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Assessment of Hydraulic Transport of Pesticides at the Watershed: Case study Tonle Sap and Mekong River

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Abstract: *Pesticides are essential tools for agricultural productivity, yet their inherent toxicity and high mobility pose significant environmental and health risks. This study investigates the mechanisms of hydraulic transport for soluble pesticides within Cambodia's major river systems: the Bassac (BSR), Tonle Sap (TSR), and Mekong (MKR). Our analysis integrates a re-analysis of published data from 48 surface-water samples (May-June 2020, covering BSR and MKR dry and wet seasons) with new, original data (March 2025 dry season, 16 locations, 48 samples) that extends coverage to the TSR. The reinterpreted 2020 data suggested potential groundwater influence or accumulation in low-flow areas, supporting localized elevated concentrations of highly soluble pesticides, including Cypermethrin. The new 2025 data established critical hydraulic propagation pathways, confirming BSR's primary connection to MKR and its disconnection from TSR. Concurrently, a localized peak in electrical conductivity (EC) at S11-BC suggests a significant influence from sewage discharge on BSR's contaminant profile. The 2025 campaign's contaminant profile was dominated by Cypermethrin, found at an extreme localized concentration of at site 10-mk. This peak concentration results in an ecological risk of RQ ,placing it at the threshold of minimal ecological risk to aquatic life. The non-detection of other monitored pesticides, resulting in minimal to low ecological risk (RQ threshold), suggests minimal use, rapid degradation, or analytical limitations. These findings highlight the continued, risky use of banned or restricted pesticides and emphasize the critical role of localized inputs and hydraulic context in pesticide distribution. Targeted, spatio-temporal monitoring is critically needed to safeguard aquatic ecosystems in identified high-risk zones.*

Keywords: Pesticides, Transportation, Tonle Sap River, Hydraulic Connectivity, Water Management

1. INTRODUCTION

Pesticides are defined as any chemical substances, mixtures of substances or natural agents that are used in agriculture to control or kill pests, insects, rodents, weeds, and diseases. While they offer advantages like boosting productivity, safeguarding harvests, preserving food, and preventing the spread of vector-borne illnesses [1], Despite their economic benefits, the widespread application of these compounds generates significant environmental challenges, primarily stemming from their toxicity and potential to contaminate environmental compartments such as soil, air, and water [2]. The fate and transport of pesticides post-application are fundamentally governed by their intrinsic chemical properties, notably water solubility and adsorption coefficients. Highly water-soluble compounds exhibit high mobility, making them susceptible to rapid leaching into groundwater or surface runoff and subsequent transport through river networks [3], [4].

Conversely, hydrophobic compounds tend to adsorb strongly to soil and sediment particles,limiting their movement in the dissolved phase but facilitating transport when associated with suspended solids [5]. Understanding these contrasting transport dynamics is crucial for effective water resource management in agricultural regions.

In Cambodia, pesticide use has escalated significantly, with an estimated of farmers utilizing these products by 2022, leading to an estimated total annual use of 160,000 tons in 2024, primarily sourced from neighboring [6], [7]. The country 's central watershed-composed of the Tonle Sap River (TSR), the Mekong River (MKR), and the Bassac River (BSR) is a vital resource vulnerable to agricultural and urban pollution inputs.

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Previous environmental screening of the Mekong River (MKR), and the Bassac River (BSR) primary focused on pesticide occurrence in water and soil [8]. However, a dedicated analysis of the hydraulic propagation patterns that is, how flow connectivity and water chemistry influence contaminant transport is lacking. Specifically, integrating data on physical parameters (like electrical conductivity) with chemical concentrations provides a powerful approach to pinpointing sources and understanding mixing dynamics at the watershed scale. In this study, we provide a comprehensive assessment of pesticide transport dynamics in the Cambodian river system. Our objectives are to:

i) Present a targeted re-analysis of previously published pesticide data (2020 campaign) from the MKR and BSR, focusing specifically on the hydraulic transport and mobility of highly soluble compounds to establish a necessary seasonal baseline.

ii) Report new, original data from a targeted sampling campaign (March 2025) that successfully expanded coverage to include the emblematic TSR and provided full spatial coverage.

iii) Perform a quantitative analysis of detected pesticide concentrations, including their spatial distribution, ecological risk assessment, and the influence of localized factors and hydraulic connectivity on their fate within the watershed.

