Supplementary Information

Development of a UPLC-MS/MS Method for Pesticide Analysis in Paddy Water and Evaluation of Anodic TiO_2 Nanostructured Films for Pesticide Photodegradation and Antimicrobial Applications

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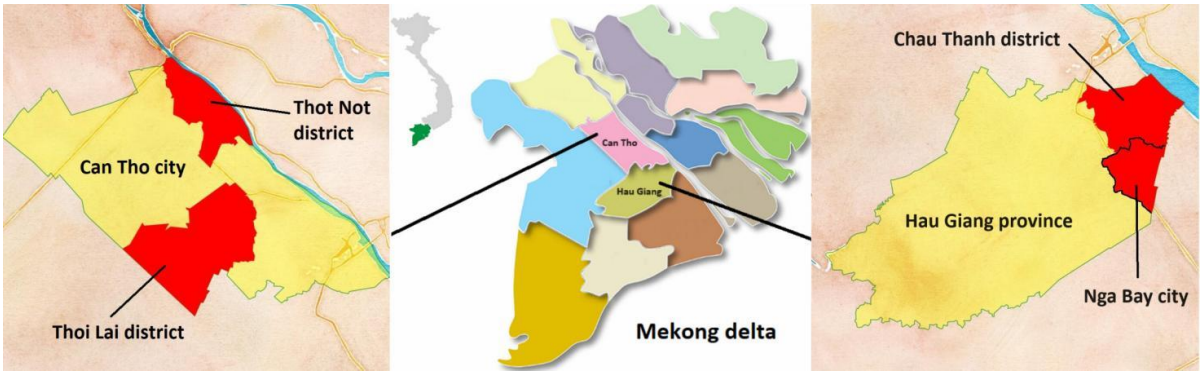

Figure S1. Locations of agricultural wastewater and canal water sampling sites in Can Tho City and Hau Giang Province, Mekong Delta, Vietnam.

Table S1. Retention times, MS/MS parameters, precursor and product ions for the five targeted pesticides and an internal standard (IS).

Compounds	Retention time (min)	Precursor ion $[M+H]^+$	Cone voltage (V)	Quantitative ion	Collision energy - quantitative ion (V)	Identified ion	Collision energy - identified ion (V)
Carbaryl	2.71	202.19	18	145.02	10	127.01	26
Methiocarb	3.03	225.31	16	169.07	8	121.13	22
Diazinon	4.58	305.12	12	168.97	22	152.98	22
Chlorpyrifos	5.85	351.82	28	96.77	30	199.79	30
Cypermethrin	6.26	416.02	30	191.15	10	163.16	25
Triphenylphosphate (IS)	5.17	327.20	52	76.99	42	152.02	36

Table S2. Composition of mobile phases used for chromatographic separation.

Time (min)	Flow rate (mL/min)	Methanol (%)	Water with 0.12% formic acid (%)
0.0	0.3	65	35
3.0	0.3	65	35
3.1	0.5	97	3
6.5	0.5	97	3
6.6	0.3	65	35
10.0	0.3	65	35

Table S3. Recovery rates of target pesticides under two different extraction conditions.

Process	Extraction recovery (%)					Signal strength	Sample processing time (min)
	CBR	MTC	DZN	CLO	CYPER		
1	78.75%	88.93%	79.35%	92.35%	80.52%	6.44×10^6	60
2	85.55%	84.87%	96.50%	90.30%	85.90%	12.5×10^6	5

Table S4. Validation parameters for the developed LC-MS/MS method, including a linearity range of 0.1 to 250 ng/mL.

Parameter		CBR	MTC	DZN	CLO	CYPER
r^2		0.996	0.997	0.997	0.995	0.998
MDL (ng/mL)		0.125	0.05	0.001	0.025	0.003
MQL (ng/mL)		0.30	0.10	0.005	0.012	0.015
Precision	Intra-day [a]	4.58	6.32	5.06	5.35	4.42
	Inter-day [b]	3.52	4.76	4.07	4.87	6.31
Accuracy [c]	10 ng/mL	95.61	89.32	103.08	102.08	85.54
	50 ng/mL	103.77	104.67	103.20	97.89	89.45
	100 ng/mL	100.69	98.44	101.73	102.05	90.27

[a] Maximum deviation within a single day, determined by peak area percentage (n = 9); [b] Deviation over three days, determined by peak area percentage (n = 3); [c] Expressed as percentage recovery rates.

Table S5. Presence and concentration (C, ng/mL) of pesticides detected in agricultural wastewater samples collected from two districts in Can Tho City and two districts in Hau Giang Province, Vietnam.

