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Ecological risk estimation of organophosphorus pesticides in riverine ecosystems

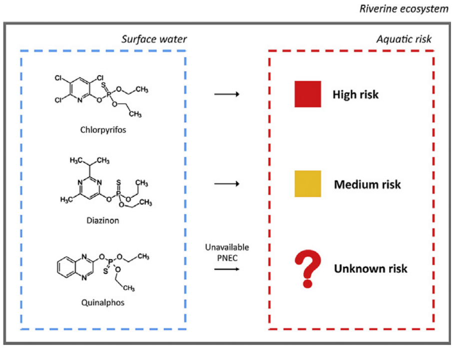
Sze Yee Wee, Ahmad Zaharin Aris*

Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

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 $RQ_{ex} = 0.66$; $0.1 \leq RQ < 1$) of overall diazinon. The overall chlorpyrifos exposure was observed at high risk ($RQ \geq 1$) 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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* Corresponding author.
E-mail address: zaharin@upm.edu.my (A.Z. Aris).

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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 $\mu g\ L^{-1}$; diazinon = 0.0030 $\mu g\ L^{-1}$; chlorpyrifos = 0.0060 $\mu g\ L^{-1}$). Sample analyses revealed that chlorpyrifos (0.0202 $\mu g\ L^{-1}$) was the dominant OPP, followed by quinalphos and diazinon, with mean concentrations of 0.0178 $\mu g\ L^{-1}$ and 0.0094 $\mu g\ L^{-1}$, 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.

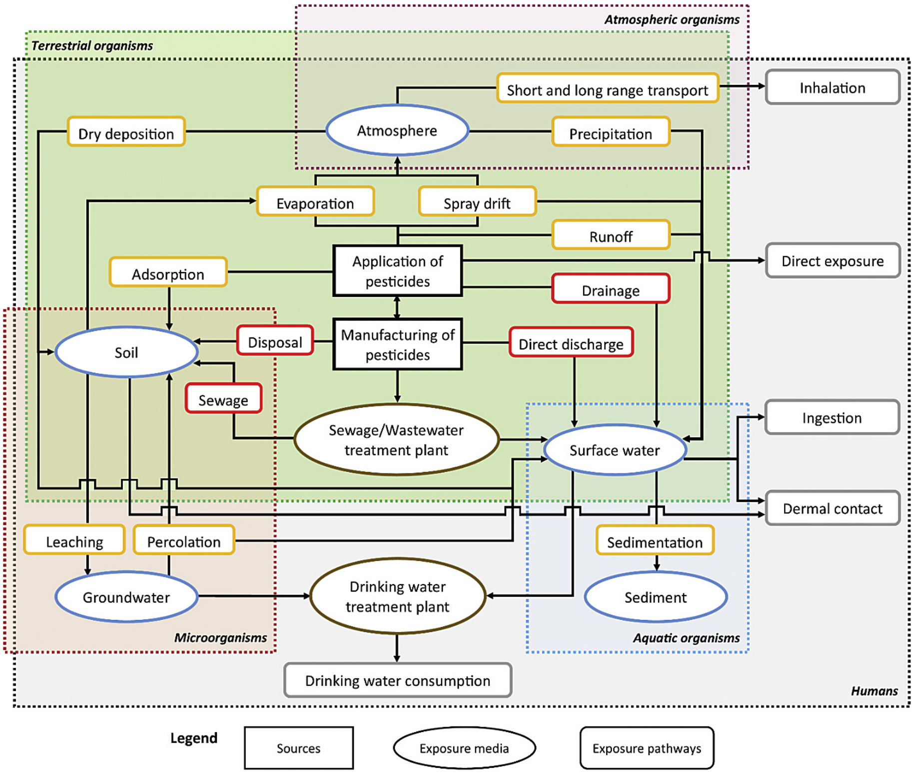


Fig. 1. Overview of organisms and humans exposure to pesticides.