2. METHODOLOGY

2.1 Data Reinterpretation and Target Selection

The previous pesticide screening of the Mekong (MKR) and Bassac (BSR) river areas covered the dry and wet seasons of May-June 2020, involving 48 surface-water samples [8],[9]. For the purpose of the current study, this dataset was re-analyzed with a specific emphasis on characterizing hydraulic transport and the behavior of compounds based on their solubility. Ten representative pesticides were selected for both the re-analysis and the new campaign, comprising three herbicides (Atrazine, Isocarbamid, Fluroxypyr), five fungicides (Carbendazim, Iprobenfos, Triadimefon, DMST, Cyproconazole), and two insecticides (Cypermethrin, Tebufenozide), chosen based on local crop protection programs and their chemical properties. The core focus remained on compounds with high potential for aquatic mobility.

2.2 Sample collection

Water samples were collected during the dry season (March 2025) from sixteen distinct locations across the Tonle Sap River (sites S1 to S8), Mekong River (sites S9 and S10), and Bassac River (sites S11 to S16). All samples were collected in triplicate, totaling 48 samples. Sampling points were located 3 meters from the riverbanks at a depth of 50 cm. In-situ measurements of electrical conductivity (EC), pH, and temperature were recorded. Water flow and water level were subsequently calculated (tracking) from existing data obtained from the Mekong River Commission (MRC) database. One-liter polypropylene bottles were used for collection, and samples were immediately filtered on-site using glass microfiber filters (Whatman, GF/CTM) to remove suspended solids. Filtered samples were transported under iced conditions to the SATREPS laboratory at the Institute of Technology of Cambodia and stored at prior to extraction as shown as Figure 1.

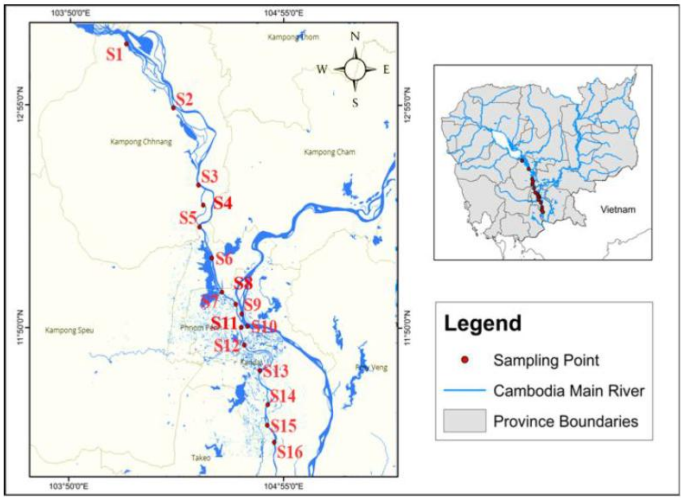

Fig. 1 Mapping of sampling sites at TSR, MKR and BSR.083

2.3 Chemicals and reagents

Sample preparation utilized a sodium phosphate buffer solution (pH = 7.0), dichloromethane (ACS BASIC), acetone, n-hexane (HPLC grade), sodium sulfate, nitrogen gas, PLS3 sorbent, and an AC cartridge.

2.4 Sample Preparation (Solid-Phase Extraction)

Solid-phase extraction (SPE) was performed on the filtered water samples. The SPE cartridge (PLS3 attached to an AC cartridge) was activated sequentially with 5 mL of dichloromethane, 5 mL of acetone, and two 5 mL aliquots of purified water. The pH of each liter of filtered sample was adjusted to 7.0 using 1 mL of sodium phosphate buffer solution. Samples were passed through the activated cartridges using a vacuum pump at approximately . Cartridges were then dried under a nitrogen gas stream for 30 minutes. Elution was performed sequentially with 2 mL of acetone and 5 mL of dichloromethane through the PLS3 cartridge, followed by 5 mL of acetone through the assembled PLS3 and AC cartridge set. The combined eluted solvent was concentrated to under a nitrogen stream. of n-hexane was added, dehydrated by passing the mixture through anhydrous sodium sulfate, and finally concentrated to for storage at prior to GC-MS analysis.

