Supplementary Material

Experimental design approaches to optimize ultrasound-assisted simultaneous-silylation dispersive liquid-liquid microextraction for the rapid determination of parabens in surface water samples

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Reagents, chemicals and standards

Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany) supplied all chemicals and solvents (highest available purity) that were used in this study. Analytical standards (purity greater than 98%), viz., methyl-paraben (MeP), ethyl-paraben (EtP), propyl-paraben (PrP), and butyl-paraben (BuP) were obtained from Alfa Aesar (Lancashire, UK), and were used for the evaluation and validation of the developed method. Their name, structures, chemical and physical properties are listed in Table S1. *p*-Terphenyl-d_{14} (purity ≥ 98%, used as an internal standard), *N*-Methyl-(*tert*-butyldimethylsilyl)-trifluoroacetamide with 1% *tert*-butyldimethylchlorosilane (MTBSTFA+1% t-BDMCS, or simplified as MTBSTFA in this study) and *N,O*-bis(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane (BSTFA+1% TMCS, or simplified as BSTFA in this study) were obtained from Sigma-Aldrich. Stock solutions of each analyte (1.0 mg/mL) were prepared in methanol. Mixtures of the analytes for working standard preparations and sample fortification were prepared in methanol. All stock solutions and mixtures were stored in the dark at 4 °C. Deionized water was further purified using a Millipore water purification system (Billerica, MA, USA).

Table S1. Name (abbreviation), chemical structure, physical and chemical properties of four parabens used for the method development and validation.

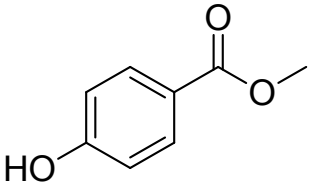
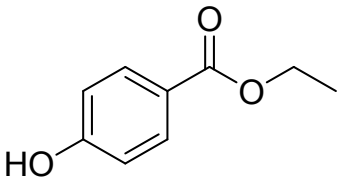
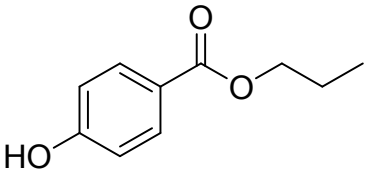
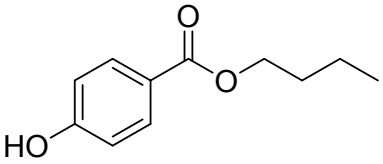
Name (Abbreviation):	**Structure**	**MW (g/mol)**	**pK_a**	**$LogK_{ow}$**	**Vapor pressure mm Hg (25°C)**
Methyl-paraben (MeP)		**152.1**	8.5	1.96	2.37×10^{-4}
Ethyl-paraben (EtP)		**166.2**	8.5	2.47	9.29×10^{-5}
Propyl-paraben (PrP)		**180.2**	7.91	3.04	3.07×10^{-4}
Butyl-paraben (BuP)		**194.2**	8.47	3.57	2.51×10^{-4}

Table S2. Analysis of variance (ANOVA) for the Factorial Multilevel Categoric Design

Source	Sum of Squares	df	Mean Square	F Value	*p*-value Prob > F
Model	7.076×10^{14}	7	1.011×10^{14}	26.12	<0.0001*
A-Extractant	2.725×10^{14}	2	1.362×10^{14}	35.21	<0.0001*
B-Dispersant	3.704×10^{14}	2	1.852×10^{14}	47.87	<0.0001*
C-Silylating agent	4.481×10^{13}	1	4.481×10^{13}	11.58	0.0067*
BC	1.982×10^{13}	2	9.912×10^{12}	2.56	0.1264

Table S3. Analysis of variance (ANOVA) for the Box-Behnken Design.

source	Sum of squares	df	Mean square	F Value	p-value Prob > F
Model	2.532×10^{14}	9	2.813×10^{13}	11.95	0.0069*
A-C_2Cl_4	5.064×10^{13}	1	5.064×10^{13}	21.50	0.0056*
B-Acetone	1.524×10^{13}	1	1.524×10^{13}	6.47	0.0483*
C-Salt added	8.460×10^{12}	1	8.460×10^{12}	3.59	0.1165
AB	6.317×10^{12}	1	6.317×10^{12}	2.68	0.1624
AC	3.650×10^{10}	1	3.650×10^{10}	0.015	0.9058
BC	1.075×10^{13}	1	1.075×10^{13}	4.56	0.0857
A^2	5.958×10^{13}	1	5.958×10^{13}	25.30	0.0040
B^2	6.463×10^{13}	1	6.463×10^{13}	27.45	0.0034
C^2	3.137×10^{13}	1	3.137×10^{13}	13.32	0.0187
Lack-of-fit	1.101×10^{13}	3	3.669×10^{12}	9.57	0.0960

*Significant

The *F*-value for "Lack-of-Fit" was insignificant (at the 95% confidence level) which confirmed that the model fit the response variables with a near-perfect prediction.