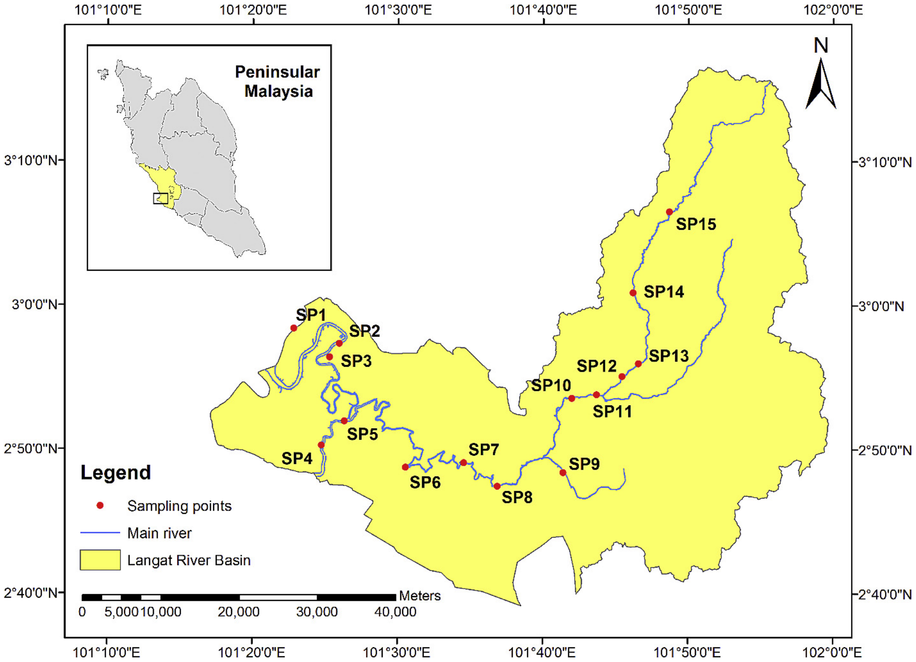


Fig. 2. Map of the sampling points in the Langat River Basin.

2.2. Risk assessment

The aquatic risk assessment of OPPs (quinalphos, diazinon, and chlorpyrifos) was performed using a deterministic method, the risk quotient (RQ) method (Xu et al., 2013; Palma et al., 2014; Montuori et al., 2016). RQ is established based on Eq. (1).

$$RQ = \mathrm{MEC}/\mathrm{PNEC} \tag{1}$$

where MEC is the mean or maximum measured environmental concentration and PNEC is the predicted no-effect concentration. PNEC is derived from the lowest toxicity value (i.e., no-observed effect concentration (NOEC) value) observed for the most

