample preparation
Name of your method:	Modified Salting-out assisted liquid-liquid microextraction (SALLME)
Name and reference of original method:	Salting-out assisted liquid-liquid microextraction (SALLME)
Resource availability:	Liquid Chromatography-tandem mass spectrometry (LC-MS/MS)

## Background

Pesticide residues in surface water are a global concern due to their adverse ecotoxicological consequences on the ecosystem. Pesticide drifts into the riverine environment can cause chemical contamination, alter water quality, and pose a threat to non-target organisms via bioaccumulation and biomagnification. Therefore, the European Union sets the maximum acceptable concentration (MAC) for each pesticide (0.1 µg/L) and for the sum (0.5 µg/L) of all individual pesticides detected in water for human consumption [1]. Bangladesh particularly have national legislations to regulate pesticide use, such as, “Pesticide Ordinance, 1971”; “Pesticide Rules (1985)”; and “Pesticide (Amendment) Act 2009” [2]. Unfortunately, because of lack of formers consciousness, the pesticides are used in Bangladesh without following the ordinance and rules. Hence, pesticide residue monitoring in river water is crucial to understand the spatiotemporal distribution and evaluate potential risks to regulate pesticide use.

Pesticide residues occur in trace quantities in environmental waters as a variety of pesticides are extensively used for agricultural yield improve, vector diseases control, and aquacultural weed control purposes in Bangladesh. Hence, the optimization of sample preparation (extraction, clean-up) is integral to enhance the sensitivity of an analytical method with better recovery of target analytes in complex environmental matrices. Conventional liquid-liquid extraction (LLE) is the most commonly used method to facilitate the efficient separation of aqueous solutions and non-polar pesticides in environmental water samples. However, LLE is time-consuming and requires a huge amount of organic solvent [3,4]. Alternatively, different modifications of salting-out assisted liquid-liquid microextraction (SALLME) techniques were introduced for the efficient extraction of multi-class pesticide residues simultaneously in various environmental waters [5–7]. SALLME is a comparatively preferable method for residue analysis in river water as the QuEChERS sample preparation technique is more efficient to extract residues from complex matrices. In SALLME, the salting-out effect influences the solubility of different molecules and facilitates the partitioning of the target compounds into the organic phase by separating the aqueous phase. Here, Acetonitrile (ACN) is used as the organic solvent due to its low toxicity, high extraction efficiency for polar to moderately polar compounds, and compatibility for direct injection into LC-MS/MS without reconstitution. For instrumentation, LC-MS/MS is more sensitive toward a wide range of non-volatile, polar, semi-polar, and thermolabile pesticides, except the OCPs [4,8,9]. Though SPE cartridges perform better purification of non-target compounds, these are expensive for routine analysis in developing countries, and cartridge clogging can be a problem for analyzing environmental water with suspended solids [10]. Alternatively, a combination of dSPE (dispersive solid phase extraction) adsorbents reduces the effects of the co-extracted matrix components, enhances the sensitivity of the analytical method, and reduces the cost for routine analysis [2,11,12].

The objective of this study is to optimize and validate a modified SALLME-dSPE method followed by LC-MS/MS instrumentation for the simultaneous determination of azoxystrobin (Az), buprofezin (BUP), carbofuran (CAR), dimethoate (DMT), pymetrozine (PYM), difenoconazole (DFN), and chlorantraniliprole (CLP) in river water. The chemical structures of the studies CUPs are represented in Fig. 1.

## Method details

## Chemicals and reagents

All the following used reagents were of recognized chemical purity and quality control was assured to prevent any possible contamination:

1. **Solvents:** LC-MS grade acetonitrile (ACN) (CAS: 75–05–8)
2. **Water:** Ultrapure deionized (DI) water (18 MΩ cm)
3. **Inorganic salts:** Analytical-grade sodium chloride (NaCl) (≥99.9 %, CAS: 7647–14–5), anhydrous magnesium sulphate (MgSO<sub>4</sub>) (≥99.0 %, CAS: 7487–88–9)
4. **dSPE adsorbents:** Graphitized carbon black (GCB) (CAS: 7440–44–0), primary secondary amine (PSA) (CAS: 1,318,259–33–4), and octadecylsilane (C18) (CAS: 71,889–02–6), were purchased from CNW Technologies, ANPEL Laboratory Technologies (Shanghai), China.

## Standards

The below mentioned standards were used:

1. **Reference standards:** Certified reference materials (purity ≥ 98.0 %) of Azoxystrobin (CAS: 131860–33–8), Buprofezin (CAS: 69327–76–0), Dimethoate (CAS: 60–51–5), Carbofuran (CAS: 1563–66–2), Pymetrozine (CAS: 123312–89–0), Chlorantraniliprole (CAS: 500008–45–7), Difenoconazole (CAS: 119446–68–3) were obtained from Sigma-Aldrich (St Louis, MO, USA).

