Pyrethroid residues in Indonesian river Citarum : A simple analytical method applied for an ecological and human health risk assessment

Chemosphere

Ariyani, Miranti; Yusiasih, Retno; Endah, Een Sri; Koesmawati, Tiny Agustini; Ridwan, Yohanes Susanto et al

https://doi.org/10.1016/j.chemosphere.2023.139067

Chemosphere 335 (2023) 139067

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Pyrethroid residues in Indonesian river Citarum: A simple analytical method applied for an ecological and human health risk assessment

Miranti Ariyani [a,b], Retno Yusiasih [a], Een Sri Endah [c], Tiny Agustini Koesmawati [a], Yohanes Susanto Ridwan [a], Oman Rohman [a], Diana Rahayuning Wulan [a], Muhammad Bachri Amran [d], Mariska Margaret Pitoi [a,d,*]

[a] *National Research and Innovation Agency Indonesian - Research Center for Environmental and Clean Technology, KST Samaun Samadikun, Jl. Sangkuriang, Bandung, 40135, Indonesia*

[b] *Water System and Global Change Group, Wageningen University & Research, Droevendaalsesteeg 4, Wageningen, 6708 PB, Netherlands*

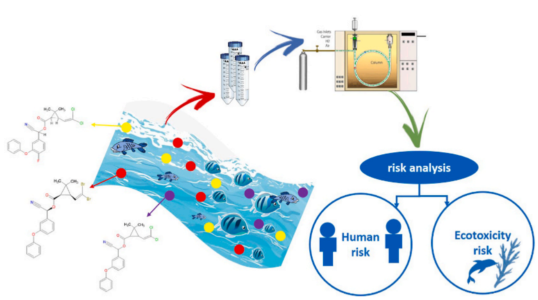
[c] *National Research and Innovation Agency Indonesian - Research Center for Applied Microbiology, KST Samaun Samadikun, Jl. Sangkuriang, Bandung, 40135, Indonesia*

[d] *Analytical Chemistry Research Group, Institut Teknologi Bandung, Bandung, 40132, Indonesia*

HIGHLIGHTS

- Pyrethroids occurrence and risk assessment in the Citarum River was first reported.
- A simple and efficient method was built and validated for pyrethroids analysis.
- β-cyfluthrin, cypermethrin, and deltamethrin, were detected in the Citarum River.
- β-cyfluthrin and deltamethrin have exceeded the Citarum river water capacity.
- Chronic non-carcinogenic risk associated to β-cyfluthrin is likely.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: A. Gies

Keywords:
Pyrethroid
Pyrethroid analysis
Water assimilative capacity
Ecotoxicity risk
Human risk

ABSTRACT

Pyrethroid residues in the Citarum River, Indonesia, was first investigated based on their occurrences, water assimilative capacity, and risk assessment. In this paper, first, a relatively simple and efficient method was built and validated for analysis of seven pyrethroids in a river water matrix: bifenthrin, fenpropathrin, permethrin, β-cyfluthrin, cypermethrin, fenvalerate, and deltamethrin. Next, the validated method was used to analyze pyrethroids in the Citarum River. Three pyrethroids, β-cyfluthrin, cypermethrin, and deltamethrin, were detected in some sampling points with concentration up to 0.01 mg/L. Water assimilative capacity evaluation shows that β-cyfluthrin and deltamethrin pollution exceed the Citarum river water capacity. However, due to hydrophobicity properties of pyrethroids, removal through binding to sediments are expected. Ecotoxicity risk assessment shows that β-cyfluthrin, cypermethrin and deltamethrin pose risks to the aquatic organisms in the Citarum River and its tributaries through bioaccumulation in food chain. Based on bioconcentration factors of the detected pyrethroids, β-cyfluthrin poses the highest adverse effect to humans while cypermethrin is the safest. Human risk assessment based on hazard index suggests that acute non-carcinogenic risk associated to consuming fish from

* Corresponding author. National Research and Innovation Agency Indonesian - Research Center for Environmental and Clean Technology, KST Samaun Samadikun, Jl. Sangkuriang, Bandung, 40135, Indonesia.

E-mail addresses: mari013@brin.go.id, mariska.pitoi@gmail.com (M.M. Pitoi).

https://doi.org/10.1016/j.chemosphere.2023.139067
Received 9 March 2023; Received in revised form 20 May 2023; Accepted 27 May 2023
Available online 4 June 2023

the study location polluted with β-cyfluthrin, cypermethrin and deltamethrin is unlikely. However, hazard quotient shows that chronic non-carcinogenic risk associated to consuming fish from the study location polluted with β-cyfluthrin is likely. However, since the risk assessment was performed separately for each pyrethroid, further assessment on the impact of mixture pyrethroid to aquatic organisms and humans should be performed to explore the real impact of pyrethroids to the river system.

1. Introduction

The application of synthetic pyrethroids is of increasing concerns in the environment. These chemicals are preferred over organophosphorus, organochlorines, and carbamates due to their higher effectivity to pests and disease and their selective toxicity (Tang et al., 2018). More reports have documented their toxicity (Xia et al., 2004; Aydın et al., 2005; Hladik and Kuivila, 2009; Kim et al., 2010; Maund et al., 2011; Abdel-Daim et al., 2013; Ogaly et al., 2015; El Ayari et al., 2022; Rivera-Dávila et al., 2022; Hutton et al., 2023) especially in mammals, such as rats. For instance, deltamethrin is neurotoxic and hepatotoxic (Anadon et al., 1996; Kim et al., 2010; Romero et al., 2012; Abdel-Daim et al., 2013; Ogaly et al., 2015; Lu et al., 2019), cypermethrin is neurotoxic, teratogenic (El Ayari et al., 2022) and is proven to exert central brain systems (Singh et al., 2012), and β-cyfluthrin is neurotoxic, hepatotoxic, and teratogenic.

Pyrethroids are hydrophobic with high *n*-octanol-water partition coefficients (K_{ow}) and high bioconcentration potential. They are less soluble in water and rapidly dissipate and accumulate into sediment and aquatic organisms thus enter the food chain (Katagi, 2011; Kumar et al., 2012; Werner and Young, 2018). Although they are biodegradable, their accumulation in sediments making them unavailable for the biodegradation. Some of them have half-lives greater than 60 days and are resistant to degradation (Werner and Young, 2018; Aznar-Alemany, 2020). Moreover, increasing application of pyrethroids along with their physical-chemical properties have allowed these compounds to enter the aquatic environment through leaching and runoff (Bao et al., 2015; Werner and Young, 2018; Firouzsalari et al., 2019).

Pyrethroids occurrences are well documented in Asian river systems and their risks to humans and aquatic organisms have been noted in China (Liu and Zhang, 2014; Zhao, 2014; Wang et al., 2023), India (Jabeen et al., 2015), Spain (Peris et al., 2022), Vietnam (Van Toan et al., 2013; Chau et al., 2015), and Pakistan (Mahboob et al., 2015). Unfortunately, the occurrence and risk assessment of pyrethroids in Indonesia were limited with only one report in soil (Ariyani et al., 2020) and none was performed for the aquatic environment.

Normally, the water ecosystem is capable to reduce concentration of pollutants based on self-purification, known as assimilative capacity (Jamshidi, 2019). The water assimilative capacity can be estimated through grey water footprint concept (Hoekstra et al., 2009). Several studies have been performed to assess the water assimilative capacity for contaminants from agricultures such as nutrients (Chapagain et al., 2006; Mekonnen and Hoekstra, 2011; Munro et al., 2016; Novo, 2017), pesticides other than pyrethroids (Paraiba et al., 2014; Vale et al., 2019), chemicals sourced from domestic waste such as pharmaceuticals (Martínez-Alcalá et al., 2018; Wöhler et al., 2020), and heavy metals (Novo, 2017). However, none of these studies assessed the water assimilative capacity of pyrethroids as pollutants.