2.5 Calibration and GC-MS Analysis

An aliquot of of internal standard (IS) solution was added to each sample prior to GC-MS analysis. External standards were prepared at six concentrations (to) to quantify the target compounds. Pesticide screening was performed using a gas chromatography-mass spectrometry (GC-MS) system (Shimadzu TQ8040 series) equipped with a DB-5ms column. The GC-MS method utilized splitless injection, a temperature program from to , and ultra-pure helium as the carrier gas. Identification was based on comparison against an MS database.

2.6 Quality Control and Method Validation

Pesticide compounds were screened using a gas chromatography-mass spectrometry (GC-MS) system, model TQ8040 series (Shimadzu, Japan), utilizing an MS database containing 451 pesticide compounds for identification. A DB-5ms column (30 m length, 0.25 µm film thickness, and 0.25 mm internal diameter) was employed for separation. Samples were injected with a 1 µL volume into the GC-MS system using split less injection mode. The column oven temperature was initially held at 40 °C for 2 minutes, then increased to 310 °C at a rate of 8 °C/min and held at the final temperature for 5 minutes. Ultra-pure helium was used as the carrier gas at a flow rate of 1.23 mL/min. The ion source temperature was maintained at 200 °C, and the interface temperature was set to 300 °C. Mass spectra was acquired in scan mode over a mass-to-charge ratio (m/z) range of 33-600. Identification of pesticide residues was performed using the system's data processing software, which calculates the monoisotopic mass, predicts the structural formula of compounds, and compares these against the MS database.

2.7 Environmental risk assessment

The environmental risk assessment for the pesticides detected in the surface-water samples was performed by calculating the risk quotient (RQ) using

$$RQ = MEC \div PNEC \quad \text{(Eq.1)}$$

Where:

RQ = is the risk quotientation.

MEC = is the maximum measured environmental concentration (detected maximum concentration of each pesticide at all sites) [10] .

PNEC = is the predicted no-effect concentration (PNEC) for fresh water was obtained from various databases, such as the Norman Ecotoxicology and Pesticide Properties Database [11], (Table.1).

In the case that no lowest PNEC fresh water values were available in databases, this was calculated by dividing the no-observed-effect concentration (NOCE) value by an assessment factor (AF) obtained from Van Leeuwen and Vermeire [12].When $RQ < 0.01$ the targeted pesticide has a very low risk to aquatic organisms, and when $0.01 \leq RQ < 0.1$, the ecological risk level is low. When $0.1 \leq RQ < 1$ the targeted pesticide has a moderate risk to aquatic organisms. When $1 \leq RQ < 10$, the targeted pesticide has a high risk to aquatic organisms, and when $RQ \geq 10$, the ecological risk level is very high [12].

Table1. The value of PNEC (ug/L).

Pesticides	PNEC (ug/L)
Cypermethrin	0.0004
Atrazine-diethyl	0
Carbendazim	0.44
Cyproconazole	1.3
DMST	100
Fluroxypyr	123
Iprobenfos	0.0035
Isocarbamid	0
Tebufenozide	0.57
Triadimefon	1.5

3. RESULTS AND DISCUSSION

3.1 Physico-chemical parameters (2025 campaign)

The temperature profiles (Fig. 2) across the TSR, MKR, and BSR showed relative stability during the March 2025 dry season sampling, fluctuating narrowly between and . While this consistency minimizes the direct role of thermal variation on concentrations during the campaign, temperature remains a key factor influencing the long-term degradation and volatility of pesticides [12].

Increased temperatures lead to a faster loss of pesticide effectiveness, primarily due to accelerated degradation and physical loss. Warmer conditions enhance pesticide volatilization, solubility, and breakdown on plants. They also boost uptake by plants and increase microbial/animal activity in soil, all of which hasten degradation. While higher temperatures generally reduce pesticide adsorption in soil, the drying effect they cause can complicate this, often leading to increased adsorption. These temperature increases are generally linked to higher radiation and climatic changes [13].