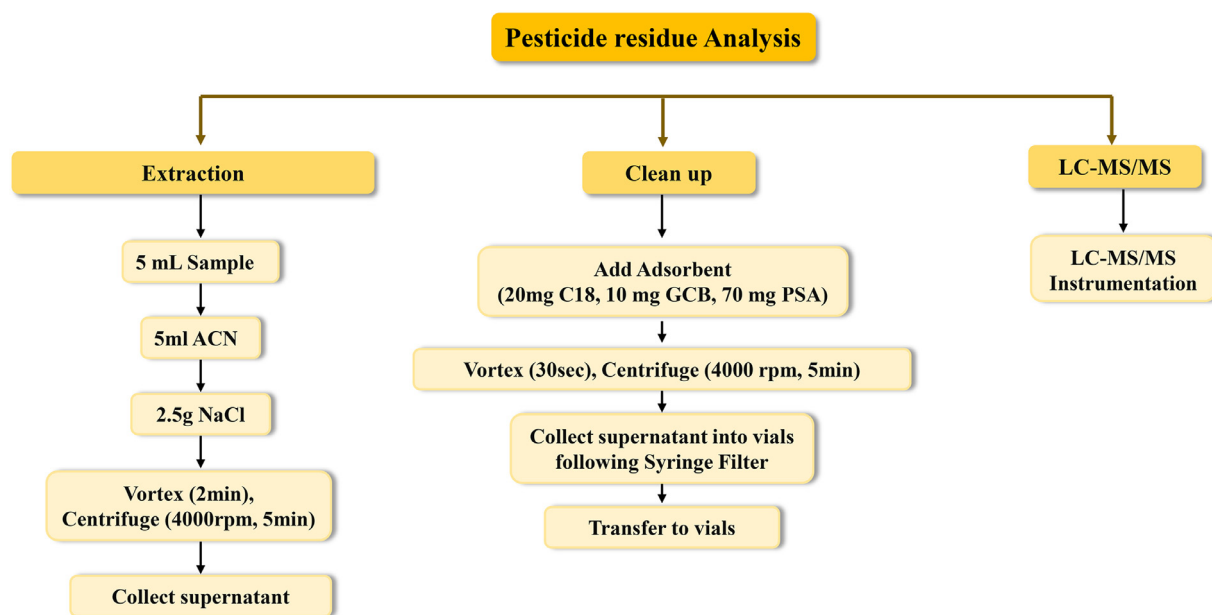


Fig. 1. Schematic diagram of the optimized SALLME-dSPE method for analyzing the selected pesticide residues in river water.

- Individual stock solution:** Standard stock solutions (100 mg/L) of AZ, BUP, CAR, DMT, PYM, DFN, and CLP were prepared individually in 100 mL volumetric flasks by adding 10.0 g of each pesticide standard and filling it with LC-MS grade ACN up to the lower meniscus.
- Intermediate standard solution:** Next, an intermediate working solution of 10 mg/L was prepared by diluting the standard stock solution with same solvent. In a 50 mL volumetric flask, a working standard solution (2 mg/L) was prepared by mixing an appropriate volume from the intermediate working solutions of the seven pesticides and filling up to the mark with LC-MS grade ACN.
- Calibration standards:** Finally, solvent-matched calibration curves were constructed using a series of dilution of 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, 0.001, 0.0005, 0.0002, and 0.0001 mg/L from the 2 mg/L mixed working standard solution. All standard solutions were stored in a freezer at  $-20^{\circ}\text{C}$  for further analysis.
- Spiking solution:** Varying volumes of mixed working standard solution were diluted in blank water to prepare spiking solutions with concentrations ranging from 20 to 400  $\mu\text{g/L}$  for the selected CUPs.

#### Apparatus

- Filters:** 0.22  $\mu\text{m}$ , from CNW Technologies, ANPEL Laboratory Technologies (Shanghai), China
- Analytical Column:** ZORBAX RRHD Eclipse plus C18 column (2.1  $\times$  100 mm, 1.8  $\mu\text{m}$  particle size)
- Liquid Chromatograph (LC):** The chromatography system used an Agilent 1290 LC system (1290 Infinity II)

#### Sample preparation

The targeted pesticides were extracted using an optimized salting-out assisted liquid-liquid microextraction (SALLME) method (Fig. 1). In brief, 5 mL of representative water sample were weighed and taken into a 15 mL falcon centrifuge tube. After adding 5 mL acetonitrile into the tube, the tube was closed tightly and manually shaken for 1 min. Thereafter, 2.5 g NaCl were added to the tube and vortexed (Model: AVM-2000-C, Brand: Digisystem, Origin: Taiwan) for 2 min followed by centrifugation (Model: DSC-200A-2, Brand: Digisystem, Origin: Taiwan) at 4000 rpm for 5 min. 1.5 mL supernatant were collected into a 2 mL centrifuge tube. A combination of 70 mg PSA, 10 mg GCB, and 20 mg C18 were previously weighed precisely and kept into the 2 mL centrifuge tube. The tubes are vortexed and centrifuged (Model: D3024, Brand: Scilogex, Origin: Germany) at 4000 rpm for 5 min for clean-up. Finally, the supernatants were syringe filtered (0.22  $\mu\text{m}$ , CNW Technologies, ANPEL Laboratory Technologies (Shanghai), China) and collected into 2 mL vials for LC-MS/MS analysis.