Several analytical methods were proposed to analyze pyrethroids in water. Liquid-liquid extraction is the most popular method due to its simplicity and efficiency (Oudou and Hansen, 2002; Gil-García et al., 2006; Feo et al., 2010). However, this method is time-consuming, uses large volumes of organic solvents, and disposes large amounts of toxic chemicals (Albaseer et al., 2010). Furthermore, since pyrethroids are toxic at extremely low water concentrations, analytical methods with relatively low detection limit is required.

The aim of this study is to develop a simple and efficient liquid-liquid extraction method to assess the risk of pyrethroids to human health and ecological risk in the Citarum River. In this study, (i) a simple and efficient analytical method was developed, validated, and used to measure pyrethroid concentration in the Citarum River, (ii) the assimilative capacity of the Citarum River to pyrethroids was assessed using the grey water footprint approach, and (ii) human and ecotoxicological risk of pyrethroids was assessed based on risk quotient, hazard index, hazard quotient and carcinogenic risk.

2. Material and methods

2.1. Water sampling

The water samples were randomly collected from 7 locations in the upstream Citarum River, consisting of 6 tributaries of the Citarum River: Citarik (S1); Cirasea (S2); Cikeruh (S3); Cikapundung (S4); Cisangkuy (S5); Ciwidey (S6), and a location in the Citarum River (S7) (Fig. 1). These locations were selected because they are located downstream of the agriculture practices known to have used pyrethroids (Ariyani et al., 2020, 2022). Water sampling was conducted once in August 2021, representing the driest month according to the 10-years monthly rainfall data. While previous study shows that dry season was not a driver for pyrethroid concentration in the water (Harbourt et al., 2014), we are aware that sampling in several period of times, especially when pesticides are used with the greatest intensity, and at more locations, will result a better judgement. In this study, sampling was conducted at the dry season where the assimilative capacity of river to pyrethroids is minimum. Also, samples were taken from the upstream of the Citarum River, so the effect of pesticides residues investigated in this study is mainly from agriculture practices and not from urban life.

Water samples were collected through grab sampling. A horizontal water sampler was used to collect water. For each sampling location, water samples were grabbed from 3 different points and the water was combined as a composite sample. Samples for pyrethroids analysis taken from the composite samples were filtered and collected in pre-cleaned glass bottles. After sampling, the bottles were covered with aluminium foil and stored on ice (<4 °C). The pyrethroids analysis was performed immediately after the sampling. The quality of water for each composite sample was measured *in situ* with a water quality checker.

2.2. Apparatus and chemical

Standards of seven pyrethroids (bifenthrin, 98%; fenpropathrin, 99.5%; permethrin, 73.8% trans, 25.8% cis; β-cyfluthrin, 99.5%; cypermethrin, 99.2%; fenvalerate, 99.5% and deltamethrin, 99.3%), were all sourced from Chem Service, West Chester, USA (Table 1). These pyrethroids were chosen in preferences due to their usage and their availability in Indonesia. All solvents used in this experiment were gas chromatography (GC) or liquid chromatography (LC) grade and sourced from Merck Darmstadt, Germany. Magnesium sulphate anhydrous and other chemicals used in this study were sourced from Merck unless otherwise stated. Pyrethroids solutions were prepared in either acetone or *n*-hexane. Individual solutions were prepared for each pyrethroid at 100 ± 5 mg/L and then mixed to obtained a mix solution with final concentration of 5 mg/L for each pyrethroid. The standard solutions were then prepared by diluting the mix solution in *n*-hexane, while the spiking solutions were prepared in acetone.

2.3. Pyrethroid analysis

Method validation was conducted through spike experiment where blank samples were fortified with pyrethroids. For the spike experiment, a 30 mL of sample was transferred to a 50-mL centrifuge tube and the spiking solution was added into the sample at the desired concentrations before being submitted for extraction. For the extraction, a 3 mL solution of 1% acetone in *n*-hexane was added for each sample as the solvent. The extraction was performed in a rotary agitator spinning at 15 rpm for 60 min. The mixture was then centrifuged at 4000 rpm for 1 min and the supernatant was separated. An aliquot of the supernatant was transferred into the column containing the small piece of magnesium sulphate anhydrous to remove water before injected into the gas chromatography - electron capture detector (GC-ECD) for quantification.

For analysis of water samples, the extraction was conducted as for the spike experiment. However, in water samples analysis, no addition of pyrethroids was done.

The target pyrethroids were detected by an Agilent 7890 B gas chromatography coupled with a micro-electron capture detector (GC-μECD). Separations were performed in an Agilent HP-5 column (30 m × 0.320 mm x 0.25 μm). The separation was optimized at these conditions: injector temperature at 250 °C; injection at 1 μL with a ratio of 1:1; carrier gas He at 2 mL/min; make-up gas (N_2) at 30 mL/min; the oven temperature was initially set at 200 °C then increased to 315 °C. The oven was programmed by: (i) ramping up the initial temperature at 5 °C/min to 245 °C and hold for 1 min; (ii) ramping up at 5 °C/min to 265 °C and hold for 5 min; (iii) ramping up at 5 °C/min to 275 °C; (iv) ramping up at 20 °C/min to 315 °C and hold at 5 min.

2.4. Method validation

For method validation, parameters of linearity, accuracy, precision, and limit of detection (LoD) were evaluated. Linearity was evaluated for every target pyrethroid at concentration range of 1–500 μg/L by plotting the peak areas of each pyrethroid to their respective concentrations. Accuracy was evaluated as percent recovery values in the spiked samples at 8 μg/L. Precision was evaluated as percent relative standard (RSD) of six replicates of the blank water sample spiked with pyrethroids. LoD for every pyrethroid was established as the minimum concentration that could be detected from spiked samples at the lowest tested concentration.

2.5. Water assimilative capacity

In this study, the water assimilative capacity was adapted from the grey water footprint concept. The assimilative capacity for each pyrethroid was calculated based on maximum assimilative capacity (MAC) in the following equation (Novo, 2017):

$$MAC = \frac{C}{C_{max} - C_{nat}} \tag{1}$$

in which C (mg/L) denoted the pyrethroid concentration in the water body and C_{max} (mg/L) was the acceptable concentration for each pyrethroid. The values of C_{max} are also known as maximum residues limit (MRL). In this study the C_{max} for deltamethrin (0.004 μg/L) and permethrin (0.0004 μg/L) were generated from Canadian Water Quality Guidelines (Pawlisz et al., 1998) while other pyrethroids were obtained either from World Health Organization (Albaseer et al., 2010) or EU directive on drinking water quality (98/83/CE) (Prammer, 1998). Since anthropogenic chemicals do not naturally occur in the water, the natural concentration of pyrethroids in the receiving water body (C_{nat}) is equal to zero (Franke et al., 2013).

