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Ecological risk estimation of organophosphorus pesticides in riverine ecosystems

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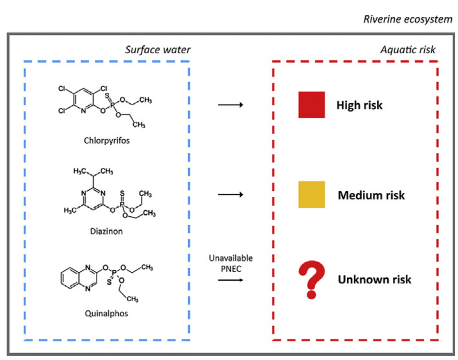
HIGHLIGHTS

- Preliminary screening of risk is vital for sustainability of riverine ecosystems.
- RQ suggests a potential risk of chlorpyrifos and diazinon in riverine ecosystems.
- Organisms and humans can be exposed to high OPP concentrations.
- Quinalphos is concerning due to the unregulated pollution risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticides are of great concern because of their existence in ecosystems at trace concentrations. Worldwide pesticide use and its ecological impacts (i.e., altered environmental distribution and toxicity of pesticides) have increased over time. Exposure and toxicity studies are vital for reducing the extent of pesticide exposure and risk to the environment and humans. Regional regulatory actions may be less relevant in some regions because the contamination and distribution of pesticides vary across regions and countries. The risk quotient (RQ) method was applied to assess the potential risk of organophosphorus pesticides (OPPs), primarily focusing on riverine ecosystems. Using the available ecotoxicity data, aquatic risks from OPPs (diazinon and chlorpyrifos) in the surface water of the Langat River, Selangor, Malaysia were evaluated based on general (RQ_m) and worst-case (RQ_{ex}) scenarios. Since the ecotoxicity of quinalphos has not been well established, quinalphos was excluded from the risk assessment. The calculated RQs indicate medium risk ($RQ_m = 0.17$ and $RQ_{ex} = 0.66$; $0.1 \le RQ < 1$) of overall diazinon. The overall chlorpyrifos exposure was observed at high risk ($RQ \ge 1$) based on RQ_m and RQ_{ex} at 1.44 and 4.83, respectively. A contradictory trend of RQs > 1 (high risk) was observed for both the general and worst cases of chlorpyrifos, but only for the worst cases of diazinon at all sites from downstream to upstream regions. Thus, chlorpyrifos posed a higher risk than diazinon along the Langat River, suggesting that organisms and humans could be exposed to potentially high levels of OPPs.

1. Introduction

Besides their conventional uses in agricultural production,

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pesticides are also used in public health control (e.g., malathion for malaria control), commercial applications (e.g., triclosan as a water disinfectant), and homes. Recently, climate change has been identified as a potential factor to ubiquitous sources and has increased the impacts of pesticides on the environment. Based on the work of Chiu et al. (2017), a future increase in pesticide use is projected based on increasing atmospheric temperatures. Thus, the ecological impacts of pesticides are likely to increase in the future. Due to the altered rainfall patterns, higher impacts are predicted in less intensive agricultural areas. The physical (e.g., altered temperature and wind pattern), chemical (e.g., degradation and transformation), and biological (e.g., changes in soil and water microbial activity) stressors are continuously affecting the environmental distribution and toxicity of pesticides (Noyes et al., 2009).

Pesticides are introduced to the environment via nonpoint (e.g., agricultural runoff and leachate) and point sources (e.g., industrial and municipal discharges) (Tankiewicz et al., 2010). Nonpoint source pollution from agricultural practices caused by natural attenuation such as rainfall, is the basis of pesticide fate and transport as well as surface water quality deterioration (Luo et al., 2008). In addition, current treatment technologies are relatively incapable of completely removing pesticides (Kuster et al., 2008; Köck-Schulmeyer et al., 2013). Besides surface water and groundwater, pesticides in the atmosphere are also of great concern due to the atmospheric transportation (long- and short-range), deposition (dry and wet), and adsorption pathways (Tankiewicz et al., 2010; Wee and Aris, 2017). Increased occurrence of pesticides causes ecological changes and a higher risk of exposure for the organisms (i.e., terrestrial, aquatic, and micro-organisms) and humans. Subsequent occurrence of pesticides in riverine ecosystems not only impacts the ecological communities but also the health of the population living in direct and/or indirect contact with pesticides. The deteriorating water quality in most water resources contributes to relatively incomplete pollutant removal in drinking water treatment plants (DWTPs) (Simazaki et al., 2015; Gou et al., 2016). Consequently, drinking water could be a potential exposure pathway for humans. Furthermore, humans are increasingly susceptible to a wide range of diseases (acute and chronic), which vary across regions and by food preferences of exposed individuals (Noyes et al., 2009). An overview of organisms and humans exposure to pesticides is demonstrated in Fig. 1. Occupational exposure (direct exposure) is a major concern because it poses a high risk for endocrine system dysfunction in workers as well as in their children (Maqbool et al., 2016). Currently, several pesticides have been listed as endocrine disrupting compounds (EDCs) due to their modes of action and mechanisms in endocrine system disruption (Mnif et al., 2011). Risk assessments are required for risk prioritization and mitigation to achieve the overall protection of the human health and ecosystems.