The temperature profiles presented in the (Fig.2) provide baseline environmental data for the 3 Rivers. The temperature in Cambodia is normally from from 25°C to 35°C, it means that temperature of the 3 Rivers (TSR, MKR &BRR) is relatively stable. Therefore, the temperature in this study is not significantly affecting the pesticides concentrations.

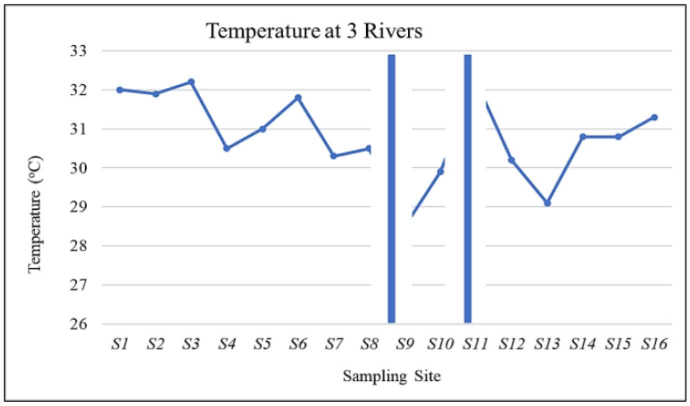

Fig. 2. The temperature along 3Rivers (TSR, MKR & BSR)

Vertical blue lines in Figures 3 and 5 represent the change from one river to another. In (Fig.3), the first one is located between sampling points (S8-TS) and (S10-MK), at the spatial location of the confluence Tonle Sap and Mekong Rivers. The second vertical line is located between sampling points (S10-MK) and (S11-BC), at the confluence between the Mekong and Bassac Rivers. The electrical conductivity (EC) from sampling point S1-TS to S8-TS remains relatively low and stable, generally fluctuating between around 110 and 130 µS/cm. There is a significant and abrupt increase in electrical conductivity between sampling point S8-TS and S10-MK, where the EC rises from around 130 µS/cm to over 300 µS/cm. It reveals that TSR and MKR have very different EC, thus allowing for an efficient differentiation of waters flow pattern in the watershed. From S12-BC to S16-BC, the electrical conductivity remains relatively stable, fluctuating between approximately 300 and 360 µS/cm, which is notably higher than the values observed in the initial Tonle Sap River samples.

Based on the Electric conductivity related to water flow from MKR, it is found that BSR receives water, and potentially pesticides, only from MKR and not from TSR. So, hydraulic transport of pesticides could not occur from TSR to BSR. This information is crucial when discussing pesticides results. These results are similar to results from [9], concentration from Mekong upstream (M1-M4) is lower than either Mekong downstream (M5-M8) and BSR (B1-B2). According to these arguments, the pesticides could not be transported through regional water flow; otherwise it moved from nearby agriculture activities

The high EC at sampling point S11-BC, reaching a peak of approximately 600 µS/cm, is potentially due to the contribution of sewage water (domestic wastewater) some location of the BSR, thus having a potentially high effect on the origin and fate of pesticide compounds.

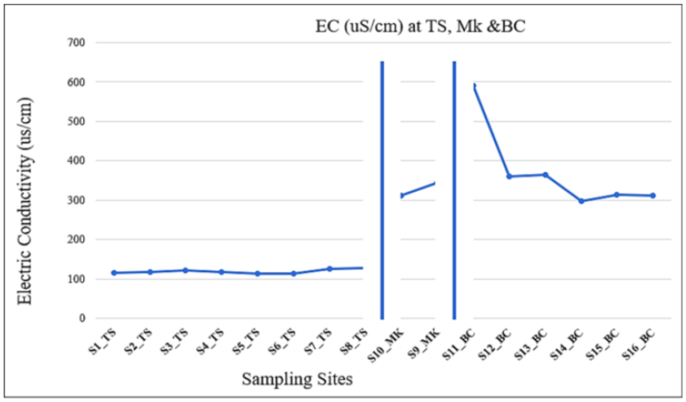

Fig. 3. Electrical conductivity EC (µS/cm)

3.2 Pesticide residues detected around 3Rivers (TSR, MKR &BSR)

(Fig.4) illustrates the spatial distribution of ten distinct pesticide compounds across various sampling sites along the three-river systems. The y-axis quantifies concentration in micrograms per liter (ug/L), ranging from 0 to 30, while the x-axis denotes sampling sites, encompassing 1-Ts through 8-Ts, 9-mk, 10-mk, and 11-Bc through 16-Bc. The pesticides analyzed included Cypermethrin, Atrazine-desethyl, Carbendazim, Cyproconazole, DMST, Fluroxypyr, Iprobenfos, Isocarbamid, Tebufenozide, and Triadimefon.

