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Absence of Detectable Organochlorine Pesticide Residues in Cabano River, Guimaras, Philippines: A Two- Season Assessment with Regulatory Benchmarking

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Abstract

Organochlorine pesticides (OCPs) are persistent organic pollutants known for their environmental stability, hydrophobicity, and strong potential for bioaccumulation. Although many OCPs have been banned or restricted under international agreements such as the Stockholm Convention, residues may still persist in aquatic systems due to historical use. In the Philippines, studies on pesticide contamination have largely focused on major agricultural areas, with limited data available for insular watersheds like Guimaras. This study assessed the occurrence and spatial–seasonal distribution of OCP residues in the surface waters of Cabano River. Surface water samples were collected from upstream, midstream, and downstream stations during both dry and rainy seasons using a grab-composite method. Samples were preserved and analyzed in an accredited laboratory for 22 OCP compounds, including DDT and its metabolites, cyclodienes, hexachlorocyclohexane isomers, and endosulfans, using gas chromatography. Detection limits ranged from 0.0052 to 0.20 µg/L. All target OCP compounds were below their respective detection limits across all sampling sites and seasons. No spatial or seasonal variation was observed. The results indicate the absence of detectable dissolved-phase OCP residues within the analytical limits of the method. Measured values complied with Philippine DENR Administrative Order 2016-08 Class C freshwater standards, with no exceedances of European Union environmental quality thresholds, although some EU limits were lower than the detection capability. These findings provide baseline data for Cabano River and suggest low current risk from dissolved OCP contamination, while highlighting the need for continued monitoring.

Clinical Trial Number: not applicable

1 Introduction

Organochlorine pesticides (OCPs) are synthetic chlorinated hydrocarbons formerly used on a wide scale for crop protection, vector control, and other pest-management applications. Representative compounds include dichlorodiphenyltrichloroethane (DDT), aldrin, dieldrin, endrin, chlordane, hexachlorocyclohexane (HCH) isomers, toxaphene, and heptachlor. Their low water solubility, high lipophilicity, and resistance to degradation favor environmental persistence and bioaccumulation, particularly in sediments, aquatic food webs, and other organic-rich compartments (Blus, 1995; Pereira et al., 2016).

Because of these properties, many OCPs have been listed under the Stockholm Convention on Persistent Organic Pollutants. Their environmental and public-health relevance remains high because exposure has been associated with endocrine disruption, neurotoxicity, carcinogenicity, and reproductive impairment in both wildlife and humans (Keswani et al., 2022). Even after restriction or prohibition, residues may remain detectable through legacy contamination and long-range transport.

OCPs enter aquatic systems through multiple pathways, including surface runoff, soil erosion, atmospheric deposition, and sediment remobilization. Only a fraction of an applied pesticide reaches the target organism, whereas a substantial proportion may remain in soils and later migrate into adjacent

water bodies (Damalas & Eleftherohorinos, 2011). In riverine environments, dissolved concentrations may therefore reflect not only current use but also historical accumulation and watershed mobilization.

In the Philippines, published pesticide-monitoring studies remain limited in spatial coverage. Bouman et al., (2002) documented pesticide residues in groundwater under rice-based cropping systems in Luzon. Varca (2012) reported pesticide contamination in tributaries draining to Laguna de Bay, with detections linked to application timing and rainfall. Navarrete et al. (2018) further demonstrated measurable organochlorine residues in surface water and groundwater along the Pampanga River, with some compounds exceeding regulatory thresholds. These studies show that pesticide occurrence in Philippine waters can vary substantially with land use, hydrology, and intensity of agricultural activity.

Despite this evidence from major agricultural basins, information remains scarce for small island watersheds such as those in Guimaras. Cabano River traverses agricultural and residential landscapes where pesticide application may occur directly or indirectly within the watershed. Generating baseline data for such systems is important for local water-quality management, regulatory benchmarking, and future trend assessment.

This study therefore assessed the occurrence, spatial distribution, and seasonal variability of 22 organochlorine pesticide compounds in the surface waters of Cabano River, Guimaras, Philippines. Specifically, it aimed to determine whether OCP residues were detectable across upstream, midstream, and downstream stations during dry and rainy seasons and to evaluate the results against Philippine and selected European regulatory benchmarks.