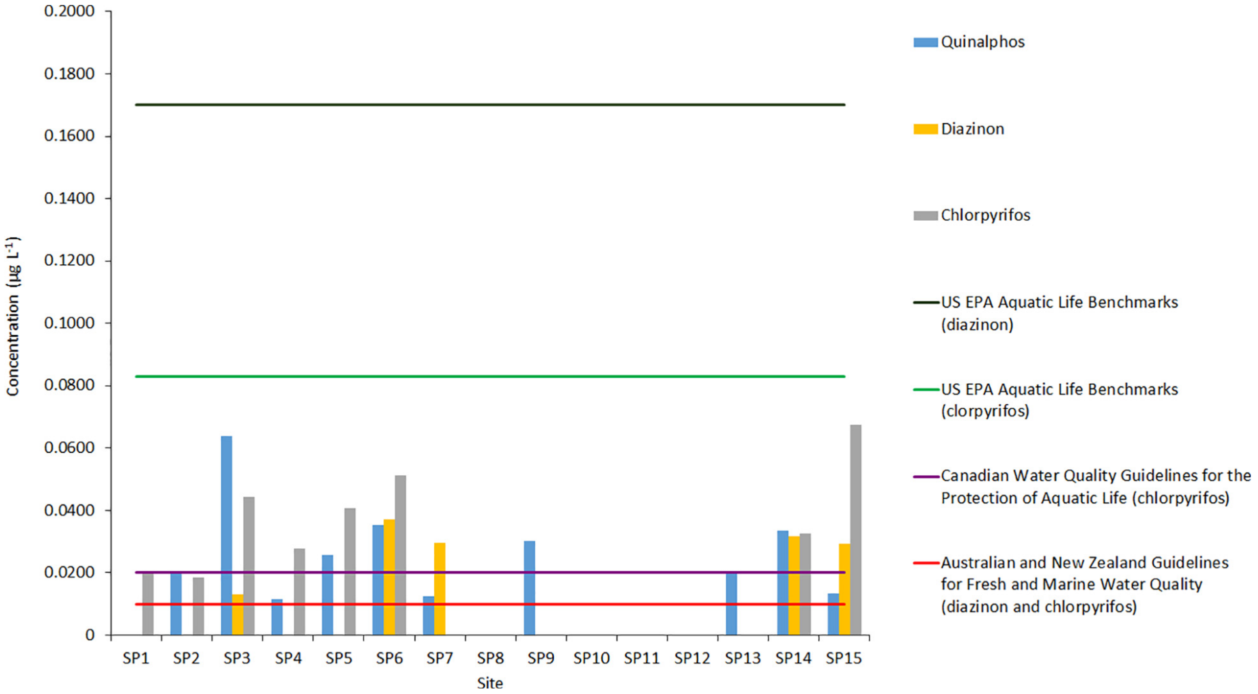


Fig. 3. Distribution of OPPs (quinalphos, diazinon, and chlorpyrifos) in surface water of the Langat River compared to (i) trigger values established under United States Environmental Protection Agency (US EPA) Aquatic Life Benchmarks (diazinon = 0.0100 µg L^{-1}; chlorpyrifos = 0.0100 µg L^{-1}), (ii) limit of Canadian Water Quality Guidelines for the Protection of Aquatic Life (chlorpyrifos = 0.0200 µg L^{-1}), and (iii) criteria maximum concentration (CMC) established under Australian and New Zealand Guidelines for Fresh and Marine Water Quality (diazinon = 0.1700 µg L^{-1}; chlorpyrifos = 0.0830 µg L^{-1}). No guideline is available for quinalphos.

sensitive species. In this aquatic risk assessment, the respective NOEC values for three trophic levels (primary producers i.e., algae; primary consumers i.e., aquatic invertebrates; secondary consumers i.e., fish) were evaluated to determine the PNEC. The ecotoxicological data were obtained from Lewis et al. (2016). An assessment factor of 10 was applied based on the available data on long-term toxicity NOECs of three species (European Commission, 2003). The mean and maximum detected concentrations were used for the general (RQ_m) and the worst-case (RQ_{ex}) scenarios, respectively. The risk ratios were classified into four risk levels: negligible risk ($RQ < 0.01$), low risk ($0.01 \leq RQ < 0.1$), medium risk ($0.1 \leq RQ < 1$), and high risk ($RQ \geq 1$) (Sánchez-Bayo et al., 2002; Palma et al., 2014). The risk quotient of the mixture (RQ_{mix}) of OPPs was calculated based on the summation of individual RQ values of each OPP (Palma et al., 2014).

3. Results and discussion

Previous studies revealed the toxic, carcinogenic, genotoxic, and neurotoxic effects of OPP exposure on the central nervous system, from neuronal responses to physiological stresses, based on the biomarkers such as the inhibition of AChE and butyrylcholinesterase (BChE) (Lionetto et al., 2013; Jin et al., 2015; Yuan et al., 2016). As demonstrated by Jin et al. (2015), chlorpyrifos induced developmental toxicity (i.e., morphological abnormality), behavioral changes, oxidative stress, and immunotoxicity in the early life stages of zebrafish. Organic matter processing and energy cycling in streams, which can lead to further alterations of freshwater ecosystems, were examined in a diazinon exposure study (Flores et al., 2014). The study presented the promoted effects of diazinon on fungus (i.e., enhanced sporulation and reduced species richness) and amphipod (i.e., reduced shredding performance and increased mortality). The effects were also observed in humans, causing diazinon-induced cytotoxicity and oxidative damage (generation of free radicals) and inducing lipid peroxidation and DNA fragmentation (Boussabbeh et al., 2016). The cytotoxic effects of quinalphos were examined by Zerin et al. (2015).

Concerns for the environmental and human health effects of OPPs led many countries to implement environmental quality standards for prioritized OPPs. Particularly, the European Union mandates risk assessments for risk mitigation through several regulations (i.e., Regulations 793/93 and 1488/94) and directives (i.e., Directive 67/548, 93/67 and Directive 98/8). However, regional regulatory actions may be less relevant in other regions because of seasonal variations, different usage patterns, and ubiquitous sources, resulting in different contamination levels and distribution of pollutants (Montuori et al., 2016). The observed concentrations of diazinon and chlorpyrifos were below the criterion maximum concentration (CMC) (diazinon = 0.1700 µg L^{-1}; chlorpyrifos = 0.0830 µg L^{-1}) established under the United States Environmental Protection Agency (US EPA) Aquatic Life Benchmarks, but exceeded the trigger values (diazinon = 0.0100 µg L^{-1}; chlorpyrifos = 0.0100 µg L^{-1}) established under the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (Fig. 3). Furthermore, most of the detected chlorpyrifos exceeded the Canadian Water Quality Guidelines for the Protection of Aquatic Life (0.0200 µg L^{-1}). Although quinalphos had demonstrated oxidative damage, antioxidant response, genetic damage, and nuclear changes in freshwater fish (*Cyprinus carpio* and *Barbonymus gonionotus*), it is not regulated in any of those guidelines (Hemalatha et al., 2015; Sadiqul et al., 2016). Based on the findings of Kegley et al. (2016), quinalphos is susceptible to rapid aerobic degradation in soil (half-life, quinalphos = 21 d; diazinon = 40 d; chlorpyrifos = 30.5 d) and hydrolysis (half-life, quinalphos = 39 d; diazinon = 138 d; chlorpyrifos = 2118 d). Zerin et al. (2015) also reported the relatively low persistence of quinalphos.