The most prominent finding from these data is that laboratory analyses indicate no detectable concentrations for any of the 10 pesticides compounds except Cypermethrin across the monitored sampling sites. Cypermethrin was found with distinct prevalence at two sampling locations. Site 10-mk exhibits an exceptionally high concentration of Cypermethrin, reaching approximately 26 ug/L. A lower, yet still noticeable, concentration of about 2.5 ug/L of Cypermethrin is also detected at site 9-mk.

This pattern of concentration strongly suggests a highly localized point source of Cypermethrin contamination at or very near sampling site 10-mk. Considering laboratory analyses as representative, the magnitude of the concentration at this specific site indicates a substantial and concentrated release into the river. Such a point source could originate from a variety of anthropogenic activities, including, but not limited to, direct discharge from industrial facilities utilizing or producing the compound, agricultural runoff from areas of intense Cypermethrin application particularly following rainfall events, inadequately treated wastewater discharge, or an accidental spill during the storage, transport, or application of

Cypermethrin products within the immediate vicinity of this sampling point.

The observed concentration gradient, provides critical insights into the transport and attenuation dynamics of this pesticide within the river network. Assuming site 9-mk is hydrologically upstream from site 10-mk, the lower concentration at 9-mk suggests either very limited upstream dispersion from the major source at 10-mk, or possibly a minor, intermittent upstream source that is largely overshadowed by the substantial input at 10-mk. More critically, the complete absence of detectable Cypermethrin at all other sampling locations further removed from site 10-mk (e.g., 1-Ts to 8-Ts) and (11-Bc to 16-Bc) would demonstrate robust natural processes of transport and attenuation. Advective transport, driven by the bulk movement of water, is the primary mechanism distributing any dissolved and suspended Cypermethrin downstream from its point of entry. Concurrently, significant dilution occurs as the contaminated water mixes with the large volumes of relatively uncontaminated water within the river system. Turbulent mixing within the river further contributes to the dispersion of the contaminant both longitudinally and laterally. Given Cypermethrin's extremely low water solubility (approximately 0.009 mg/L) and its strong tendency to adsorb to organic matter and clay particles due to its hydrophobic nature, sorption to suspended sediments plays a crucial role in its environmental fate. This process can facilitate the transport of the compound attached to solid particles, and upon subsequent sedimentation, lead to its accumulation in the riverbed, potentially serving as a long-term secondary source. While less dominant over short river stretches or in highly dynamic systems, biodegradation and photodegradation also contribute to the gradual reduction in Cypermethrin concentrations as it travels through the aquatic environment.

The consistent absence of detectable concentrations for all monitored pesticides at the majority of sampling sites highlights a crucial aspect of pesticide transport at a broader scale. This pattern indicates that the Cypermethrin contamination is likely confined to a very localized area within the immediate vicinity of site 10-mk. It strongly suggests that widespread, diffuse contamination is not occurring across the entire monitoring network for these specific pesticides at the time of sampling. Moreover, it implies that natural attenuation processes within the river system are sufficiently effective in reducing Cypermethrin concentrations below detection limits before it reaches more distant sampling points. The non-detection of the other nine pesticides throughout the study area suggests that they are either not utilized in the investigated catchments, or their environmental fate, including rapid degradation or strong immobilization in soil, prevents their significant transport into and subsequent detection within the river water.

The implications for environmental management and water resource protection are significant. The data strongly underscore the critical importance of targeted investigation and management efforts within the specific area immediately surrounding sampling site 10-mk. Strategies for controlling and mitigating Cypermethrin pollution should therefore focus on precisely identifying and addressing the exact source(s) at this localized hot-spot. Understanding the specific transport pathways, such as drainage networks or direct discharge points, will be essential for developing effective pollutant entry control strategies and safeguarding the health of the broader river ecosystem.