2 Materials and Method

2.1 Study Area

Cabano River is located in Guimaras, Philippines, and the sampling design covered three river sections intended to represent upstream, midstream, and downstream conditions. The upstream station was identified in Brgy. San Miguel, Jordan, whereas the midstream and downstream stations were located in Brgy. M. Chavez and Brgy. Cabano, San Lorenzo, respectively. Sampling was conducted during the dry and rainy seasons to account for possible hydrologic influences on contaminant transport, dilution, and remobilization. Because watershed runoff and flow dynamics can vary seasonally in tropical river systems, the two-season design was used to capture potential temporal differences in dissolved OCP occurrence.

2.2 Surface Water Sampling

Surface-water samples were collected using a grab-composite approach adapted from (Navarrete et al., 2018). At each station, a pre-cleaned polyethylene bucket attached to a nylon rope was lowered into the mid-channel area at approximately 20–30 cm below the water surface to avoid surface films and to minimize disturbance of bottom sediments. The collected water was transferred to a larger acid-washed

container, and the procedure was repeated three times to generate a homogenized composite sample representative of the station.

From each composite sample, three 1-L amber glass bottles were filled for OCP analysis. Bottles were filled carefully to minimize volatilization losses and photodegradation. Field duplicates and procedural blanks were prepared as part of quality-control procedures intended to assess contamination during sample handling and transport. After collection, samples were immediately stored at approximately 4°C in an insulated cooler and were transported to the laboratory within 24 h.

2.3 Sample Preservation, Transport, and Laboratory Submission

All sample containers were securely capped, labeled, and maintained under cooled conditions from the time of collection until laboratory turnover. Samples were transported by air on the day of collection, and two separate shipment events were conducted to correspond with the dry- and rainy-season sampling campaigns. Upon arrival at Ninoy Aquino International Airport, the samples were received by authorized personnel of Intertek Testing Services Philippines, Inc., Makati City, Philippines. Chain-of-custody procedures were observed throughout transfer to preserve sample integrity prior to analysis.

2.4 Determination of Organochlorine Pesticides by Gas Chromatography

Organochlorine pesticide residues were determined by Intertek Testing Services Philippines, Inc. using gas chromatography, as indicated in the laboratory certificate of analysis. Instrumental analysis was performed entirely by the accredited laboratory in accordance with its validated procedures for water-matrix OCP determination. The present study therefore reports laboratory-generated results and interprets them within the environmental and regulatory context of the Cabano River watershed.

The target analytes were 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, aldrin, alpha-, beta-, delta-, and gamma-BHC (lindane), alpha- and gamma-chlordane, technical chlordane, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, and toxaphene. Results were reported in micrograms per liter (µg/L). Concentrations below the method detection limit (MDL) were reported using the symbol '<'. Across analytes, MDLs ranged from 0.0052 to 0.20 µg/L.

2.5 Data Treatment and Regulatory Benchmarking

Because all reported concentrations were below their respective MDLs, the dataset was interpreted descriptively rather than through inferential statistics. Spatial and seasonal comparisons were therefore based on the occurrence of detectable versus non-detectable results across stations and sampling periods. Measured values were compared with the Philippine DENR DAO 2016-08 Class C freshwater criterion for total organochlorine pesticides and with selected European Union annual average environmental quality standards to provide regulatory context. This benchmarking approach was used to

distinguish between demonstrated compliance under national standards and the analytical limitations associated with selected ultra-trace international thresholds.

3 Results and Discussion

3.1 Occurrence and Distribution of Organochlorine Pesticides

Twenty-two OCP compounds were included in the analytical panel for surface-water samples collected from the upstream, midstream, and downstream stations of Cabano River during both dry and rainy seasons. The analytes comprised DDT and its metabolites, cyclodiene pesticides, HCH isomers, endosulfan-related compounds, methoxychlor, toxaphene, and related chlorinated pesticides commonly associated with legacy agricultural contamination.