#### Method optimization

A 5 mL solvent volume was preferred to ensure the dilution of analytes and applied in subsequent experiments. On the other hand, NaCl, as a suitable salting-out agent, increased the ionic strengths of the sample solution and facilitated the partitioning of target

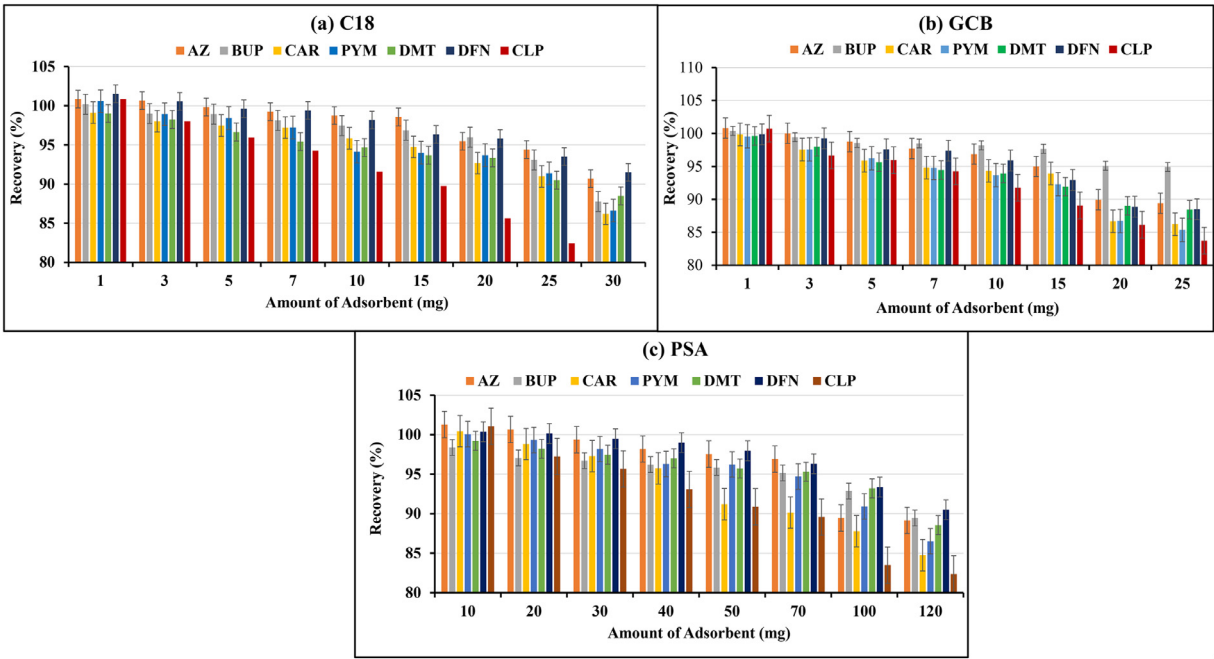


Fig. 2. Recovery optimization of adsorbent doses for dSPE clean-up: (a) C18, (b) GCB, and (c) PSA.

pesticides from the aqueous to the organic solvent phase [13]. The modified SALLME was followed by dSPE clean-up to enhance the recovery of the target pesticide and minimize the matrix effect. However, PSA can adsorb many polar matrix components including sugars, organic acids, while, C18 can remove non-polar compounds and fat. Additionally, GCB can facilitate the removal of pigments, sterols, etc. Hence, a cost-effective and efficient D-SPE clean-up is utilized in the present study through an optimized dose of adsorbents (PSA, GCB, C18) displayed in Fig. 2.

LC-MS/MS instrumentation

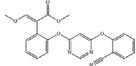


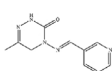
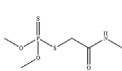
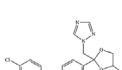
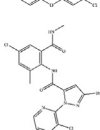
LC-MS/MS analysis was conducted using a triple quadrupole (QQQ) mass spectrometer (6420LC/TQ) equipped with an Agilent 1290 LC system (1290 Infinity II). The instrumental conditions for LC-MS/MS are briefed in Table 1.

The total run time for each sample was 12.1 min, and the injection volume was 5  $\mu$ L. The detection parameters i.e., the qualitative ion, quantitative ion, collision energies (CE), and fragmentation voltage (FP) for the target compounds were optimized to attain the maximum sensitivity for identification and quantification. Two transitions were monitored for each target analyte where the more abundant ion used for quantification and a second ion as the qualifier for confirmation as shown in Table 2. For mass spectrometric detection, the QQQ mass spectrometer data were acquired in the positive mode of multiple reaction monitoring (MRM) and processed through the Agilent Mass Hunter Workstation Software for qualitative analysis.