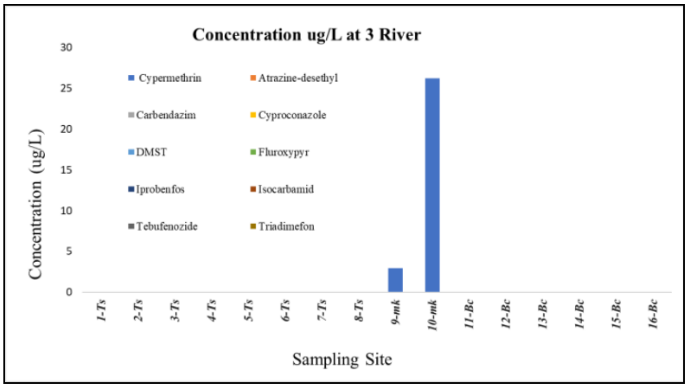

Fig. 4. Pesticides concentrations at the 3rivers (TSR, MKR &BSR) in 2025

3.3 Pesticide detected Around MKR and BSR

This section illustrates a re-interpretation from a screening of a series of pesticide compounds along the MKR and BSR was recently published by [9], state that there are 10 pesticide compounds consists of Atrazine-desethyl, Carbendazim Cyproconazole, DMST, Fluroxypyr, Iprobenfos, Isocarboxazid, Tebufenozide, Cypermethrin and Triadimefon. This research focuses on soluble pesticides and studies the spatial variation of these compounds along river flow and mixing.

Table2 . The soluble value of pesticides (g/L) [8].

No	Pesticide	Solubility (mg/L)	Level soluble
1	Atrazine	3200	High soluble.
2	Carbendazim	29	Low solubility
3	Cyproconazole	140	Moderate solubility.
4	DMST	0.9	Low solubility
5	Fluroxypyr	5700	Highly soluble,
6	Iprobenfos	430	Moderate soluble.
7	Isocarbamid	1300	Highly soluble.
8	Tebufenozide	0.83	Low solubility.

9	Triadimefon	75.6	Moderate soluble.
10	Cypermethrin	0.026	Low solubility

The reinterpreted 2020 data (Figs. 5A and 5B) showed more widespread, albeit lower, contamination for a broader range of pesticides, including Carbendazim, Cyproconazole, and Tebuconazole (measured in ng/L). This previous campaign revealed that, despite expectations for higher concentrations during the wet season due to agricultural runoff, some locations showed elevated levels during the dry season, suggesting the influence of groundwater inputs or slow-release accumulation in low-flow areas.

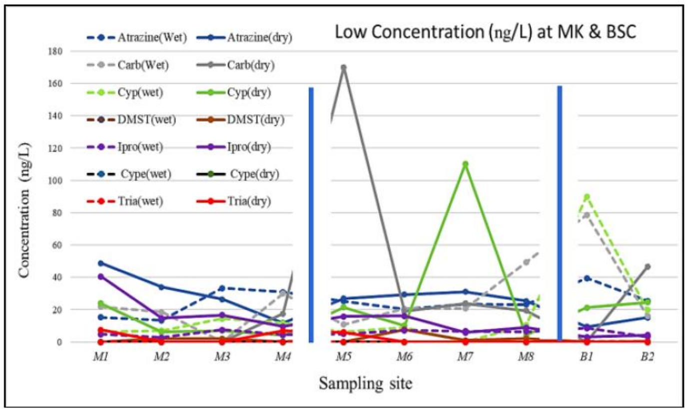

Fig. 5A. Low concentration (ng/L) at MKR and BSR.

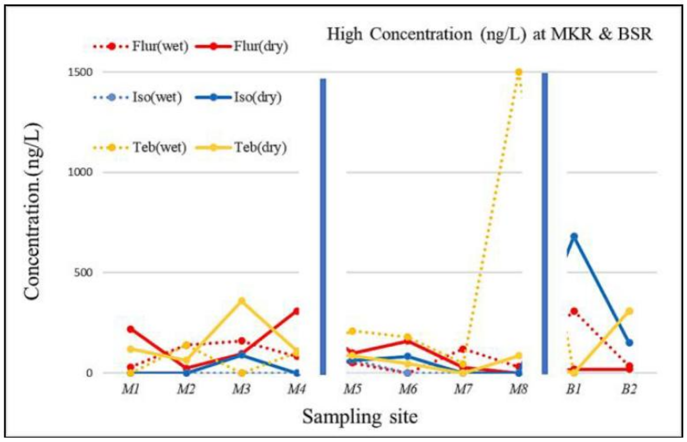

Fig. 5B. High concentration (ng/L) at MKR and BSR.