Across all stations and in both sampling periods, none of the target compounds were detected above their respective MDLs. All laboratory reports indicated concentrations below detection, demonstrating that measurable dissolved-phase OCP residues were absent within the analytical sensitivity applied in this study. Likewise, no spatial trend was evident along the upstream-to-downstream gradient, and no seasonal contrast was observed between the dry and rainy sampling periods.

These results suggest that Cabano River did not experience measurable dissolved OCP contamination during the study period. The findings contrast with reports from larger Philippine agricultural basins, where organochlorine residues have been observed in surface water or groundwater (Bouman et al., 2002; Navarrete et al., 2018; Varca, 2012). Relative to those systems, Cabano River appears to have a lower detectable OCP burden, at least in the dissolved phase and within the period covered by this assessment.

3.2 Environmental Persistence and Watershed Interpretation

The absence of dissolved-phase detections should be interpreted cautiously. OCPs are strongly hydrophobic and tend to partition preferentially into sediments, suspended particulates, and biota rather than remain in the water column (Blus, 1995; Pereira et al., 2016). Consequently, non-detection in surface water does not necessarily imply complete absence within the broader watershed.

Several explanations may account for the observed non-detectable concentrations. First, historical use of legacy OCPs in the Cabano River watershed may have been limited. Second, residues from past applications may already be strongly sequestered in soils or sediments, thereby reducing their dissolved-phase expression. Third, any residual concentrations may be present at levels below the MDLs of the analytical method. A fourth possibility is that currently used pesticides in the watershed belong predominantly to newer chemical classes, such as organophosphates, carbamates, or pyrethroids, which were outside the scope of the present analyte panel.

Notably, no measurable increase in concentration was observed during the rainy season, when runoff-driven mobilization of legacy residues might be expected. This may indicate low watershed loading, effective attenuation and dilution, or the predominance of non-dissolved environmental compartments for any residual OCPs. However, this interpretation should remain conservative because only two seasonal snapshots were included, and episodic contamination can be missed when sampling frequency is limited.

3.3 Spatial and Seasonal Considerations

The consistent non-detectable results across upstream, midstream, and downstream stations indicate that no discrete source or cumulative downstream enrichment of OCPs was evident during sampling. In more intensively cultivated catchments, downstream increases are often associated with cumulative agricultural runoff, drainage discharge, or sediment transport. The absence of such a pattern in Cabano River supports the inference that substantial dissolved OCP inputs were not present at the time of collection.

Similarly, the lack of contrast between dry- and rainy-season results suggests that rainfall-driven remobilization of OCP residues did not produce measurable concentrations in the water column during the study period. This outcome differs from observations in other Philippine watersheds where rainfall and pesticide application schedules influenced surface-water detections (Varca, 2012). For Cabano River, the present results indicate either very low watershed contamination, concentrations below detection, or a tendency for residues to remain associated with particulate or benthic compartments rather than dissolved water.

3.4 Regulatory Compliance and Benchmarking

3.4.1 Philippine Standards (DAO 2016-08, Class C)

Under DENR DAO 2016-08, Class C freshwater bodies are subject to a cumulative criterion of 50 µg/L for total organochlorine pesticides. Because all analytes in this study were reported below their respective MDLs, the results indicate compliance with the applicable Philippine standard at all stations and in both sampling seasons. Within the regulatory framework used for fisheries, irrigation, recreation, and livestock watering, Cabano River therefore met the national water-quality benchmark for OCPs during the monitoring period.

3.4.2 European Union Environmental Quality Standards

Comparison with selected European Union annual average environmental quality standards also showed no measured exceedance for the compounds and groups assessed. However, interpretation requires caution because several EU thresholds are set at ultra-trace concentrations that are substantially lower than the MDLs used in this study. This is especially relevant for heptachlor and heptachlor epoxide, for which the benchmark values are several orders of magnitude lower than the laboratory detection limits.