Table 1  
Instrumental conditions for LC-MS/MS.

Parameters	Condition
LC-MS/MS column	ZORBAX RRHD Eclipse plus C18 column (2.1 $\times$ 100 mm, 1.8 $\mu$ m particle size) at an oven temperature of 30 $^{\circ}$ C
Gradient	Time (min) A (%) 0.1 % Formic Acid B (%) Acetonitrile
	0.00 50 50
	3.01 50 50
	7.01 10 90
	12.00 50 50
Gas flow rate	7 L/min
Injection volume	5 $\mu$ L
Ionization mode	Electrospray Ionization (ESI), positive mode
Capillary Voltage	3,500 V
Nebulizer pressure	15 psi
gas temperature	300 C

**Table 2**  
Fragmentation Pattern of the pesticides in MRM mode in LC-MS/MS.

Pesticide	Molecular Formula	Molecular Weight	Molecular structure	LogKow	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy, eV	Dwell Energy, eV	Fragmentation Energy, eV
AZ	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	403.4		2.50	404.1	329.1 <sup>b</sup> 372.0 <sup>a</sup>	12 36	200	110
BUP	C <sub>16</sub> H <sub>23</sub> N <sub>3</sub> OS	305.44		4.5	306.2	116 <sup>b</sup> 201.0 <sup>a</sup>	12 12	200	110
CAR	C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>	221.26		1.8	222.1	123.0 165.1 <sup>a</sup>	13 29	200	135
PYM	C <sub>18</sub> H <sub>11</sub> N <sub>5</sub> O	217.23		-0.19	218.1	79.0 <sup>b</sup> 105.0 <sup>a</sup>	8 20	200	110
DMT	C <sub>5</sub> H <sub>12</sub> NO <sub>3</sub> PS <sub>2</sub>	229.26		0.75	230.1	125.0 <sup>a</sup> 199.0 <sup>b</sup>	20 20	200	135
DFN	C <sub>19</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub>	406.26		4.36	406.0	337.0 <sup>b</sup> 251.0 <sup>a</sup>	30 30	200	135
CLP	C <sub>18</sub> H <sub>14</sub> BrCl <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	483.15		2.86	484.2	453.1 <sup>b</sup> 286.1 <sup>a</sup>	11 11	200	135

N.B.: AZ = Azoxystrobin, BUP = Buprofezin, CAR = Carbofuran, PYM = Pymetrozine, DMT = Dimethoate, DFN = Difenconazole, CLP = Chlorantraniliprole.

<sup>a</sup> Quantifier.

<sup>b</sup> Qualifier.

### Method validation

The validation of the optimized SALLME method was performed based on specificity, limit of detection, limit of quantification, and recoveries following European Commission SANTE/11312/2021 guidelines [14,15].

### Linearity

Linearity range for individual analyte was selected considering the determination coefficient ( $r^2$ ) value obtained from the matrix-matched calibration curve plotted for each pesticide. Further, the linearity of the optimized SALLME method was studied by constructing the external standard calibration curve of eleven points in the concentration range of 0.1–200 µg/L. The MS/MS detectors exhibited excellent linearity with a determination coefficient of  $r^2 \geq 0.9994$  within the established linear range of each target pesticide as shown in Table 3.

### Specificity

In addition, specificity was assessed, evaluating the absence of any unwanted peak from other compounds (i.e., impurities, degradants, matrix, etc.) in the blank sample at the retention time of target analytes [9,16].

### LOD and LOQ

Here, the optimized method's LOD and LOQ were estimated as the minimum concentration of analyte at which the analyte yielded a signal-to-noise ratio (S/N) of three and nine, respectively [17,18]. The LOD and LOQ values of the present method were 0.0333 µg/L to 0.333 µg/L and 0.1 µg/L to 1 µg/L, respectively. However, the obtained LOQ values for all targeted pesticides were satisfactory when compared with the MAC in drinkable water.

### Trueness and precision

Moreover, the trueness and precision of this method were assessed based on the recovery percentage (%) and relative standard deviation (RSD) (%). Subsequently, recovery (%) for the developed analytical technique was calculated at four spiking (0.4, 0.2, 0.04,

**Table 3**

Method validation data of the studied CUPs in water samples using the optimized SALLME-dSPE method.