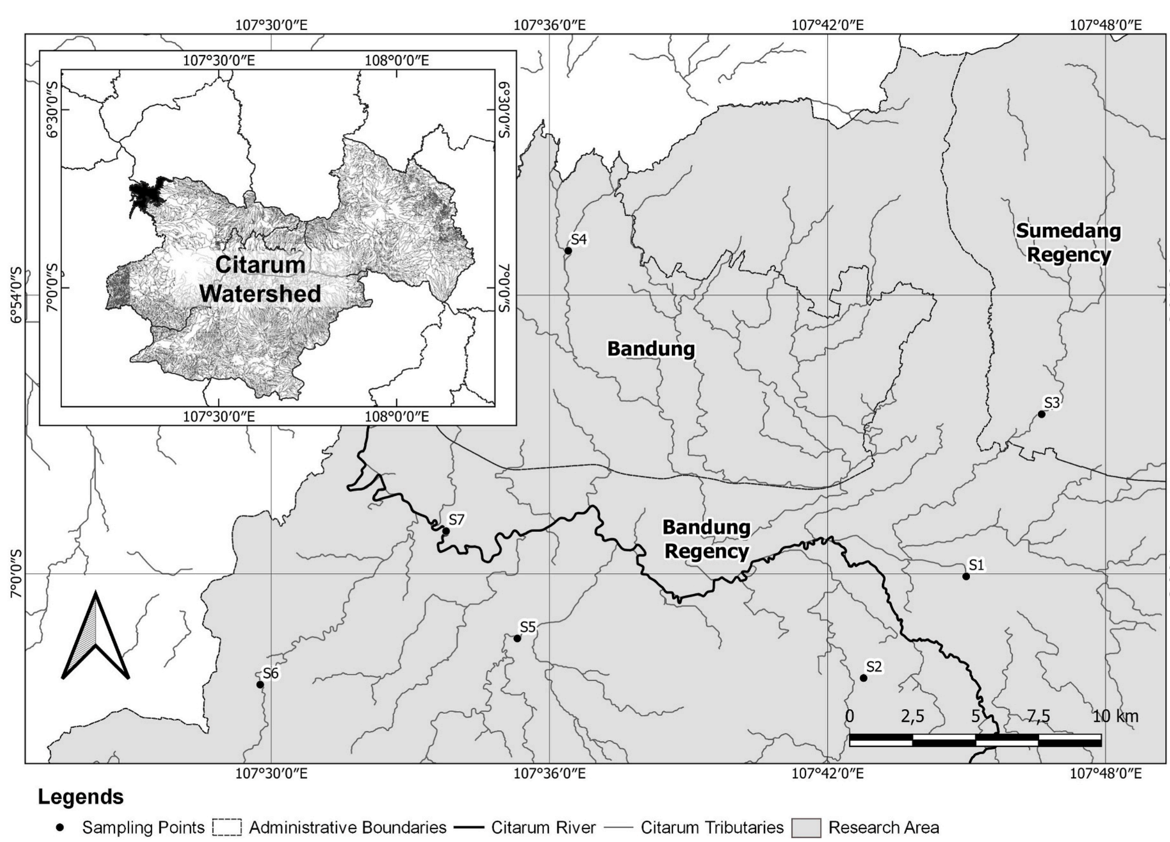
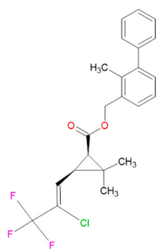
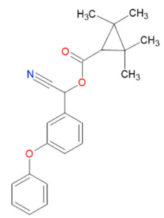
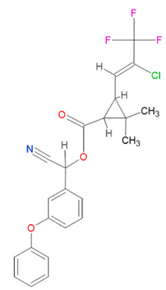
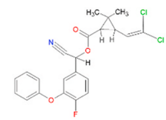
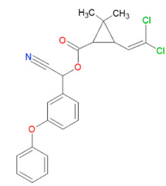
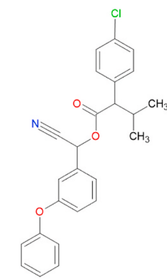
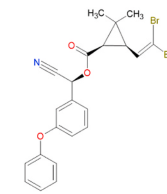


Fig. 1. Map of sampling points.

Table 1
Properties of pyrethroids.

Properties	Pyrethroids						
	bifenthrin	fenpropathrin	permethrin	β-cyfluthrin	cypermethrin	fenvalerate	deltamethrin
chemical structure							
CAS No	82657-04-3	39515-41-8	52645-53-1	68359-37-5	52315-07-8	51630-58-1	52918-63-5
IUPAC Name	(2-methyl-3-phenylphenyl) methyl (1*R*,3*R*)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate	[cyano-(3-phenoxyphenyl) methyl] 2,2,3,3-tetramethylcyclopropane-1-carboxylate	(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	[cyano-(4-fluoro-3-phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	[cyano-(3-phenoxyphenyl) methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	[cyano-(3-phenoxyphenyl) methyl] 2-(4-chlorophenyl)-3-methylbutanoate	[(*S*)-cyano-(3-phenoxyphenyl)methyl] (1*R*,3*R*)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-1-carboxylate
formula	$C_{23}H_{22}ClF_3O_2$	$C_{22}H_{23}NO_3$	$C_{21}Cl_2H_{20}O_3$	$C_{22}H_{18}Cl_2FNO_3$	$C_{22}H_{19}Cl_2NO_3$	$C_{25}H_{22}ClNO_3$	$C_{22}H_{19}Br_2NO_3$
Type	I	I/II	I	II	II	II	II
Used isomers (percentage)	1	1	2 (73.8%; 25.8%)	2 (80.0%; 19.8%)	2 (58.5%; 40.8%)	1	1
log *n*-Octanol-Water Partition Coefficient (log K_{oc})	6.00	6.00	6.50	5.95	6.60	6.20	6.20

2.6. Risk assessment

The risk assessment was conducted based on the human risk and the ecotoxicological risk. The human risk and ecotoxicological risk for the aquatic organisms inhabited in the Citarum River were assessed for each pyrethroid based on their maximum detected concentrations. The ecotoxicological risk was performed using risk quotient (RQ, **Eq. (2)**) (Papadakis et al., 2015; Peake et al., 2016):

$$RQ = \frac{MEC}{PNEC} \tag{2}$$

where MEC was the measured concentration and PNEC is the predicted no effects concentration for each pyrethroid in water for aquatic organisms. PNEC was used due to the absence of ambient water quality standard for pyrethroids (Martínez-Alcalá et al., 2018) and was calculated based on **Eq. (3)** (Smit et al., 2005).

$$PNEC = \frac{10^{-3}}{A_{SF}} \times \{LC_{50}/EC_{50}i \quad (\text{algae, daphnids, fish})\} \tag{3}$$

In this study, the assessment factor (A_{SF}) of 1000 was employed to calculate the uncertainty as a result of extrapolation of the single-species laboratory data to multi-species ecosystem (Li et al., 2020; Reis et al., 2021). The minimum value of the lethal concentration 50 (LC_{50}) or the median effective concentration (EC_{50}) of the three taxa aquatic organisms (algae, daphnia, fish) inhabited the Citarum River was also used (Smit et al., 2005).

The short term non-carcinogenic effect, long-term non-carcinogenic effect, and carcinogenic risk for each pyrethroid were represented by the hazard index (HI), hazard quotient (HQ), and carcinogenic risk (R) consecutively (USEPA, 2000; Hu et al., 2011; Shi et al., 2011; Kim et al., 2013; Liu et al., 2016). The HI ((Eq. (4))) showed the pyrethroid intake through fish consumption per kilogram body weight and was calculated from estimated short-term intake (ESTI, **Eq. (5)**) and acute reference dose (ARfD) which was adjusted based on European Union and USEPA regulations (Prammer, 1998; USEPA, 2000):

$$HI = \frac{ESTI}{ARfD} \tag{4}$$

$$ESTI = \frac{C \times DI}{BW} \tag{5}$$

where C was the highest measured concentration for each pyrethroid in fish (mg/kg). In this study, the bioconcentration factor was used to estimate the pyrethroid concentration in fish (Laskowski, 2002; Katagi, 2011). The daily intake (DI) of fish rate was adjusted to 0.086 kg, while body weight (BW) of 60 kg was used (Yusiasih et al., 2019).

The HQ (**Eq. (6)**) was calculated from the chronic daily intake (CDI, **Eq. (7)**), the amount of pyrethroid intake per kilogram body weight, and the chronic reference dose (RfD):

$$HQ = \frac{CDI}{RfD} \tag{6}$$

$$CDI = ESTI \times \frac{EF \times ED}{AT} \tag{7}$$

in which EF was the exposure frequency (days), ED was the exposure duration (years), and AT was the average lifespan (Hu et al., 2011).