Accordingly, the present results support the conclusion that no measurable OCP contamination was detected, but they do not allow strict confirmation of compliance with every ultra-trace benchmark where analytical sensitivity was insufficient. This distinction is important for scientific transparency: non-detection reflects concentrations below method capability, not definitive zero concentration. Table 1 presents the comparison of reported organochlorine pesticide concentrations in Cabano River with Philippine DENR DAO 2016-08 (Class C) and selected EU annual average environmental quality standards.

3.5 Implications for Monitoring and Watershed Management

The present findings provide a useful baseline for an island watershed where published pesticide data are limited. From a management perspective, the absence of measurable dissolved-phase OCPs is encouraging and suggests that acute regulatory concern for legacy organochlorines in the water column is currently low. Nevertheless, OCP monitoring in tropical river systems should not rely exclusively on dissolved surface water because hydrophobic residues may persist in sediment and biota, where ecological exposure can still occur.

Future monitoring should therefore expand matrix coverage to include bottom sediments, suspended particulates, and representative aquatic organisms. Screening should also be broadened to encompass currently used pesticide classes that may better reflect present agricultural practice. Finally, the use of more sensitive analytical techniques and repeated sampling across multiple hydrologic events would improve the ability to detect episodic or ultra-trace contamination and would strengthen long-term watershed risk assessment.

Table 1

Comparison of reported organochlorine pesticide concentrations in Cabano River with Philippine DENR DAO 2016-08 (Class C) and selected EU annual average environmental quality standards.

Compound	Measured concentration (µg/L)	DAO 2016-08 Class C (µg/L) [a]	EU AA-EQS inland surface waters (µg/L) [b]
4,4'-DDT	< 0.0083	Included in total OCP (50 µg/L)	0.01 (p,p'-DDT)
4,4'-DDD	< 0.0083	Included in total OCP (50 µg/L)	0.025 (DDT total)
4,4'-DDE	< 0.0084	Included in total OCP (50 µg/L)	0.025 (DDT total)
Aldrin	< 0.0076	Included in total OCP (50 µg/L)	Included in cyclodiene pesticides (Σ = 0.01)
Dieldrin	< 0.0092	Included in total OCP (50 µg/L)	Included in cyclodiene pesticides (Σ = 0.01)
Endrin	< 0.0086	Included in total OCP (50 µg/L)	Included in cyclodiene pesticides (Σ = 0.01)
Heptachlor	< 0.0096	Included in total OCP (50 µg/L)	2×10^{-7} µg/L
Heptachlor epoxide	< 0.0096	Included in total OCP (50 µg/L)	2×10^{-7} µg/L
Lindane (γ-HCH)	< 0.0069	Included in total OCP (50 µg/L)	0.02 (hexachlorocyclohexane)
Alpha-, beta-, delta-BHC	< 0.0052–0.0084	Included in total OCP (50 µg/L)	0.02 (hexachlorocyclohexane)
Endosulfan I and II	< 0.0062–0.0070	Included in total OCP (50 µg/L)	0.005
Endosulfan sulfate	< 0.0092	Included in total OCP (50 µg/L)	Not listed
Chlordane (all forms)	< 0.10	Included in total OCP (50 µg/L)	Not separately listed
Endrin aldehyde	< 0.0076	Included in total OCP (50 µg/L)	Not listed
Endrin ketone	< 0.0073	Included in total OCP (50 µg/L)	Not listed
Methoxychlor	< 0.0089	Included in total OCP (50 µg/L)	Not listed

Note: [a] DENR DAO 2016-08, Table 6, secondary parameters (organics), Freshwater Class C: total organochlorine pesticides = 50 µg/L.

Compound	Measured concentration (µg/L)	DAO 2016-08 Class C (µg/L) [a]	EU AA-EQS inland surface waters (µg/L) [b]
Toxaphene	< 0.20	Included in total OCP (50 µg/L)	Not listed

Note: [a] DENR DAO 2016-08, Table 6, secondary parameters (organics), Freshwater Class C: total organochlorine pesticides = 50 µg/L.

[b] Directive 2008/105/EC as amended by Directive 2013/39/EU, annual average environmental quality standards for inland surface waters. Not listed indicates compounds without specific EU EQS values, while Not separately listed indicates compounds regulated under grouped standards. All reported concentrations were below detection limits.