Pesticides	CT-TL[1-10]		CT-TN[1-10]		HG-CT[1-10]		HG-NB[1-10]	
	occur	C (ng/mL)	occur	C (ng/mL)	occur	C (ng/mL)	Occur	C (ng/mL)
CBR	2/10	2.1-6.7	3/10	1.3-14.3	3/10	1.9-7.9	*not detectable*	
MTC	1/10	5.4	1/10	4.7	2/10	6.8-7.7	2/10	4.1-5.4
CLO	3/10	1.7-7.4	4/10	2.5-7.6	4/10	2.2-8.5	2/10	4.6-10.9
DZN	2/10	6.5-.7.8	1/10	10.5	1/10	2.8	1/10	6.3
CYPER	*not detectable*				3/10	3.4-8.1	4/10	2.6-9.4

Table S6. Comparison of this study with previous research

Aspect	**This study**	**Previous studies**	**Advantages of this study**
Water sample types and geographical scope	Agricultural wastewater and river/canal water from rice-growing areas in Mekong Delta, Vietnam	• Water in the lower reaches of Dong Nai River system, Vietnam [1] • River water of Can Tho River, Vietnam, and Cagayan de Oro River Basin, Philippines [2] - Fresh water of aquaculture systems Mekong Delta, Vietnam [3]	This study provides a specific focus on agricultural wastewater and river/canal water from rice-growing areas in the Mekong Delta, addressing a critical research gap in local environmental studies.
Pesticides assessed	Five pesticides in 03 main groups: • The organophosphates: diazinon and chlorpyrifos • The carbamates: carbaryl and methiocarb The pyrethroid: cypermethrin	• Six pesticides in the organochlorine group: dichlorodiphenyl-trichloroethane, hexachloro-cyclohexane, aldrin, heptachlor, dieldrin, endrin [1] • Hydrophobic and hydrophilic organic pesticides [2] Three pesticides: quinalphos, trifluralin and dichlorvos [3]	This study provides a broader spectrum by analyzing pesticides from multiple groups that are directly relevant to local agricultural practices, contributing to a deeper understanding of pesticide contamination in the region.

Analytical method used	UPLC-MS/MS	• GC-ECD [1] • GC-MS/MS and LC-MS/MS [2] GC-MS and GC-ECD [3]	The UPLC-MS/MS method employed in this study offers exceptional sensitivity and precision, enabling the detection of ultra-trace pesticide levels (ng/mL) with high accuracy and reproducibility.
Detection limits of pesticides	MDL: 0.001–0.125 ng/mL, MQL: 0.05–0.30 ng/mL	• Not mentioned [1,2] MDL 0.002-0.016 ng/mL and MQL 0.007-0.053 ng/mL [3]	The study ensures sensitivity, allowing for the detection of ultra-trace pesticide levels and ensuring precise identification even at extremely low concentrations (ng/mL).
Accuracy and precision of measurements	85.54% – 104.67%, RSD <6.32%	• Not mentioned [1,2] 85.3% - 101.0%, RSD < 13% [3]	Rigorous method validation ensures highly reliable and reproducible results, confirming the robustness of the analytical process.
Sample size and distribution	40 water samples were collected, including 10 from Thot Not District and 10 from Thoi Lai District in Can Tho City, as well as 10 from Chau Thanh District and 10 from Nga Bay City in Hau Giang Province.	• 48 water samples from the 12 sampling stations [1] • 3 sampling sites in Can Tho River, Vietnam and 03 sampling sites in the CDO River Basin, Philipines [2] 13 samples from rice field, 10 samples collected from cat fish ponds and 10 samples collected from red tilapia cages [3]	This study offers a larger and more comprehensive sample size, ensuring robust data that better represents regional conditions and provides valuable insights for policymakers and stakeholders in agriculture and environmental management.
Sample analysis duration	10 minutes per 50 mL sample	Not mentioned [1-3]	Fast sample analysis with improved throughput for high sample volumes.
Utilize the developed UPLC-MS/MS method to investigate photocatalytic materials for multiple applications	Investigated TiO_2 nanostructured films (i.e., TNAs and TNWs/TNAs) for pesticide degradation and antibacterial applications	Not mentioned [1-3]	Integrating pesticide analysis with TiO_2-based photocatalytic degradation and antibacterial properties provides a comprehensive strategy for detecting and removing pesticide contamination while effectively controlling microbial growth.

[1] Nguyen, T. X.; Nguyen, B. T.; Tran, H. T. T.; Mai, H.; Duong, T. T.; Bach, Q. V., Seasonal, Spatial Variation, and Potential Sources of Organochlorine Pesticides in Water and Sediment in the Lower Reaches of the Dong Nai River System in Vietnam. *Arch Environ Contam Toxicol* **2019,** *77* (4), 514-526.

[2] Salingay, M. L. B.; Zevenbergen, C.; Pathirana, A., Assessment of residual pesticides and other organic pollutants using passive samplers in Can Tho River, Vietnam, and Cagayan de Oro River Basin, Philippines. *Frontiers in Water* **2024,** *6*, 1474499.

[3] Nguyen, Q. T.; Douny, C.; Tran, M. P.; Brose, F.; Nguyen, P. T.; Huong, D. T. T.; Kestemont, P.; Scippo, M. L., Screening of quinalphos, trifluralin and dichlorvos residues in fresh water of aquaculture systems in Mekong Delta, Vietnam. *Aquaculture Research* **2018,** *50* (1), 247-255.