Contrasting Temporal Patterns: The 2020 data showed more distributed, lower-level contamination across the MKR and BSR, with notable seasonal peaks (e.g., Tebuconazole reaching over at M8 in the wet season). In sharp contrast, the 2025 dry season data exhibited a pattern dominated by a single, extreme, and highly localized Cypermethrin point source, while nearly all other monitored pesticides were non-detectable. This temporal difference underscores the dynamic nature of contamination, where the wet season facilitates diffuse runoff and mobilization of various compounds, while the dry season highlights the immediate, severe impact of localized point source inputs

3.4 Environmental risk assessment

The environmental risk quotient (RQ) calculation was based on the Maximum Measured Environmental Concentration (MEC) from the 2025 data, as is standard practice for assessing acute ecological risk at a confirmed contamination hotspot. While a single-time MEC is a conservative approach for chronic risk assessment, it is essential for identifying and quantifying the immediate threat posed by a catastrophic localized release.

As shown in Fig.6, Cypermethrin's calculated risk quotient is RQ . This value places Cypermethrin at the threshold between the Very Low and Low Ecological Risk categories. This indicates that while a localized concentration of was detected, the resulting risk to aquatic life, based on this specific RQ value, is minimal. The RQ values calculated for the other nine pesticides are also consistently at or below the low-risk threshold of , confirming that they pose a minimal to low ecological risk to aquatic organisms under the observed conditions. The presence of Cypermethrin, a pesticide that is reportedly restricted or banned in Cambodia, still warrants monitoring for regulatory and enforcement purposes.

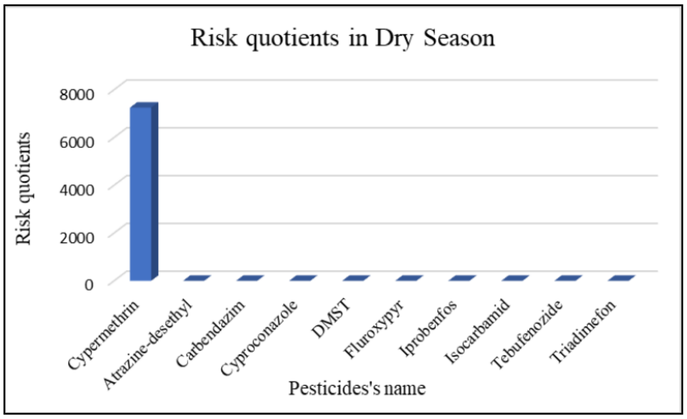

Fig. 6. The risk quotients in dry season

4. CONCLUSIONS

This study successfully analyzed pesticide propagation dynamics across the Tonle Sap, Mekong, and Bassac Rivers by integrating reinterpreted historical data with a new, targeted campaign.

The key finding from the 2025 dry season campaign is the identification of an extreme, highly localized Cypermethrin point source at site 10-mk, which reached a concentration of .

This peak concentration results in an ecological risk of RQ , indicating a minimal ecological risk to aquatic organisms.

The contrasting non-detection of the other monitored pesticides suggests either highly effective natural attenuation processes or minimal usage in the sampled catchments during the dry season. Our EC analysis clarified critical hydraulic connectivity, confirming that the Bassac River's flow and contaminant load are governed by the Mekong River. Furthermore, the localized EC peak at S11-BC demonstrated the significant influence of urban inputs, such as potential sewage contributions, on local water quality and contaminant profiles.

The findings underscore two immediate needs for water management in this vital watershed: 1) the necessity for source identification and control measures at the Cypermethrin hotspot at site 10-mk, and 2) the implementation of continuous spatio-temporal monitoring to accurately capture the seasonal variability and the complex interplay between hydraulic factors and contaminant inputs.

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