Toxicological effects of pesticides on organisms and humans have been proven in previous studies. Matzrafi et al. (2016) demonstrated an increased herbicide resistance in weeds caused by the modifications on their development (i.e., altered growth and morphology) and responses to herbicides (i.e., suppressed sensitivity and enhanced detoxification). Aquatic organisms, such as juvenile *Oncorhynchus kisutch* (coho salmon) experienced inhibition of brain acetylcholinesterase (AChE) (improper nervous system function) and declination of liver carboxylesterase (CaE) (impaired detoxifying ability) under organophosphorus pesticide (OPP) mixture exposure (Laetz et al., 2014). In addition, an increase in neurotoxicity was observed at elevated freshwater temperatures. Food web interactions are of great concern because insecticide chlorpyrifos-induced behavioral changes may impair predator-prey interactions (Van et al., 2014). Especially humans, being at the top of the food chain, are at a higher risk of exposure to pesticides via food ingestion, drinking water consumption, inhalation of air, and dermal contact (Fig. 1). Li et al. (2016) reported formation and adsorption of ubiquitous OPP byproducts in drinking water treatment plants. OPP pollution can be serious because OPPs are susceptible to various natural attenuation processes (e.g., volatilization, adsorption, oxidation, biodegradation, hydrolysis, and photolysis) and the degradation byproducts may have higher toxicity and persistence compared to their parent compounds (Gupta et al., 2011; Žabar et al., 2016).

This study aims to evaluate the environmental risk of exposure to OPPs (quinalphos, diazinon, and chlorpyrifos) in riverine ecosystems in the Langat River, Selangor. The Langat River Basin is located in the southern part of the Klang Valley, a national key economic area (NKEA) with large urban development. Increasing population and development makes the Langat River Basin the most populated and urbanized river basin in Malaysia that experiences significant land use changes. This study highlights the nature and the effects of OPPs, and the priorities for future research on OPP pollution in riverine ecosystems. The outcomes are relevant for effective pesticide risk mitigation measures and for decision-making in monitoring, management, and policy ratification.

2. Materials and methods

2.1. Study area

The Langat River Basin (approximately 2352 km^2) acts as a catchment area supporting 1.2 million people. The Langat River (approximately 141 km) is one of the longest rivers in the Langat River Basin, along with the Semenyih River and the Labu River. The Langat River flows from the mountainous north towards the flat west coast and ends in two estuaries: the Malacca Strait and Lumut Strait. Because of the tropical monsoon climate, the Langat River Basin experiences several periods of heavy rainfall and high humidity throughout the year. Increasing trends in annual and seasonal precipitation and temperature have been observed in the past 40 years (Amirabadizadeh et al., 2015). The OPP existence (i.e., concentration and distribution) in the surface water of the Langat River has been reported in an earlier publication (Wee et al., 2016). In this work, the study sites included the pesticide-impacted and non-impacted stretches along the Langat River ($n = 15$). The map of the sampling points is shown in Fig. 2. Several OPPs (quinalphos, diazinon, and chlorpyrifos) were quantified using an optimized analytical method based on solid phase extraction and high performance liquid chromatography coupled with diode array detector (SPE-HPLC-DAD). The developed analytical method was validated based on method accuracy (spike recovery, quinalphos = 100.21%; diazinon = 100.15%; chlorpyrifos = 32.40%), sensitivity (correlation coefficient of calibration curve, quinalphos = 0.9999; diazinon = 0.9998; chlorpyrifos = 0.9997), precision (inter-day reproducibility and intra-day repeatability, relative standard deviation < 20.00%), and limits of detection (LOD) (method detection limit, quinalphos = 0.0030 μg L^{-1}; diazinon = 0.0030 μg L^{-1}; chlorpyrifos = 0.0060 μg L^{-1}). Sample analyses revealed that chlorpyrifos (0.0202 μg L^{-1}) was the dominant OPP, followed by quinalphos and diazinon, with mean concentrations of 0.0178 μg L^{-1} and 0.0094 μg L^{-1}, respectively. The common occurrence of OPPs downstream is caused by urban discharge to tributaries that drain domestic wastes, industrial wastes, and oil palm plantation effluents to the river. OPPs upstream are mostly originated from domestic waste from residential areas, effluent waste from crop plantations, and leachate from illegal waste dumping.