The carcinogenic risk (**Eq. (8)**) was calculated from chronic daily intake (CDI), slope factor (SF) (USEPA, 2006), and age dependent adjustment factor (ADAF) (Kim et al., 2013):

$$R = CDI \times SF \times ADAF \tag{8}$$

In this study, the carcinogenic risk was only estimated for permethrin since it was the only pyrethroid in this study that has been classified as a carcinogenic compound (USEPA, 2006).

3. Result and discussion

3.1. Validation of the analytical procedure

The proposed method only used small amount of solvent (3 mL) during extraction and did not involve clean-up step, where materials or adsorbent usually used, afterwards. Evaporation, which is usually involved in pesticide analysis (Yusiasih et al., 2021), was also eliminated from this method. Therefore, in terms of the number and amount of chemicals used in this method, this method is relatively simple and efficient. However, it must be noted that the extraction time is 60 min thus it is relatively time consuming. The analytical performance of the GC- μECD method (Table 2) was satisfied for the target pyrethroids, with wide linear ranges and the correlation coefficients of seven calibration curves were also satisfied, ranging from 0.9936 to 0.9997. The percent recoveries of pyrethroids fell from 80.70 to 114.1%. These values were below the values suggested by both European Commission (EC, 2010) and AOAC International (AOAC, 2016). The repeatability (% RSD) of the method for all pyrethroids were from 1.87 to 6.72%. These values were all below the suggested value of AOAC International (AOAC, 2016) which was 16%. The LoD of pyrethroid ranged from 1.67 to 8.67 μg/L. Compare to other studies (Hu et al., 2015; Yang et al., 2016a, 2016b; Han et al., 2018; Lu et al., 2018; Qian et al., 2018; Riaz et al., 2018; Wang et al., 2018; Liu et al., 2019), the LoD obtained in this study is higher. However, it must be note that other methods use either special adsorbent, advanced material, or eutectic solvents that must be synthetized or relatively toxic solvents.

3.2. Pyrethroid concentrations and water assimilative capacity

In this study, only three pyrethroids: β-cyfluthrin, cypermethrin, and deltamethrin, were detected in sampling points with concentrations up to 0.01 mg/L (see Table 3). For other pyrethroids with "not detected" status, their concentration in the sampling points were defined as LOD/2 (Liu et al., 2020). Concentrations of β-cyfluthrin, and deltamethrin in Citarik (S1), Ciwidey (S6), and the Citarum River (S7) were exceeded their MRLs. However, pyrethroids are hydrophobic so they are likely to be removed from the water and bind to sediments (Jabeen et al., 2015).

Pyrethroid were frequently detected in surface water in several regions. For example in Bangladesh (Hossain et al., 2015); Mexico (Moreno-Villa et al., 2012); Vietnam (Van Toan et al., 2013); China (Wang et al., 2013; Zhao, 2014); and United States (Delgado-Moreno et al., 2011) and most of the time, their concentrations were below 5 μg/L (Tang et al., 2018). However, in some cases, pyrethroids were detected at higher concentrations up to 13 mg/L (Tang et al., 2018). Due to their hydrophobicity characteristic, pyrethroids are likely to be accumulated in the solid particles such as sediments (Li et al., 2017; Tang et al., 2018). Therefore, the levels of pyrethroids residues in surface water were likely

Table 2
Method evaluation.

Pyrethroids	% RSD	% Rec	Linear regression (r)	LoD (μg/L)
bifenthrin	4.92	106.3–111.5	y = 5.57E5 x + 1.84E7 (0.9936)	8.33
fenpropathrin	4.49	91.5–96.3	y = 9.52E5 x + 8.17E6 (0.9988)	8.47
permethrin	3.52	94.6–100.2	y = 3.27E5 x + 1.09E7 (0.9987)	8.43
β-cyfluthrin	2.67	102.5–108.5	y = 1.31E6 x −5.81E6 (0.9997)	1.69
cypermethrin	1.87	91.7–95.1	y = 8.92E5 x + 1.15E7 (0.9983)	1.79
fenvalerate	5.72	80.7–86.8	y = 9.34E5 x + 2.02E7 (0.9959)	8.67
deltamethrin	6.72	108.4–114.1	y = 1.03E6 x + 8.60E6 (0.9992)	1.67

Table 3
Concentration (mg/L) of pyrethroid in Citarum river.

Location	Residues (mg/L)		
	β-cyfluthrin	cypermethrin	deltamethrin
Citarik (S1)	n.d (8.45×10^{-4})	n.d (8.95×10^{-4})	0.005 ± 2.82
Cirasea (S2)	n.d (8.45×10^{-4})	n.d (8.95×10^{-4})	n.d (8.35×10^{-4})
Cikeruh (S3)	n.d (8.45×10^{-4})	n.d (8.95×10^{-4})	n.d (8.35×10^{-4})
Cikapundung (S4)	n.d (8.45×10^{-4})	n.d (8.95×10^{-4})	n.d (8.35×10^{-4})
Cisangkuy (S5)	n.d (8.45×10^{-4})	n.d (8.95×10^{-4})	n.d (8.35×10^{-4})
Ciwidey (S6)	0.01	0.004	n.d (8.35×10^{-4})
Citarum (S7)	0.009	n.d (8.95×10^{-4})	0.004

n.d = not detected.

to be lower than in sediments. Also, high hydrophobicity of pyrethroids is likely resulting in elevated bioconcentration in biota. In this study, pyrethroids concentrations in several sampling points in the Citarum River and its tributaries were relatively high (up to 10 μg/L) and due to their hydrophobicity properties, their concentrations in the sediments are likely to be higher than detected in this study.

Data from Table 3 was then used to calculate MAC and the result was given in Table 4. If MAC is equal to 1, the water capacity is the same as the pollution level, thus higher MAC values indicate pollution level that are higher than the water capacity (Novo, 2017). In this study, MAC values were only calculated for the detected pyrethroids (>LOD): β-cyfluthrin, cypermethrin, and deltamethrin. MAC values of β-cyfluthrin and deltamethrin are >1, implying that the concentrations of β-cyfluthrin and deltamethrin in water have exceeded the water capacity. Therefore, the water system is under stress (Keller and Cavallaro, 2008; Novo, 2017). On the contrary, the MAC value of cypermethrin is less than 0.1, suggesting that cypermethrin pollution is lower than the water capacity. It is important to note that from the seven studied pyrethroids, deltamethrin has the lowest C_{max} value (Table 4). Therefore, deltamethrin has the highest chance to put the system under stress.

Unlike other contaminants that are easily break down through natural process, pyrethroids will remain in the long-term either in water or sediment and prolong the attenuation process through natural assimilative capacity (Hossain et al., 2015). While pyrethroids are biodegradable, they tend to be bind to sediments thus are not available for biodegradation and making them persistent. For instance, the maximum half-life for cypermethrin is 619 days and β-cyfluthrin is 183 days. The persistency of pyrethroids making them available to aquatic organisms and enter the food chain through bioaccumulation.

3.3. Risk assessment

Using the maximum concentration of each detected pyrethroid in the water, the ecotoxicity risk based on RQ values and the human risk based on HQ and HI values were assessed. The toxicological properties which were used to estimate the PNEC are presented in Table 4. Our study showed that the detected pyrethroids have high RQ values. RQ value of less than 1 is considered to have insignificant risk to the environment thus immediate management is not required (Peake et al., 2016). The high RQ values for β-cyfluthrin, cypermethrin, and deltamethrin (>8000000) suggesting that these pyrethroids pose high risks to the aquatic organisms in Citarum River and its tributaries. This result is in line with the studies conducted in Europe where several pyrethroids, including deltamethrin, are identified as contaminants with high RQ (Lettieri et al., 2016; Werner and Young, 2018; Peris et al., 2022). Since the RQ values for the detected pyrethroids are 6 order of magnitude higher than the insignificant risk value, immediate management for contamination of the detected pyrethroids is needed for the Citarum River system.