4 Conclusion and Recommendations

This study provides the first baseline assessment of dissolved-phase organochlorine pesticide (OCP) occurrence in the surface waters of Cabano River, Guimaras, Philippines, across spatial gradients and seasonal conditions. All 22 target compounds were consistently below their respective method detection limits at upstream, midstream, and downstream stations during both dry and rainy seasons, with no observable spatial or temporal variation. These results demonstrate compliance with the Philippine DENR DAO 2016-08 Class C freshwater criterion and indicate that the river is not measurably impacted by dissolved-phase legacy OCP residues within the analytical limits applied.

While the absence of detectable concentrations suggests a low current risk in the water column, this finding should be interpreted as an early-stage environmental condition rather than a definitive absence of contamination. Given the known persistence and sediment affinity of OCPs, the results highlight the importance of proactive monitoring in relatively less-disturbed island watersheds before contamination becomes evident.

In this context, it is recommended that local government units (LGUs), in coordination with the Department of Environment and Natural Resources (DENR), institutionalize periodic pesticide monitoring programs in Cabano River and similar watersheds to support early detection and evidence-based water resource management. Additionally, future monitoring frameworks should be expanded to include sediments, aquatic biota, and currently used pesticide classes, and should adopt higher-sensitivity analytical methods to improve detection capability and align with international environmental quality standards. These measures will strengthen long-term watershed protection and ensure that emerging contamination risks are identified and managed at an early stage.

Declarations

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References

1. Blus, L. J. (1995). Organochlorine Pesticides. In *Handbook of Ecotoxicology* (2nd ed., pp. 275–300). Lewis Publishers.
2. Bouman, B. A. M., Castañeda, A. R., & Bhuiyan, S. I. (2002). Nitrate and pesticide contamination of groundwater under rice-based cropping systems: Past and current evidence from the Philippines. *Agriculture, Ecosystems & Environment*, *92*(2), 185–199. https://doi.org/10.1016/S0167-8809(01)00297-3
3. Damalas, C. A., & Eleftherohorinos, I. G. (2011). Pesticide Exposure, Safety Issues, and Risk Assessment Indicators. *International Journal of Environmental Research and Public Health*, *8*(5), 1402–1419. https://doi.org/10.3390/ijerph8051402
4. Department of Environment and Natural Resources. (2016). *Water quality guidelines and general effluent standards of 2016 (DENR Administrative Order No. 2016-08)*. https://www.denr.gov.ph/
5. European Parliament and Council of the European Union. (2008). *Directive 2008/105/EC on environmental quality standards in the field of water policy*. *Official Journal of the European Union, L348*, 84–97. (As amended by Directive 2013/39/EU)
6. Keswani, C., Dilnashin, H., Birla, H., Roy, P., Tyagi, R. K., Singh, D., Rajput, V. D., Minkina, T., & Singh, S. P. (2022). Global footprints of organochlorine pesticides: A pan-global survey. *Environmental Geochemistry and Health*, *44*(1), 149–177. https://doi.org/10.1007/s10653-021-00946-7
7. Navarrete, I. A., Tee, K. A. M., Unson, J. R. S., & Hallare, A. V. (2018). Organochlorine pesticide residues in surface water and groundwater along Pampanga River, Philippines. *Environmental Monitoring and Assessment*, *190*(5), 289. https://doi.org/10.1007/s10661-018-6680-9
8. Pereira, V., Cunha, J. P., Morais, T., Ribeiro-Oliveira, J. P., & Morais, J. (2016). Physical-chemical properties of pesticides: Concepts, applications, and interactions with the environment. *Bioscience Journal*, *32*, 627–641. https://doi.org/10.14393/BJ-v32n3a2016-31533
9. Varca, L. M. (2012). Pesticide residues in surface waters of Pagsanjan-Lumban catchment of Laguna de Bay, Philippines. *Agricultural Water Management, Assessing Off-Site Migration of*

Sediments and Agrochemicals from Agricultural/Horticultural Catchments in Philippines and Australia, *106*, 35–41. https://doi.org/10.1016/j.agwat.2011.08.006