Table S4. Spiked recoveries (%) of individual target analyte for each experimental condition of Box-Behnken Design

Run	C_2Cl_4 (μL) (A)	Acetone (μL) (B)	NaCl (%) (C)	(%)			
				MeP	EtP	PrP	BuP
1	15	800	5	72	68	65	69
2	20	600	5	97	92	93	93
3	15	600	10	72	71	78	79
4	15	600	1	80	81	78	79
5	30	600	1	55	52	53	61
6	20	800	1	72	69	66	71
7	20	400	10	55	53	61	51
8	20	600	5	92	86	88	94
9	30	800	5	68	65	65	64
10	20	600	5	93	95	91	95
11	30	400	5	45	43	51	49
12	15	400	5	69	65	62	63
13	20	800	10	72	69	71	70
14	20	400	1	78	72	78	79
15	30	600	10	52	49	55	50

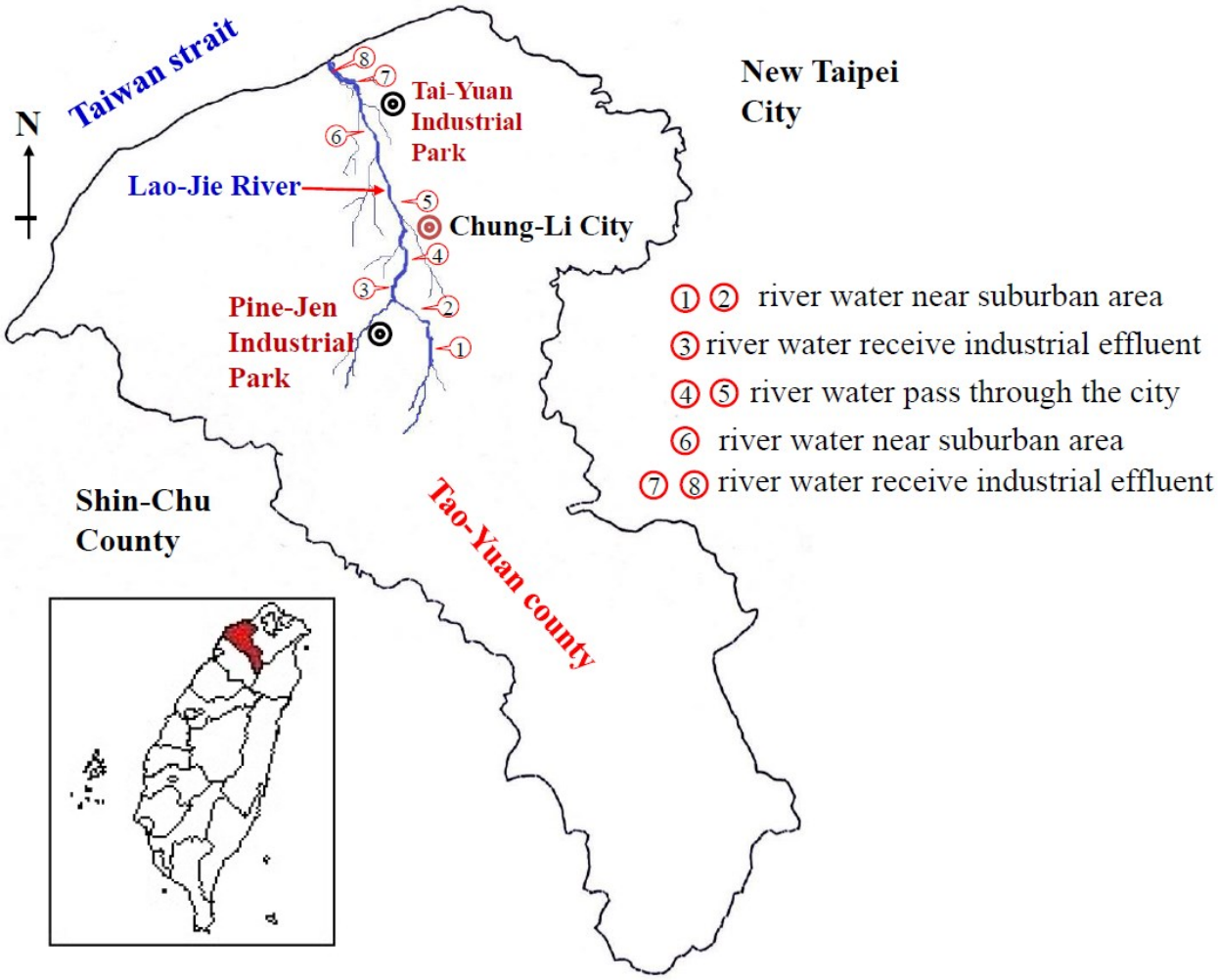


Figure S1. Sampling sites and locations at the Lao-Jie River.