Table 4
Ecotoxicological risk and water assimilative capacity assessment.

Pesticide	MEC (mg/L)	PNEC (mg/L)	Cmax (mg/L)	RQ	MAC
bifenthrin	ND	1.26E-09	1E-04	–	–
fenpropathrin	ND	5.3E-10	1E-04	–	–
permethrin	ND	1.26E-09	4E-06	–	–
B-cyfluthrin	0.01	2.9E-10	2E-04	3.79 E+07	55
cypermethrin	0.004	4.8E-10	5E-02	8.33 E+06	0.8
fenvalerate	ND	1.35E-09	5E-02	–	–
deltamethrin	0.005	7.4E-11	4E-07	6.76 E+07	12500

Several studies have demonstrated that the Citarum River is the habitat for aquatic organisms from various tropic levels such as green algae, crustaceans, to various species of fish (Putra and Lili, 2012; Sunardi et al., 2012; Muntalif et al., 2016). Due to their K_{OW} and K_{OC} properties, pyrethroid with log $K_{OW} > 4.5$ such as cypermethrin (6.5) and β-cyfluthrin (5.94) may dissipate from the water column and bind to the solid particles in sediments (Laskowski, 2002; Werner and Young, 2018). These properties also responsible to pyrethroids risk to the aquatic sediment-dwelling organisms (Li et al., 2017), since they may bio-accumulate into the organisms from the higher trophic level through the food chain mechanism. Moreover, metabolism and elimination of pyrethroids in fish are slower than in mammals or birds due to insufficient hydrolytic enzymes for pyrethroids in fish (Aydın et al., 2005; Kumar et al., 2012; Richterova and Svobodová, 2012; Brander et al., 2016). Therefore, pyrethroids are more toxic to fish than to other aquatic organisms.

In this study, the bioconcentration factor for each pyrethroid (Laskowski, 2002) was used to calculate the concentrations of pyrethroids in fish (Table 5 and 6). The maximum values of the concentrations were then used for the human risk assessment in Table 6. Assuming that fish in study locations was consumed, using fish daily intake data for Indonesia, the acute and chronic risk represented by HI and HQ were estimated. However, since permethrin; the one and only pyrethroid which considered as carcinogenic compound; was not detected in all study location, the carcinogenic risk due to pyrethroid contamination in fish was neglected. The HI for β-cyfluthrin, cypermethrin, and deltamethrin are 0.57; 0.017; and 0.5 respectively while the HQ are 2.27; 0.342; and 0.5 respectively. For adults with 60 kg of bodyweight, the HI values are lower than 1, suggesting no short-term non-carcinogenic effect are likely to be resulted from fish consumption from the sampling points (Yusiasih et al., 2021). Similarly, the HQ values for cypermethrin and deltamethrin do not exceed 1, suggesting no long-term non-carcinogenic effect are likely. However, the HQ value of β-cyfluthrin is higher than 1, suggesting that long-term non-carcinogenic effect related to β-cyfluthrin contamination is possible and cannot be neglected. Fortunately, the chronic toxicity due to the exposure of low-concentration of pyrethroid does not cause any specific symptoms, unless it is combined with the nerve disease (Aznar-Alemany, 2020).

Several studies have reported the presence of deltamethrin, and cypermethrin in fish tissue. For instance, deltamethrin and cypermethrin were detected in fish from Indus River (Jabeen et al., 2015). Similar to our study, the toxicity risk due to the daily intake was negligible. Moreover, the accumulation of pyrethroid in human shall become of concerns since pyrethroid has been documented in humans' urine (Heudorf et al., 2004), hair and blood of pregnant women (Ostrea et al., 2009; Channa et al., 2012), and humans' breast milk (Zehringer et al., 2001; Corcellas et al., 2012) and these may lead to reproductive system disorders (Aznar-Alemany, 2020). However, since the ecotoxicity and human risk assessment in this study are performed individually, further study is required to investigate the impact of mixed pyrethroids contaminations.

4. Conclusion

A relatively simple and efficient method, which did not include

Table 5
Toxicology properties of each pyrethroid to aquatic organism from different taxa.

Taxa	Organism	EC_{50}/LC_{50} (mg/L)						
		bifenthrin	fenpropathrin	permethrin	β-cyfluthrin	cypermethrin	fenvalerate	deltamethrin
Algae	Green algae	0.43	–	0.004	2.37	0.0272	–	9.1
Crustacean	*Daphnia magna*	0.001	0.0005	0.001	0.0003	0.0005	0.002	0.004
Fish	*Poecilia reticulata*	–	–	0.245	0.02	0.122	–	0.005
	Oreochromis niloticus	–	–	0.027	0.016	0.64	0.015	0.001
	Oreochromis mossambicus	–	–	0.004	–	0.01	0.026	0.0008
	Clarias gariepinus	–	–	–	0.21	0.21	0.001	0.004
	Cyprinus carpio	0.075	0.003	0.006	0.25	0.25	0.002	0.00007
	Xiphophorus helleri	–	–	–	–	–	–	

Table 6
Human risk assessment.

	β Cyfluthrin	Cypermethrin	Deltamethrin
Concentration (mg/L) C	0.011	0.004	0.005
Concentration in fish (mg/L) C	7.9	2.38	3.49
Daily intake (kg/day) DI	0.086	0.086	0.086
Exposure frequency (days) EF	365	365	365
Exposure duration (years) ED	70	70	70
Body weight (kg) BW	60	60	60
Average lifespan AT	25550	25550	25550
Acute reference dose (mg/kg) ARfD	0.02	0.2	0.01
Estimated short time intake ESTI	0.011	0.003	0.005
Hazard index HI	0.57	0.017	0.5
Chronic daily intake CDI	0.011	0.003	0.005
Chronic reference dose (mg/kg) RfD	0.005	0.01	0.01
Hazard quotient HQ	2.27	0.342	0.5
Slope factor SF	–	–	–
Age-dependent adjustment factor ADAF	–	–	–
Carcinogenic risk R	–	–	–

clean-up step and evaporation, was validated for pyrethroid analysis in river water. Three pyrethroids, β-cyfluthrin, cypermethrin, and deltamethrin, were detected in samples. From those pyrethroids, β-cyfluthrin, and deltamethrin pollution have exceeded the river water capacity. However, since pyrethroids are relatively hydrophobic, they may be removed from water and bind to sediment. The ecotoxicity risk analysis showed that β-cyfluthrin and deltamethrin pose adverse risk to the aquatic organisms in the Citarum River and its tributaries through bioaccumulation in the food chain. Hazard index of adults for β-cyfluthrin, deltamethrin, and cypermethrin were less than 1 thus acute risk associated with fish consumption from the study location contaminated with these pyrethroids is unlikely. However, hazard quotient value shows that chronic non-carcinogenic risk to human resulted from consuming fish contaminated with β-cyfluthrin is likely thus pyrethroid contamination in fish from the study location should be considered. Moreover, further study on the risk assessment of mixed pyrethroids to aquatic organisms should be performed in the future.

Author contribution

Miranti Ariyani: Writing - Original Draft, Investigation, Formal analysis. **Retno Yusiasih**: Conceptualization, Methodology, Investigation. **Een Sri Endah**: Investigation. **Tiny Agustini Koesmawati**: Resources. **Yohanes Susanto Ridwan**: Resources. **Oman Rohman**: Investigation. **Diana Rahayuning Wulan**: Resources. **Muhammad Bachri Amran**: Writing - Review & Editing. **Mariska Margaret Pitoi**: Conceptualization, Visualization, Formal analysis, Writing - Review & Editing.

Funding

This research was partly supported by INSINAS 2020–2021 Research Grant Program from the Ministry of Research and Technology Indonesia.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors wish to thank Muhamad Hanif Resgi Putranto for his help for map preparation. The authors also acknowledge the facilities and scientific support through E-Layanan Sains, National Research and Innovation Agency.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139067.