In this study, quinalphos was excluded from the risk assessment because of inadequate toxicity data (e.g., NOEC and PNEC). Toxicity

Table 1
Ecotoxicity endpoints for fish, aquatic invertebrates, and algae and RQ evaluation for OPPs (diazinon and chlorpyrifos) in surface water of the Langat River.

Compound	NOEC (μg L^{-1})				Assessment factor	PNEC (μg L^{-1})	Concentration (μg L^{-1})		RQ_m	RQ_{ex}
	Fish	Aquatic invertebrates	Algae	Critical concentration			Mean	Maximum		
Diazinon	700.00	0.56	10000	0.56	10	0.056	0.0094	0.0372	0.17	0.66
Chlorpyrifos	0.14	4.60	43	0.14	10	0.014	0.0202	0.0676	1.44	4.83
								RQ_{mix}	1.61	5.49

NOEC: No-observed effect concentration; PNEC: Predicted no-effect concentration; RQ_m: Risk quotient based on mean measured environmental concentration; RQ_{ex}: Risk quotient based on maximum measured environmental concentration; RQ_{mix}: Risk quotient of the mixture.
Source: Lewis et al. (2016) and Wee et al. (2016).

Table 2
Comparisons of OPPs (diazinon and chlorpyrifos) in surface water of the Langat River relative to other regions.

Region	Method	Diazinon					Chlorpyrifos					Reference
		LOD (ng L^{-1})	Concentration (μg L^{-1})		RQ_m	RQ_{ex}	LOD (ng L^{-1})	Concentration (μg L^{-1})		RQ_m	RQ_{ex}	
			Mean	Maximum				Mean	Maximum			
Lake Amvrakia, Greece	SPE-GCMS	0.80	0.0054	0.0526	0.10	0.94	0.60	0.0025	0.0292	0.18	2.09	Thomatou et al. (2013)
Acheloos River, Greece	SPE-GCMS	8.00	0.0310	0.0703	0.55	1.26	4.00	0.0020	0.0337	0.14	2.41	Stamatis et al. (2013)
Tiber River, Italy	SPE-GCMS	0.22	0.0029	0.0421	0.05	0.75	0.20	0.0012	0.0218	0.09	1.56	Montuori et al. (2016)
Langat River, Malaysia	SPE-HPLC-DAD	3.00	0.0094	0.0372	0.17	0.66	6.00	0.0202	0.0676	1.44	4.83	Current study

LOD: Limit of detection; RQ_m: Risk quotient based on mean measured environmental concentration; RQ_{ex}: Risk quotient based on maximum measured environmental concentration; RQ_{mix}: Risk quotient of the mixture; SPE: Solid phase extraction; GCMS: Gas chromatography mass spectrometry; HPLC-DAD: High performance liquid chromatography coupled with diode array detector.