Pesticide	Linear range (µg/L) and linear equation (Linearity, R <sup>2</sup> )*	Recovery at different spike levels		LOD (µg/L)	LOQ (µg/L)	ME (%)
		Spiked levels (n = 4) (µg/L)	Recoveries [Mean ± RSD]%			
AZ	0.2 – 200 Solvent matched: y = 189362x – 2974.9 (R <sup>2</sup> = 0.9873) Matrix matched: y = 151928x + 179.34 (R <sup>2</sup> = 0.9998)	400	74.1 ± 2.1	0.0667	0.2	–19.77
		200	71.1 ± 0.5			
		40	78.1 ± 4.9			
		20	72.3 ± 7.4			
CAR	0.1 – 200 Solvent matched: y = 107760x – 981.72 (R <sup>2</sup> = 0.9954) Matrix matched: y = 99103x + 148.96 (R <sup>2</sup> = 0.9999)	400	91.1 ± 1.2	0.0333	0.1	–8.03
		200	92.4 ± 6.1			
		40	107.0 ± 4.7			
		20	100.3 ± 6.5			
BUP	0.5 – 200 Solvent matched: y = 522383x + 386.05 (R <sup>2</sup> = 0.9997) Matrix matched: y = 570100x + 3041.7 (R <sup>2</sup> = 0.9994)	400	94.8 ± 2.9	0.1667	0.5	9.13
		200	90.1 ± 5.0			
		40	95.2 ± 6.3			
		20	93.6 ± 2.0			
DMT	1 – 200 Solvent matched: y = 3521.6x + 53.773 (R <sup>2</sup> = 0.9947) Matrix matched: y = 3841.8x – 5.8761 (R <sup>2</sup> = 0.9998)	400	76.8 ± 3.3	0.333	1	9.09
		200	89.5 ± 8.6			
		40	106.7 ± 5.3			
		20	105.9 ± 6.6			
PYM	1 – 200 Solvent matched: y = 74630x + 405.02 (R <sup>2</sup> = 0.9995) Matrix matched: y = 1668.6x + 25.635 (R <sup>2</sup> = 0.9995)	400	81.7 ± 13.8	0.333	1	–97.76
		200	85.3 ± 3.5			
		40	97.8 ± 10.3			
		20	97.4 ± 13.1			
DFN	0.1 – 200 Solvent matched: y = 238660x + 847.46 (R <sup>2</sup> = 0.997) Matrix matched: y = 206785x + 387.43 (R <sup>2</sup> = 0.9996)	400	71.8 ± 11.2	0.0333	0.1	–13.35
		200	86.7 ± 8.3			
		40	102.3 ± 5.1			
		20	91.6 ± 13.2			
CLP	1 – 200 Solvent matched: y = 2085.1x – 41.636 (R <sup>2</sup> = 0.9829) Matrix matched: y = 1748.6x + 22.202 (R <sup>2</sup> = 0.9995)	400	71.5 ± 8.8	0.333	1	16.14
		200	64.8 ± 2.7			
		40	79.7 ± 11.3			
		20	72.1 ± 4.5			

and 0.02 mg/L) levels using the following Eq. (1) [3,19,20]:

$$\text{Recovery (\%)} = \left( \frac{\text{Concentration of analyte found in the sample}}{\text{initial concentration of analyte in the sample}} \right) \times 100\% \quad (1)$$

Precision was calculated as the Relative Standard Deviation (RSD) of the recoveries from the replicates executed on the same day.

The recovery percentages for all target analytes ranged between 71.1 % and 107 %, with RSD values of 0.3 % to 13.8 % at fortification levels of 400 µg/L, 200 µg/L, 40 µg/L, 20 µg/L. Overall, the optimized SALLME method resulted in satisfactory recovery percentages (70 – 120%) and RSD values (< 20) for the target analytes according to the SANTE/11,312/2021 guidelines.

### Matrix effect

Moreover, matrix effect was evaluated based on the following Eq. (2) [4,9,21]:

$$\text{ME\%} = \left( \frac{\text{Slope of matrix matched standards curve} - \text{Slope of solvent standards curve}}{\text{Slope of solvent standards curve}} \right) \times 100\% \quad (2)$$

In the present study, pesticide residue in river water was monitored through optimizing an efficient, rapid, and cost-effective analytical method without any matrix interferences. Method's selectivity was confirmed as interfering peaks were absent at the same retention time of the targeted pesticides in the chromatograms obtained from blank water samples. Here, AZ, CAR, PYM, DFN, and CLP were affected by matrix suppression as ME% were –19.77 %, –8.03 %, –97.76%, –13.35 %, and 16.14 %, respectively. In contrast, BUP and DMT showed matrix enhancement with an ME% of 9.13 % and 9.09 %. Overall, all pesticides except PYM exhibited matrix suppression or enhancement in the acceptable range of < ±20 %. Therefore, the matrix-matched calibration curve was used to quantify the concentration of pesticide residues.

The optimized method demonstrated higher sensitivity and efficiency for the simultaneous detection of the selected pesticides, and thus, ensures the trueness of results. The optimized method can accurately detect even trace-level residues in environmental water samples in comparison with few previous studies (Table 4).

**Table 4**

Worldwide reported studies on pesticide residue detection in river water.