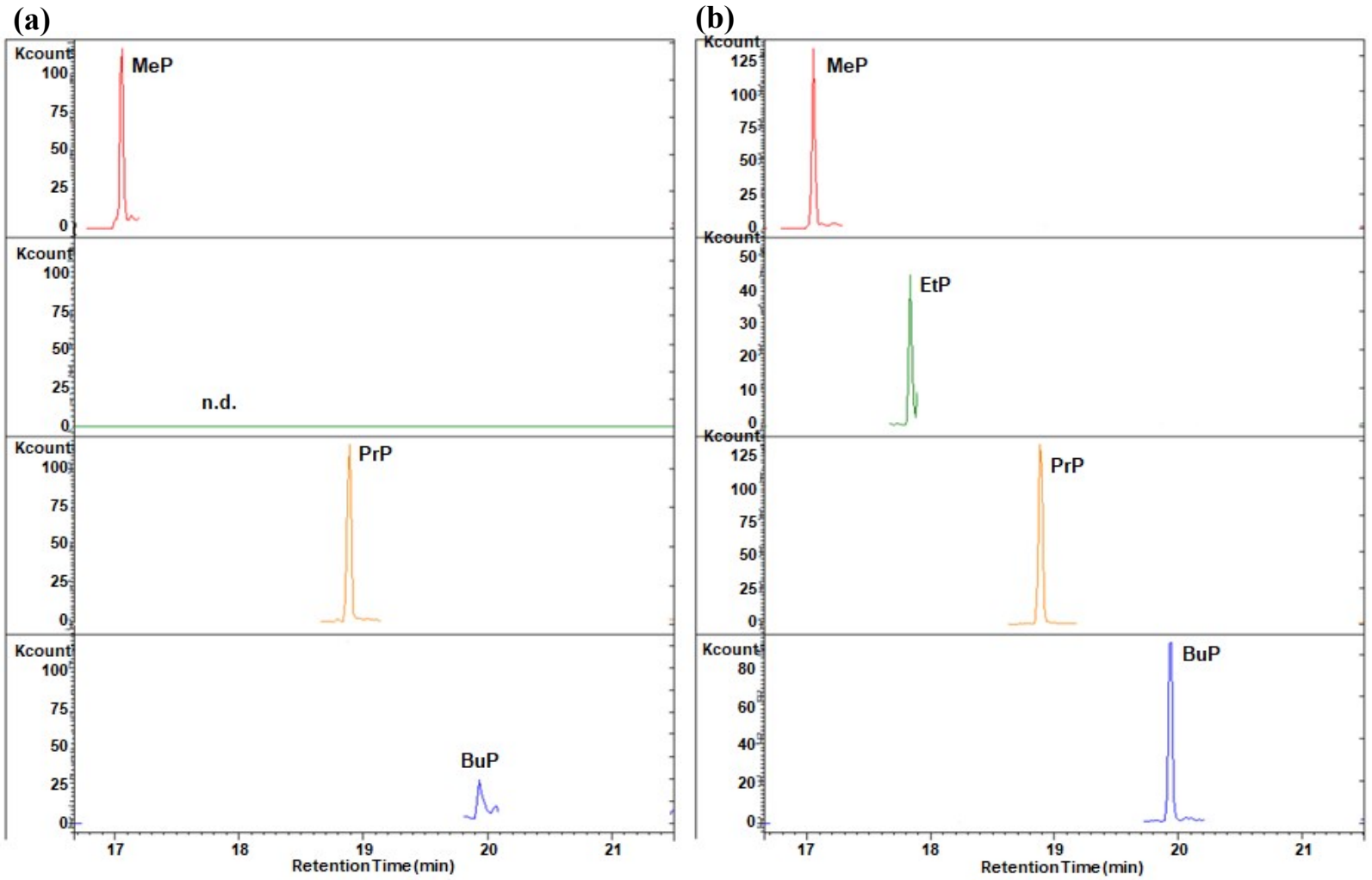


Figure S2. GC-MS/MS chromatograms for (a) non-spiked, and (b) spiked "River-5" water samples (final spiked concentration 100 ng L^{-1}). n.d.: not detected.