References

Abdel-Daim, M.M., Abuzead, S.M., Halawa, S.M., 2013. Protective role of Spirulina platensis against acute deltamethrin-induced toxicity in rats. PLoS One 8, e72991.
Albaseer, S.S., Rao, R.N., Swamy, Y., Mukkanti, K.J.J.o.C.A., 2010. An overview of sample preparation and extraction of synthetic pyrethroids from water. sediment and soil 1217, 5537–5554.
Anadon, A., Martinez-Larranaga, M., Fernandez-Cruz, M., Diaz, M., Fernandez, M., Martinez, M.J.T., Pharmacology, A., 1996. Toxicokinetics of deltamethrin and its 4′-HO-metabolite in the rat. 141, 8–16.
AOAC, 2016. Appendix F: guidelines for standard method performance requirements. In: Official Methods of Analysis of AOAC.
Ariyani, M., Pitoi, M.M., Koesmawati, T.A., Maulana, H., Endah, E.S., Yusiasih, R., 2020. Pyrethroid residues on tropical soil of an Indonesian tea plantation: analytical method development, monitoring, and risk assessment. J. Sustain. Environ. Res. 30, 1–10.
Ariyani, M., Pitoi, M.M., Yusiasih, R., Maulana, H., Mastur, A.I., Koesmawati, T.A., Sunardi, Ridwan Y.S., 2022. Water footprint analysis of Indonesian tea: exploring the impact pesticides on the grey water footprint. Environment Asia 15 (1), 47–59.
EC, 2010. Guidance Document on Pesticide Residue Analytical Methods. European Commision. SANCO/825/00 rev. 8.1).

Aydın, R., Köprücü, K., Dörücü, M., Köprücü, S.Ş., Pala, M., 2005. Acute toxicity of synthetic pyrethroid cypermethrin on the common carp (Cyprinus carpio L.) embryos and larvae. Aquacult. Int. 13, 451–458.

Aznar-Alemany, Ò., 2020. Introduction to pyrethroid insecticides: chemical structures, properties, mode of action and use. In: Eljarrat, E. (Ed.), Pyrethroid Insecticides. Springer, Switzerland, pp. 1–16.

Bao, L.-J., Wei, Y.-L., Yao, Y., Ruan, Q.-Q., Zeng, E.Y., 2015. Global trends of research on emerging contaminants in the environment and humans: a literature assimilation. Environ. Sci. Pollut. Control Ser. 22, 1635–1643.

Brander, S.M., Jeffries, K.M., Cole, B.J., DeCourten, B.M., White, J.W., Hasenbein, S., Fangue, N.A., Connon, R.E., 2016. Transcriptomic changes underlie altered egg protein production and reduced fecundity in an estuarine model fish exposed to bifenthrin. Aquat. Toxicol. 174, 247–260.

Channa, K., Röllin, H.B., Nøst, T.H., Odland, J.Ø., Sandanger, T.M., 2012. Prenatal exposure to DDT in malaria endemic region following indoor residual spraying and in non-malaria coastal regions of South Africa. Sci. Total Environ. 429, 183–190.

Chapagain, A.K., Hoekstra, A.Y., Savenije, H.H., Gautam, R.J.E.e., 2006. The water footprint of cotton consumption: An assessment of the impact of worldwide consumption of cotton products on the water resources in the cotton producing countries 60, 186–203.

Chau, N.D.G., Sebesvari, Z., Amelung, W., Renaud, F.G., 2015. Pesticide pollution of multiple drinking water sources in the Mekong Delta, Vietnam: evidence from two provinces. Environ. Sci. Pollut. Res. 22, 9042–9058.

Corcellas, C., Feo, M.L., Torres, J.P., Malm, O., Ocampo-Duque, W., Eljarrat, E., Barceló, D., 2012. Pyrethroids in human breast milk: occurrence and nursing daily intake estimation. Environ. Int. 47, 17–22.

Delgado-Moreno, L., Lin, K., Veiga-Nascimento, R., Gan, J., 2011. Occurrence and toxicity of three classes of insecticides in water and sediment in two southern California coastal watersheds. J. Agric. Food Chem. 59, 9448–9456.

El Ayari, T., Mhadhbi, L., Trigui El Menif, N., El Cafsi, M.h., 2022. Acute toxicity and teratogenicity of carbaryl (carbamates), tebufenpyrad (pyrazoles), cypermethrin and permethrin (pyrethroids) on the European sea bass (Dicentrarchus labrax L, 1758) early life stages. Environ. Sci. Pollut. Res. 29, 66125–66135.

Feo, M.L., Ginebreda, A., Eljarrat, E., Barceló, D.J.J.o.H., 2010. Presence of pyrethroid pesticides in water and sediments of Ebro River Delta 393, 156–162.

Firouzsalari, N.Z., Shakerkhatibi, M., Pourakbar, M., Yadeghari, A., Safari, G.H., Sarbakhsh, P., 2019. Pyrethroid pesticide residues in a municipal wastewater treatment plant: occurrence, removal efficiency, and risk assessment using a modified index. J. Water Process Eng. 29, 100793.

Franke, N., Boyacioglu, H., Hoekstra, A.Y., 2013. Grey Water Footprint Accounting: Tier 1 Supporting Guidelines. Unesco-Ihe Delft, The Netherlands.

Gil-García, M., Barranco-Martínez, D., Martínez-Galera, M., Parrilla-Vázquez, P., 2006. Simple, rapid solid-phase extraction procedure for the determination of ultra-trace levels of pyrethroids in ground and sea water by liquid chromatography/ electrospray ionization mass spectroscopy. Rapid Commun. Mass Spectrom. 20, 2395–2403.

Han, Q., Aydan, T., Yang, L., Zhang, X., Liang, Q., Ding, M., 2018. In-syringe solid-phase extraction for on-site sampling of pyrethroids in environmental water samples. Anal. Chim. Acta 1009, 48–55.

Hladik, M.L., Kuivila, K.M., 2009. Assessing the occurrence and distribution of pyrethroids in water and suspended sediments. J. Agric. Food Chem. 57, 9079–9085.

Hoekstra, A.Y., Chapagain, A., Martinez-Aldaya, M., Mekonnen, M., 2009. Water Footprint Manual: State of the Art 2009.

Hossain, M., Chowdhury, M.A.Z., Pramanik, M.K., Rahman, M., Fakhruddin, A., Alam, M.K., 2015. Determination of selected pesticides in water samples adjacent to agricultural fields and removal of organophosphorus insecticide chlorpyrifos using soil bacterial isolates. Appl. Water Sci. 5, 171–179.

Hu, Y., Qi, S., Zhang, J., Tan, L., Zhang, J., Wang, Y., Yuan, D., 2011. Assessment of organochlorine pesticides contamination in underground rivers in Chongqing, Southwest China. J. Geochem. Explor. 111, 47–55.

Hu, L., Zhang, P., Shan, W., Wang, X., Li, S., Zhou, W., Gao, H.J.T., 2015. In situ metathesis reaction combined with liquid-phase microextraction based on the solidification of sedimentary ionic liquids for the determination of pyrethroid insecticides in water samples 144, 98–104.

Hutton, S.J., Siddiqui, S., Pedersen, E.I., Markgraf, C.Y., Segarra, A., Hladik, M.L., Connon, R.E., Brander, S.M., 2023. Comparative behavioral ecotoxicology of Inland Silverside larvae exposed to pyrethroids across a salinity gradient. Sci. Total Environ. 857, 159398.

Jabeen, F., Chaudhry, A.S., Manzoor, S., Shaheen, T., 2015. Examining pyrethroids, carbamates and neonicotenoids in fish, water and sediments from the Indus River for potential health risks. Environ. Monit. Assess. 187, 1–11.