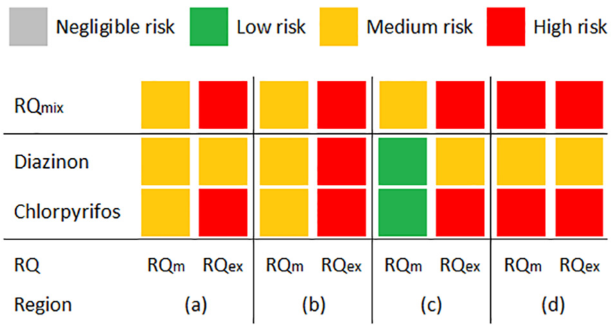


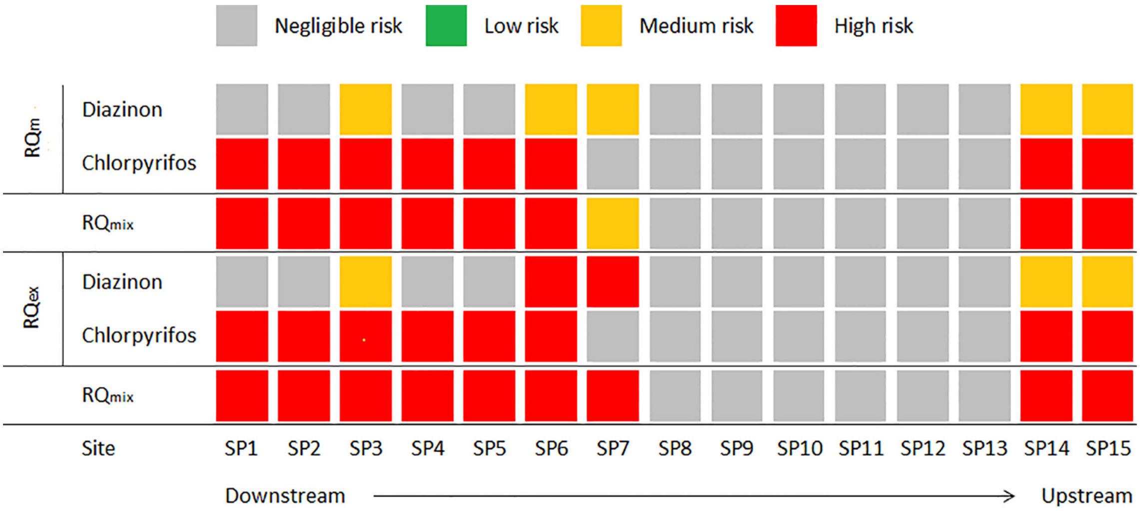
Fig. 4. RQs (RQ_m, RQ_{ex}, and RQ_{mix}) of OPPs (diazinon and chlorpyrifos) in the (a) Lake Amvrakia, (b) Acheloos River, (c) Tiber River, and (d) Langat River.

of quinalphos is yet to be elucidated although worldwide quinalphos usage and ingestion cases have been increasing because of its insecticidal and acaricidal properties (Zerin et al., 2015). Using the deterministic RQ method, higher risk from chlorpyrifos was calculated compared to the risk from diazinon. Overall, chlorpyrifos exposure was observed at high risk ($RQ \geq 1$) based on RQ_m and RQ_{ex} at 1.44 and 4.83, respectively. The calculated RQs of diazinon indicate medium risk ($RQ_m = 0.17$ and $RQ_{ex} = 0.66$; $0.1 \leq RQ < 1$). The results suggest a potential risk from diazinon and chlorpyrifos to aquatic organisms. Therefore, these two pesticides should be prioritized in risk management. Based on the higher RQ values, chlorpyrifos should be given higher priority than diazinon. RQ evaluation for OPPs in surface water of the Langat River is tabulated in Table 1. The RQ results showed that the potential risk from diazinon and chlorpyrifos should not be neglected although they are in compliance with regulations.

Table 2 shows that the observed chlorpyrifos risk in this study ($RQ_m = 1.44$ and $RQ_{ex} = 4.83$) was higher than the risk in the Tiber River ($RQ_m = 0.09$ and $RQ_{ex} = 1.56$) (Montuori et al., 2016), Acheloos River ($RQ_m = 0.14$ and $RQ_{ex} = 2.41$) (Stamatis et al., 2013), and Lake Amvrakia ($RQ_m = 0.18$ and $RQ_{ex} = 2.09$) (Thomatou et al., 2013). Stamatis et al. (2013) also calculated a high risk of diazinon (Table 2 and Fig. 4). This result indicates different mass loadings of OPPs at different regions, due to varied (a) sources of contamination, (b) instantaneous, daily, annual, or storm event loads, and (c) pesticide transport behaviors and properties (Liu et al., 2015). As reported by Montuori et al. (2016), seasonal agricultural practices with extreme meteorological and hydrological events contribute to the occurrence of OPPs in surface water. The occurrence of risk-associated OPPs in surface water of the Langat River may be due to climatic factors because the Langat River Basin experienced increasing trends in the annual and seasonal precipitation and temperature in the past 40 years (Amirabadizadeh et al., 2015). This can be a matter of great concern as Laetz et al. (2014) demonstrated the increase in the toxic effects of OPPs on juvenile coho salmon due to elevated freshwater temperatures.