River	Pesticide	Extraction	Instrument	Method Validation		References
				LOQ (ng/L)	Recovery (%)	
Shangyu River, China	DMT	–	GC-FPD	125.4	92.2	[22]
Wuchuan River, China	DMT	SPE	GC-FPD	3.267	92	[23]
Taihu lake, China	AZ	SPE	LC-MS/MS	0.06 - 20	70 – 130	[24]
	DFN				70 – 130	
Alqueva reservoir, Portugal	DMT	SPE	LC-MS/MS	1.75	110.8	[25]
Louros river, Greece	BUP	SPE	LC-MS	50	–	[26]
Mondego river estuary, Portugal	DFN	SPE	GC-MS	0.4 - 1.3	71 – 120	[27]
	DMT				71 – 120	
Ria Formosa Lagoon, Portugal	DFN	SPE	GC-MS	0.4 - 1.3	71 – 120	[28]
	DMT				71 – 120	
	AZ				71 – 120	
Mogi Guaçu River Basin, Brazil	AZ	SPE	UPLC-MS/MS	40	70.5 – 79.8	[29]
	CAR			10	80.72 – 89.2	
River Madre de Dios, Costa Rica	AZ	SPE	HPLC-DAD			[30]
	CAR					
Júcar River, Spain	BUP	SPE (Oasis HLB Cartridge)	LC-MS/MS	0.3	48.5 – 70	[31]
	CAR			0.3		
	DMT			0.03		
Feni River, Bangladesh	BUP					Present Study
	AZ	SPE	LC-MS/MS	0.2	71.1 – 78.1	
	BUP			0.5	91.1 – 107	
	CAR			0.1	90.1 – 95.2	
	PYM			1	81.7 – 97.8	
	DMT			1	76.7 – 106.7	
	DFN			0.1	71.8 – 102.3	
	CLP			1	64.8 – 79.7	

N.B.: FPD = Flame Photometric Detector, DF = Frequency of Detection, n.d. = not detected.

## Limitations

The noteworthy limitation of the modified and validated SALLME-dSPE method is that the analytical method for CUP residue determination applies only to water samples. In addition, to analyze residues in other environmental matrices except water using this method, the samples should be converted into water.

## Credit author statement

**Ananya Bhuiya:** Methodology, Data curation, Writing original draft. **Sabina Yasmin:** Conceptualization, Methodology, Supervision, Funding acquisition, Writing – review & editing. **M. Golam Mustafa:** Methodology, Supervision, Funding acquisition, Writing – review & editing. **Tajnin Jahan, Md. Atikur Rahman, Sarker Kamruzzaman, Mohammad Moniruzzaman:** Data analysis, Methodology, Writing – review & editing. **Md Humayun Kabir:** Conceptualization, Methodology, Supervision, Funding acquisition, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Acknowledgments

The authors are grateful to Institute of National Analytical Research and Service (INARS), Bangladesh Council of Scientific and Industrial Research (BCSIR) for financial support (R&D, Ref. No. [39.02.0000.011.14.169.2023/877](#) (SL. No. 131), Dated: 17.09.2023). Furthermore, the authors appreciate the assistance from the Central Analytical and Research Facility (CARF), BCSIR, to perform LC-MS/MS analysis.