Jamshidi, S., 2019. An approach to develop grey water footprint accounting. Ecol. Indicat. 106, 105477.

Katagi, T., 2011. Environmental behavior of synthetic pyrethroids. In: Pyrethroids: from Chrysanthemum to Modern Industrial Insecticide. Springer Berlin, Heidelberg, pp. 167–202.

Keller, A.A., Cavallaro, L., 2008. Assessing the US Clean Water Act 303 (d) listing process for determining impairment of a waterbody. J. Environ. Manag. 86, 699–711.

Kim, K.-B., Anand, S.S., Kim, H.J., White, C.A., Fisher, J.W., Tornero-Velez, R., Bruckner, J.V., 2010. Age, dose, and time-dependency of plasma and tissue distribution of deltamethrin in immature rats. Toxicol. Sci. 115, 354–368.

Kim, H.-H., Lim, Y.-W., Yang, J.-Y., Shin, D.-C., Ham, H.-S., Choi, B.-S., Lee, J.-Y., 2013. Health risk assessment of exposure to chlorpyrifos and dichlorvos in children at childcare facilities. Sci. Total Environ. 444, 441–450.

Kumar, A., Sharma, B., Pandey, R.J.C., Biology, M., 2012. Assessment of stress in effect to pyrethroid insecticides, λ-cyhalothrin and cypermethrin, in a freshwater fish, Channa punctatus (Bloch) 58, 153–159.

Laskowski, D.A., 2002. Physical and Chemical Properties of Pyrethroids, pp. 49–170.

Lettieri, T., Chirico, N., Carvalho, R.N., Napierska, D., Loos, R., Sanseverino, I., Marinov, D., Ceriani, L., Umlauf, G., 2016. Modelling-based Strategy for the Prioritisation Exercise under the Water Framework Directive. European Commission, Luxembourg.

Li, H., Cheng, F., Wei, Y., Lydy, M.J., You, J., 2017. Global occurrence of pyrethroid insecticides in sediment and the associated toxicological effects on benthic invertebrates: an overview. J. Hazard Mater. 324, 258–271.

Li, Y., Zhang, L., Ding, J., Liu, X., 2020. Prioritization of pharmaceuticals in water environment in China based on environmental criteria and risk analysis of top-priority pharmaceuticals. J. Environ. Manag. 253, 109732.

Liu, F.H., Zhang, S., 2014. Ecological risk of organophosphorous and synthetic pyrethroid pesticides in water from Nanfeihe River. J. Hefei Univ. Technol. (Nat. Sci.) 37, 1499–1504.

Liu, Y., Shen, D., Li, S., Ni, Z., Ding, M., Ye, C., Tang, F., 2016. Residue levels and risk assessment of pesticides in nuts of China. Chemosphere 144, 645–651.

Liu, X., Liu, C., Qian, H., Qu, Y., Zhang, S., Lu, R., Gao, H., Zhou, W., 2019. Ultrasound-assisted dispersive liquid-liquid microextraction based on a hydrophobic deep eutectic solvent for the preconcentration of pyrethroid insecticides prior to determination by high-performance liquid chromatography. Microchem. J. 146, 614–621.

Liu, N., Jin, X., Feng, C., Wang, Z., Wu, F., Johnson, A.C., Xiao, H., Hollert, H., Giesy, J. P., 2020. Ecological risk assessment of fifty pharmaceuticals and personal care products (PPCPs) in Chinese surface waters: a proposed multiple-level system. Environ. Int. 136, 105454.

Lu, N., He, X., Wang, T., Liu, S., Hou, X., 2018. Magnetic solid-phase extraction using MIL-101(Cr)-based composite combined with dispersive liquid-liquid microextraction based on solidification of a floating organic droplet for the determination of pyrethroids in environmental water and tea samples. Microchem. J. 137, 449–455.

Lu, Q., Sun, Y., Ares, I., Anadón, A., Martínez, M., Martínez-Larrañaga, M.-R., Yuan, Z., Wang, X., Martínez, M.-A., 2019. Deltamethrin toxicity: a review of oxidative stress and metabolism. Environ. Res. 170, 260–281.

Mahboob, S., Niazi, F., AlGhanim, K., Sultana, S., Al-Misned, F., Ahmed, Z., 2015. Health risks associated with pesticide residues in water, sediments and the muscle tissues of Catla catla at Head Balloki on the River Ravi. Environ. Monit. Assess. 187, 1–10.

Martínez-Alcalá, I., Pellicer-Martínez, F., Fernández-López, C., 2018. Pharmaceutical grey water footprint: accounting, influence of wastewater treatment plants and implications of the reuse. Water Res. 135, 278–287.

Maund, S., Campbell, P., Giddings, J., Hamer, M., Henry, K., Pilling, E., Warinton, J., Wheeler, J.J.P., 2011. Ecotoxicology of synthetic pyrethroids. In: Matsuo, N., Mori, T. (Eds.), Pyrethroids from Chrysanthemum to Modern Industrial Insecticide, pp. 137–165.

Mekonnen, M.M., Hoekstra, A.Y., 2011. The green, blue and grey water footprint of crops and derived crop products. Hydrol. Earth Syst. Sci. 15, 1577–1600.

Moreno-Villa, E.D., Aldana-Madrid, M.L., Silveira-Gramont, M.I., Rodríguez-Olibarría, G., Valenzuela-Quintanar, A.I., Meza-Montenegro, M., 2012. Analysis of pyrethroids in soil and water in agricultural areas and urban valleys Yaqui and Mayo. Rev. Int. Contam. Ambient. 303–310.

Munro, S.A., Fraser, G.C., Snowball, J.D., Pahlow, M., 2016. Water footprint assessment of citrus production in South Africa: a case study of the Lower Sundays River Valley. J. Clean. Prod. 135, 668–678.

Muntalif, B.S., Chasanah, N., Faza, M.F., 2016. Relationship population density of aquatic sediment macrozoobenthos to river water quality parameters: case study of upstream Citarum River in Bandung regency. J. Environ. Sci. Eng. 5, 117–125.

Novo, P.J.W., 2017. Accounting for the Assimilative Capacity of Water Systems in Scotland, vol. 9, p. 559.

Ogaly, H.A., Khalaf, A., Ibrahim, M.A., Galal, M.K., Abd-Elsalam, R.M., 2015. Influence of green tea extract on oxidative damage and apoptosis induced by deltamethrin in rat brain. Neurotoxicol. Teratol. 50, 23–31.

Ostrea Jr., E.M., Bielawski, D.M., Posecion Jr., N.C., Corrion, M., Villanueva-Uy, E., Bernardo, R.C., Jin, Y., Janisse, J.J., Ager, J.W., 2009. Combined analysis of prenatal (maternal hair and blood) and neonatal (infant hair, cord blood and meconium) matrices to detect fetal exposure to environmental pesticides. Environ. Res. 109, 116–122.

Oudou, H.C., Hansen, H.B., 2002. Sorption of lambda-cyhalothrin, cypermethrin, deltamethrin and fenvalerate to quartz, corundum, kaolinite and montmorillonite. Chemosphere 49, 1285–1294.

Papadakis, E.N., Vryzas, Z., Kotopoulou, A., Kintzikoglou, K., Makris, K.C., Papadopoulou-Mourkidou, E., 2015. A pesticide monitoring survey in rivers and lakes of northern Greece and its human and ecotoxicological risk assessment. Ecotoxicol. Environ. Saf. 116, 1–9.

Paraiba, L.C., Pazianotto, R.A.A., Luiz, A.J.B., Maia, A., Jonsson, C.M., 2014. A mathematical model to estimate the volume of grey water of pesticide mixtures. In: Embrapa Meio Ambiente-Artigo Em Periódico Indexado.