A potential high risk of the OPP mixture ($RQ_{mix} > 1$) in surface water of the Langat River was also observed (Table 1 and Fig. 5). Based on RQs calculated for all sites (Fig. 5), chlorpyrifos presented a contradictory trend of RQs > 1 (high risk) for both general (RQ_m using mean MEC) and worst cases (RQ_{ex} using maximum MEC). Meanwhile, high risk from diazinon was only observed in the worst-case scenarios. The proportions of samples classified as high risk from diazinon and chlorpyrifos in the worst-case scenarios in surface water of the Langat River were 13.3% and 53.3%, respectively. This suggested that chlorpyrifos posed a higher ecological risk than diazinon, because of its relatively high occurrence and lower PNEC (Table 1). Chlorpyrifos was the commonly used pesticide in the Langat River, as reported by Osman et al. (2012) and Zubir et al. (2014).

Exposure and toxicity assessments are necessary for risk mitigation, legislation, and policy ratification. In this context, concerns on quinalphos have increased due to inadequate data and unregulated pollution levels as well as the knowledge gap in the exposure and toxicity. The selection of a risk assessment method depends on data availability (i.e., robustness and quality), assessment approach (i.e., probabilistic and possibilistic), and the type of



⬜ Negligible risk 🟩 Low risk 🟨 Medium risk 🟥 High risk

		SP1	SP2	SP3	SP4	SP5	SP6	SP7	SP8	SP9	SP10	SP11	SP12	SP13	SP14	SP15
RQ_m	Diazinon	⬜	⬜	🟨	⬜	⬜	🟨	🟨	⬜	⬜	⬜	⬜	⬜	⬜	🟨	🟨
	Chlorpyrifos	🟥	🟥	🟥	🟥	🟥	🟥	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟥	🟥
	RQ_{mix}	🟥	🟥	🟥	🟥	🟥	🟥	🟨	⬜	⬜	⬜	⬜	⬜	⬜	🟥	🟥
RQ_{ex}	Diazinon	⬜	⬜	🟨	⬜	⬜	🟥	🟥	⬜	⬜	⬜	⬜	⬜	⬜	🟨	🟨
	Chlorpyrifos	🟥	🟥	🟥	🟥	🟥	🟥	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟥	🟥
	RQ_{mix}	🟥	🟥	🟥	🟥	🟥	🟥	🟥	⬜	⬜	⬜	⬜	⬜	⬜	🟥	🟥

Fig. 5. RQs (RQ_m, RQ_{ex}, and RQ_{mix}) of OPPs (diazinon and chlorpyrifos) in surface water of the Langat River.

assessment (i.e., ecological and human health) (Geissen et al., 2015). Ecotoxicological combined effects (additive, synergistic, potentiation, or antagonistic) of pesticide mixtures can be a matter of great concern (Walker et al., 2012). Laetz et al. (2014) suggest that the synergistic effects of OPP mixtures in salmon are likely to impact the brain and liver enzyme activity, although the precise mechanisms have yet to be determined. Hence, further research on the potential combined ecotoxicological effects of OPP mixtures is still required.

The lack of risk assessments may adversely affect environmental monitoring and management efforts. Currently, environmental regulations and policy are under the threat of emerging pollutants because they are ineffective in reducing the pollution levels and risks in large-scale catchments of these pollutants. This, in turn, impacts the environmental quality and public health. Besides exposure and toxicity studies, risk assessments are vital to prioritize risks in the guidelines and standards for effective decision-making for risk mitigation.

4. Conclusion

This study presented the status of pesticide pollution in surface water of the Langat River through aquatic risk assessment. The potential aquatic risks of chlorpyrifos and diazinon were assessed based on a deterministic approach, RQ method. The results indicated that diazinon and chlorpyrifos posed a potential risk (medium and high, respectively) to aquatic organisms in the Langat River Basin. Chlorpyrifos should be given a higher priority than diazinon based on its higher RQ values. Countries and/or regions should have their own legislative guidelines and standards to regulate the environmental pesticide pollution because the contamination levels and the distribution of pollutants vary across countries and/or regions. Risk prioritization is important for decision-making in water resources management and policy implementation. The unknown risk of quinalphos in this study depicted the lack of risk assessment due to inadequate toxicity data (e.g., NOEC and PNEC). Toxicological effects of quinalphos (i.e., oxidative damage, antioxidant responses, genetic damage, and nuclear changes) warrant future studies on the toxicity assessment of quinalphos. Preliminary screening of risk (i.e., toxicity and exposure assessment, followed by risk assessment), which provides a basis for risk management plans, is critical to direct actions towards the protection and sustainability of riverine ecosystems.

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