## References

- [1] V. Mohaupt, et al., Pesticides in European rivers, lakes and groundwaters - Data assessment, 2020, doi:[10.13140/RG.2.2.21719.60325](https://doi.org/10.13140/RG.2.2.21719.60325).
- [2] A. Bhuiya, et al., Spatiotemporal distribution, ecological risk assessment, and human health implications of currently used pesticide (CUP) residues in the surface water of Fení River, Bangladesh, *Sci. Total Environ.* 944 (2024) 173857, doi:[10.1016/j.scitotenv.2024.173857](https://doi.org/10.1016/j.scitotenv.2024.173857).
- [3] H.S. Chung, et al., Simultaneous determination of sulfoxaflor and its metabolites, X11719474 and X11721061, in brown rice and rice straw after field application using LC-MS/MS, *J. Environ. Anal. Chem.* 97 (2) (2017) 99–111, doi:[10.1080/03067319.2017.1282473](https://doi.org/10.1080/03067319.2017.1282473).
- [4] Md.M. Rahman, et al., Simultaneous quantification of methiocarb and its metabolites, methiocarb sulfoxide and methiocarb sulfone, in five food products of animal origin using tandem mass spectrometry, *J. Chromatogr. B* 1060 (2017) 387–394, doi:[10.1016/j.jchromb.2017.06.025](https://doi.org/10.1016/j.jchromb.2017.06.025).
- [5] T. Gezahegn, B. Tegegne, F. Zewge, B.S. Chandravanshi, Salting-out assisted liquid–liquid extraction for the determination of ciprofloxacin residues in water samples by high performance liquid chromatography–diode array detector, *BMC Chem.* 13 (1) (2019) 28, doi:[10.1186/s13065-019-0543-5](https://doi.org/10.1186/s13065-019-0543-5).
- [6] A.A.Z. Rodrigues, A.A. Neves, M.E.L.R. De Queiroz, A.F. De Oliveira, L.H.F. Prates, E.H.D.C. Morais, Optimization and validation of the salting-out assisted liquid–liquid extraction method and analysis by gas chromatography to determine pesticides in water, *Eclét. Quím. J.* 43 (1S1) (2018) 11, doi:[10.26850/1678-4618eqj.v43.1S1.2018.p11-21](https://doi.org/10.26850/1678-4618eqj.v43.1S1.2018.p11-21).
- [7] E. Teju, B. Tadesse, N. Megersa, Salting-out-assisted liquid–liquid extraction for the preconcentration and quantitative determination of eight herbicide residues simultaneously in different water samples with high-performance liquid chromatography, *Sep. Sci. Technol.* 56 (4) (2021) 719–729, doi:[10.1080/01496395.2016.1276596](https://doi.org/10.1080/01496395.2016.1276596).
- [8] M. H. Kabir et al., “An LLE Based LC- ESI MS/MS Analytical Method Development to Detect Azithromycin Residue in Water to Monitor Contamination Level of River and Fish Farm of Bangladesh,” In Review, preprint, 2021. doi: [10.21203/rs.3.rs-588090/v1](https://doi.org/10.21203/rs.3.rs-588090/v1).
- [9] S. Kim, et al., Simultaneous detection of sulfoxaflor and its metabolites, X11719474 and X11721061, in lettuce using a modified QuEChERS extraction method and liquid chromatography–tandem mass spectrometry, *Biomed. Chromatogr.* 31 (6) (2017) e3885, doi:[10.1002/bmc.3885](https://doi.org/10.1002/bmc.3885).
- [10] B. Nakhjavani, J. Bland, M. Khosravifard, Optimization of a Multiresidue Analysis of 65 Pesticides in Surface Water Using Solid-Phase Extraction by LC-MS/MS, *Molecules* 26 (21) (2021) 6627, doi:[10.3390/molecules26216627](https://doi.org/10.3390/molecules26216627).
- [11] A. Bhuiya, S. Yasmin, M.A.A. Shaikh, M. G. Mustafa, M.H. Kabir, Method development of multi pesticide residue analysis in country beans collected from Dhaka, Bangladesh, and their dietary risk assessment, *Food Chem.* 445 (2024) 138741, doi:[10.1016/j.foodchem.2024.138741](https://doi.org/10.1016/j.foodchem.2024.138741).
- [12] T. Jahan, et al., Development and validation of a modified QuEChERS method coupled with LC-MS/MS for simultaneous determination of difenoconazole, dimethoate, pymetrozine, and chlorantraniliprole in brinjal collected from fields and markets places to assess human health risk, *Heliyon* 9 (4) (2023) e14972, doi:[10.1016/j.heliyon.2023.e14972](https://doi.org/10.1016/j.heliyon.2023.e14972).
- [13] Y. Alemayehu, T. Tolcha, N. Megersa, Salting-out assisted liquid–liquid extraction combined with HPLC for quantitative extraction of trace multiclass pesticide residues from environmental waters, *AJAC* 08 (07) (2017) 433–448, doi:[10.4236/ajac.2017.87033](https://doi.org/10.4236/ajac.2017.87033).
- [14] H.S. Lee, Md.M. Rahman, H.S. Chung, H. Kabir, K.-S. Yoon, S.-K. Cho, A.M. Abd El-Aty, Jae-Han Shim, “An effective methodology for simultaneous quantification of thiophanate-methyl, and its metabolite carbendazim in pear, using LC-MS/MS, *J. Chromatogr. B* 1095 (2018) 1–7, doi:[10.1016/j.jchromb.2018.07.010](https://doi.org/10.1016/j.jchromb.2018.07.010).
- [15] T. Pihlström et al., “Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed SANTE 11312/2021,” 2021, Accessed: November 15, 2023. [Online]. Available: <https://gfrs.fssai.gov.in/files/docs/5-SANTE%2011312-2021-Pesticides%20method%20validation.pdf>