Pawlisz, A., Busnarda, J., McLauchlin, A., Caux, P.Y., Kent, R., 1998. Canadian water quality guidelines for deltamethrin. Environ. Toxicol. Water Qual. 13, 175–210.

Peake, B.M., Braund, R., Tong, A.Y., Tremblay, L.A.J.T.L.-C.o.P.i.t.E., 2016. The Life-Cycle of Pharmaceuticals in the Environment. Elsevier.

Peris, A., Barbieri, M.V., Postigo, C., Rambla-Alegre, M., de Alda, M.L., Eljarrat, E., 2022. Pesticides in sediments of the Ebro River Delta cultivated area (NE Spain): occurrence and risk assessment for aquatic organisms. Environ. Pollut. 305, 119239.

Prammer, B., European Union, Brussels, 1998. Directive 98/83/CE Relative to the Quality of Waters for Human Use Official Bulletin of the EC. European Union, European Union, Brussels. Brussels Pubchem, 2021. National library of medicine.
Putra, A., Lili, Z.W., 2012. Plankton community structure in the upper Citarum River in west java. J. Fish. Marine Sci. 3, 313–325.
Qian, H., Hu, L., Liu, C., Wang, H., Gao, H., Zhou, W., 2018. Determination of four pyrethroid insecticides in water samples through membrane emulsification-assisted liquid–liquid microextraction based on solidification of floating organic droplets. J. Chromatogr. A 1559, 86–94.
Reis, E.O., Santos, L.V., Lange, L.C., 2021. Prioritization and environmental risk assessment of pharmaceuticals mixtures from Brazilian surface waters. Environ. Pollut. 288, 117803.
Riaz, G., Tabinda, A.B., Kashif, M., Yasar, A., Mahmood, A., Rasheed, R., Khan, M.I., Iqbal, J., Siddique, S., Mahfooz, Y., 2018. Monitoring and spatiotemporal variations of pyrethroid insecticides in surface water, sediment, and fish of the river Chenab Pakistan. Environ. Sci. Pollut. Res. 25, 22584–22597.
Richterova, Z., Svobodová, Z., 2012. Pyrethroids influence on fish. Slovenian Vet. Res.
Rivera-Dávila, O.L., Sánchez-Martínez, G., Rico-Martínez, R., 2022. Toxicity tests, bioaccumulation and residuality of pyrethroid insecticides commonly used to control conifer bark beetles in Mexico. Ecotoxicology 31, 782–796.
Romero, A., Ramos, E., Castellano, V., Martínez, M.A., Ares, I., Martínez, M., Martínez-Larrañaga, M.R., Anadón, A., 2012. Cytotoxicity induced by deltamethrin and its metabolites in SH-SY5Y cells can be differentially prevented by selected antioxidants. Toxicol. Vitro 26, 823–830.
Shi, W., Zhang, F., Zhang, X., Su, G., Wei, S., Liu, H., Cheng, S., Yu, H., 2011. Identification of trace organic pollutants in freshwater sources in Eastern China and estimation of their associated human health risks. Ecotoxicology 20, 1099–1106.
Singh, A.K., Tiwari, M.N., Prakash, O., Singh, M.P., 2012. A current review of cypermethrin-induced neurotoxicity and nigrostriatal dopaminergic neurodegeneration. Curr. Neuropharmacol. 10, 64–71.
Smit, M., Holthaus, K., Tamis, J., Karman, C., 2005. From PEC_PNEC ratio to quantitative risk level using Species Sensitivity Distributions. In: Methodology Applied in the Environmental Impact Factor. B&O-DH.
Sunardi, Kaniawati K., Husodo, T., Malini, D.M., Astari, A.J., 2012. Distribution of fish in the Upper Citarum River: an adaptive response to physico-chemical properties. HAYATI J. Biosci. 19, 191–196.
Tang, W., Wang, D., Wang, J., Wu, Z., Li, L., Huang, M., Xu, S., Yan, D.J.C., 2018. Pyrethroid pesticide residues in the global environment: an overview 191, 990–1007.
USEPA, 2000. Supplementary Guidance for Conducting Health Risk Assessment of Chemical Mixtures. Risk Assessment Forum Technical Panel. US Environmental Protection Agency.
USEPA, 2006. In: Reregistration Eligibility Decision (RED) for Permethrin. Office of Prevention Pesticides and Toxic Substances (7508C) (EPA738-R-06-017)..
Vale, R.L., Netto, A.M., de Lima Xavier, B.T., Barreto, M.d.L.P., da Silva, J.P.S., 2019. Assessment of the gray water footprint of the pesticide mixture in a soil cultivated with sugarcane in the northern area of the State of Pernambuco, Brazil. J. Clean. Prod. 234, 925–932.
Van Toan, P., Sebesvari, Z., Bläsing, M., Rosendahl, I., Renaud, F.G., 2013. Pesticide management and their residues in sediments and surface and drinking water in the Mekong Delta, Vietnam. Sci. Total Environ. 452, 28–39.
Wang, J., Zhou, X.M., Jia, J.S., Zhao, G.C., 2013. The status and evaluation of residual 1059 pyrethroid pesticides in tobacco in central Hunan Area. Anhui Agric. Sci. Bull. 19, 1060 1098–1099.
Wang, Y., Wu, X., Zhang, L.J.M.A., 2018. Three-dimensional hollow porous raspberry-like hierarchical Co/Ni@ carbon microspheres for magnetic solid-phase extraction of pyrethroids 185, 1–9.
Wang, R., Zhang, S., Xiao, K., Cai, M., Liu, H., 2023. Occurrence, sources, and risk assessment of pyrethroid insecticides in surface water and tap water from Taihu Lake, China. J. Environ. Manag. 325, 116565.
Werner, I., Young, T.M., 2018. Pyrethroid Insecticides—Exposure and Impacts in the Aquatic Environment.
Wöhler, L., Niebaum, G., Krol, M., Hoekstra, A.Y., 2020. The grey water footprint of human and veterinary pharmaceuticals. Water Res. X 7, 100044.
Xia, Y., Bian, Q., Xu, L., Cheng, S., Song, L., Liu, J., Wu, W., Wang, S., Wang, X., 2004. Genotoxic effects on human spermatozoa among pesticide factory workers exposed to fenvalerate. Toxicology 203, 49–60.
Yang, M., Wu, X., Jia, Y., Xi, X., Yang, X., Lu, R., Zhang, S., Gao, H., Zhou, W., 2016a. Use of magnetic effervescent tablet-assisted ionic liquid dispersive liquid–liquid microextraction to extract fungicides from environmental waters with the aid of experimental design methodology. Anal. Chim. Acta 906, 118–127.
Yang, X., Zhang, P., Li, X., Hu, L., Gao, H., Zhang, S., Zhou, W., Lu, R.J.T., 2016b. Effervescence-assisted β-cyclodextrin/attapulgite composite for the in-syringe dispersive solid-phase extraction of pyrethroids in environmental water samples 153, 353–359.
Yusiasih, R., Pitoi, M.M., Ariyani, M., Koesmawati, T.A., Maulana, H., 2019. Anthraquinone in Indonesian infusion tea: analysis by HPLC–UV and risk assessment. Chem. Biol. Technol. Agric. 6, 19.
Yusiasih, R., Pitoi, M.M., Endah, E.S., Ariyani, M., Koesmawati, T.A., 2021. Pyrethroid residues in Indonesian cocoa powder: method development, analysis and risk assessment. Food Control 119, 107466.
Zehringer, M., Herrmann, A.J.E.F.R., Technology, 2001. Analysis of polychlorinated biphenyls, pyrethroid insecticides and fragrances in human milk using a laminar cup liner in the GC injector 212, 247–251.
Zhao, L., 2014. Residue and Risk Assessment of 7 Kinds of Pyrethroids in Water Environment in the Pearl River Delta. Shanghai Ocean University.