- [16] M.H. Kabir, S. Yasmin, S. Islam, M.A.A. Shaikh, M. Moniruzzaman, Residue determination of thiamethoxam and its metabolite clothianidin in okra using the modified QuEChERS method with d-SPE clean-up coupled with LC-MS/MS, *Food Chem. Adv.* 5 (2024) 100754, doi:[10.1016/j.focha.2024.100754](https://doi.org/10.1016/j.focha.2024.100754).
- [17] H.S. Chung, et al., Uptake of the veterinary antibiotics chlortetracycline, enrofloxacin, and sulphathiazole from soil by radish, *Sci. Total Environ.* 605–606 (2017) 322–331, doi:[10.1016/j.scitotenv.2017.06.231](https://doi.org/10.1016/j.scitotenv.2017.06.231).
- [18] Md.H. Kabir, et al., Dissipation pattern and risk quotients assessment of amisulbrom in Korean melon cultivated in plastic house conditions, *Environ. Monit. Assess.* 189 (6) (2017) 302, doi:[10.1007/s10661-017-6017-0](https://doi.org/10.1007/s10661-017-6017-0).
- [19] Md.H. Kabir, et al., Residual determination and risk assessment of buprofezin in plum (*Prunus domestica*) grown in open-field conditions following the application of three different formulations, *Biomed. Chromatogr.* 30 (11) (2016) 1721–1727, doi:[10.1002/bmc.3745](https://doi.org/10.1002/bmc.3745).
- [20] H.S. Lee, et al., Liquid chromatography–tandem mass spectrometry quantification of acetamiprid and thiacloprid residues in butterbur grown under regulated conditions, *J. Chromatogr. B* 1055–1056 (2017) 172–177, doi:[10.1016/j.jchromb.2017.04.021](https://doi.org/10.1016/j.jchromb.2017.04.021).
- [21] Md.M. Rahman, et al., A quick and effective methodology for analyzing dinotefuran and its highly polar metabolites in plum using liquid chromatography–tandem mass spectrometry, *Food Chem.* 239 (2018) 1235–1243, doi:[10.1016/j.foodchem.2017.07.073](https://doi.org/10.1016/j.foodchem.2017.07.073).
- [22] H. Chen, J. Zhu, Z. Li, A. Chen, Q. Zhang, The occurrence and risk assessment of five organophosphorus pesticides in river water from Shangyu, China, *Environ. Monit. Assess.* 188 (11) (2016) 614, doi:[10.1007/s10661-016-5612-9](https://doi.org/10.1007/s10661-016-5612-9).
- [23] Z.L. Zhang, H.S. Hong, J.L. Zhou, G. Yu, Occurrence and behaviour of organophosphorus insecticides in the River Wuchuan, southeast China, *J. Environ. Monitor.* 4 (4) (2002) 498–504, doi:[10.1039/b203852h](https://doi.org/10.1039/b203852h).
- [24] W. Li, B. Wang, Y. Yuan, S. Wang, Spatiotemporal distribution patterns and ecological risk of multi-pesticide residues in the surface water of a typical agriculture area in China, *Sci. Total Environ.* 870 (2023) 161872, doi:[10.1016/j.scitotenv.2023.161872](https://doi.org/10.1016/j.scitotenv.2023.161872).
- [25] P. Palma, et al., Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal), *Sci. Total Environ.* 488–489 (2014) 208–219, doi:[10.1016/j.scitotenv.2014.04.088](https://doi.org/10.1016/j.scitotenv.2014.04.088).
- [26] M. Kapsi, C. Tsoutsis, A. Paschalidou, T. Albanis, Environmental monitoring and risk assessment of pesticide residues in surface waters of the Louros River (N.W. Greece), *Sci. Total Environ.* 650 (2019) 2188–2198, doi:[10.1016/j.scitotenv.2018.09.185](https://doi.org/10.1016/j.scitotenv.2018.09.185).
- [27] C. Cruzeiro, E. Rocha, M.Á. Pardal, M.J. Rocha, Environmental assessment of pesticides in the Mondego River Estuary (Portugal), *Mar. Pollut. Bull.* 103 (1–2) (2016) 240–246, doi:[10.1016/j.marpolbul.2015.12.013](https://doi.org/10.1016/j.marpolbul.2015.12.013).
- [28] C. Cruzeiro, E. Rocha, M.Á. Pardal, M.J. Rocha, Uncovering seasonal patterns of 56 pesticides in surface coastal waters of the Ria Formosa lagoon (Portugal), using a GC-MS method, *Int. J. Environ. Anal. Chem.* 95 (14) (2015) 1370–1384, doi:[10.1080/03067319.2015.1100724](https://doi.org/10.1080/03067319.2015.1100724).
- [29] R.R.M. Barizon, et al., Surface water contamination from pesticide mixtures and risks to aquatic life in a high-input agricultural region of Brazil, *Chemosphere* 308 (2022) 136400, doi:[10.1016/j.chemosphere.2022.136400](https://doi.org/10.1016/j.chemosphere.2022.136400).
- [30] R.A. Rämö, P.J. Van Den Brink, C. Ruepert, L.E. Castillo, J.S. Gunnarsson, Environmental risk assessment of pesticides in the River Madre de Dios, Costa Rica using PERPEST, SSD, and mSPAF models, *Environ. Sci. Pollut. Res.* 25 (14) (2018) 13254–13269, doi:[10.1007/s11356-016-7375-9](https://doi.org/10.1007/s11356-016-7375-9).
- [31] V. Belenguer, F. Martinez-Capel, A. Masiá, Y. Picó, Patterns of presence and concentration of pesticides in fish and waters of the Júcar River (Eastern Spain), *J. Hazard Mater.* 265 (2014) 271–279, doi:[10.1016/j.jhazmat.2013.11.016](https://doi.org/10.1016/j.jhazmat.2013.11.016).