Environmental prioritization of pesticide in the Upper Citarum River Basin, Indonesia, using predicted and measured concentrations

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HIGHLIGHTS
• Prediction based prioritization for aquatic and human health risks of pesticides.
• Developed by using open ecotoxicity and human toxicity worldwide databases.
• Predicted and monitored concentrations agreed within 1 order of magnitude.
• Prioritizations based on modelling and monitoring yielded similar results.
• In the study area (Citarum River, Indonesia) the aquatic risks were significant.

GRAPHICAL ABSTRACT

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ABSTRACT

A novel screening method was developed to prioritize aquatic and human health risks of pesticides based on usage data, runoff modelling and effect prediction. An important asset of this new method is that it does not require measured concentration data, which are often unavailable or difficult to obtain in low- and middle-income countries like Indonesia. The method was applied to prioritize 31 agricultural pesticides used in the Upper Citarum River Basin in West Java, Indonesia. Ranking of pesticides based on predicted concentrations generally showed good agreement with ranking based on concentrations measured by passive sampling. The individual pesticide intake through the consumption of river water was predicted to cause negligible human health risks, but substantial aquatic risks (i.e. PEC/PNEC >1) were predicted for profenofos (5.2.E+01), propineb (3.6. E+01), chlorpyrifos (2.6.E+01), carbofuran (1.7.E+01), imidacloprid (9.4.E+00), methomyl (7.6.E+00) and chlorantraniliprole (3.6.E+00). In order to protect the aquatic environment, water managers are advised to take measures to reduce the use and runoff of these pesticides in the UCRB. The screening assessment can be further refined by performing additional effect studies for some pesticides, pesticide mixtures and validation of the predicted water concentrations by targeted measurements.

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1. Introduction

Rivers play an important role as a source of water in our daily lives. River pollution is one of the greatest threats to ecosystem and human
Among the different forms of pollution, Contaminants of Emerging Concern (CECs) are one of particular interest (Kuzmanović et al., 2015). CECs cover a wide range of manmade chemicals and materials which have been detected or are suspected to be present in various environmental compartments and whose toxicity or persistence are likely to significantly alter the metabolism of a living being while there is limited data on occurrence, environmental fate, toxicity and mostly not yet regulated (Sauvé and Desrosiers, 2014; US-EPA, 2019; Meador et al., 2016). CECs can have a natural or anthropogenic origin, including agricultural, industrial, and domestic activities (Schwarzenbach et al., 2006). These CECs include, but are not limited to, pesticides, pharmaceuticals and personal care products (PPCPs), veterinary products, food additives and life-style compounds like caffeine (Meador et al., 2016; Brumovský et al., 2017; Bai et al., 2018). Many of these chemicals and their transformation products enter the aqueous environment during their life cycle (Schwarzenbach et al., 2006).

Some classes of CECs were purposely designed to affect living systems even at relatively low exposure levels, e.g., pesticides, pharmaceuticals and illicit drugs. Chronic exposure to low levels of these substances might be harmful for ecosystems (e.g., Jorgenson et al., 2018) and human health (e.g., Ma et al., 2019). These impacts are sometimes obvious and directly observable, but they can also be more subtle and difficult to detect, e.g. delayed effects and bioaccumulation (Vörösmarty et al., 2010; Yeh et al., 2017; Margenat et al., 2019).

Over 394,000 chemicals are registered and regulated via the Regulated Chemicals Listing (CHEMLIST; CAS, 2019). Protecting ecosystems and humans by banning all chemicals is unrealistic (Porta et al., 2008). However, it is also unfeasible to experimentally assess the risks of all CECs in a timely manner. Luckily, this is unnecessary because the major part of the toxicity is often caused only by a limited number of substances (Harbers et al., 2006; Aubbakirova et al., 2017; Baken et al., 2018). To overcome this problem, prioritization approaches can be applied to identify which CECs likely pose the greatest risk in a particular situation and, therefore, need to be considered as a priority for further study (von der Ohe et al., 2011; Boxall et al., 2012; Guo et al., 2016; Burns et al., 2018).

Several CEC prioritizations have been applied around the world (von der Ohe et al., 2011; Guo et al., 2016; Al-Khazrajy and Boxall, 2016; Burns et al., 2018; Baken et al., 2018). A prioritization study in the United Kingdom showed that from the 146 actively used pharmaceuticals; only sixteen compounds were identified as a potential priority (Guo et al., 2016). Another risk-based prioritization study analysed 99 of the most dispensed pharmaceuticals in three Iraqi cities, i.e. Baghdad, Mosul and Basrah. The result indicated that only antibiotics, antidepressants and analgesics were of high priority in surface water, sediment and the terrestrial environment (Al-Khazrajy and Boxall, 2016). Most studies prioritize <10 compounds (Saunders et al., 2016), indicating that only a limited number of CECs cause the major part of the risk. Risk prioritization is therefore expected to increase the effectiveness of water quality management.

Prioritizing approaches require data on CEC concentrations in the environment. CEC prioritization can be particularly challenging in low- and middle-income countries such as Indonesia because of lacking monitoring data. The limited availability of suitable analysis equipment and technology, in association with the high analysis costs, can be a burden for the government budgets of these countries (Al-Khazrajy and Boxall, 2016; Burns et al., 2018). As a cost-effective alternative, predicted environmental concentrations (PECs) based on chemicals usage may be used (Liebig et al., 2006; Aubbakirova et al., 2017; Burns et al., 2017). PEC has the advantage that no monitoring is needed, that also new interventions can be modelled, but up to date usage data is required.

Several studies have compared PECs with measured environmental concentrations (MECs) (Kostich et al., 2010; Liebig et al., 2006; Burns et al., 2017; Celle-Jeanton et al., 2014; Coetsier et al., 2009; Oldenkamp et al., 2018). These comparisons have provided variable results, with some studies showing that PECs adequately represent MECs (Celle-Jeanton et al., 2014; Saunders et al., 2016; Burns et al., 2017), whereas others suggest that differences are too large to be useful or
that PECs may underestimate MECs under particular conditions, such as low spatial resolution use data or large scale environments (Kostich et al., 2010; Liebig et al., 2006; Goetzier et al., 2009; van Gils et al., 2020). The aim of the present study was to explore the performance of a prioritization approach for CECs given that measurement data are lacking compared to a situation where CECs concentrations are measured. This method can be used by authorities to be able to propose appropriate mitigation and/or control measures for environmental or health protection. The prioritization approach was applied to the Upper Citarum River Basin (UCRB) in West Java, Indonesia. We estimated the use of 31 pesticides based on a survey among farmers. PECs were estimated using a simple fate model accounting for runoff, degradation and dilution. Prioritization was based on comparing PECs with reference levels for human health and ecosystem protection. The PECs and prioritization results were partly validated using pesticide concentrations measured with passive samplers.

2. Materials & methods

2.1. Study location

The Citarum River is the longest river (269 km) in West Java and it plays an important role in many sectors (ADB, 2007). It provides surface water for about 35 million people in West Java and Jakarta (ADB and The World Bank, 2013), irrigates an area of around 420,000 ha of rice fields (Statistics Indonesia, 2015) and acts as a water source for >2000 factories (ADB and The World Bank, 2013).

The Upper Citarum River Basin (UCRB) runs from the Citarum Spring at Wayang Mountain until the inlet of the Saguling Reservoir and has a total basin area of about 1822 km² (Fig. 1; Harlan et al., 2018; Statistics Indonesia, 2015). The UCRB covers 2 cities and 6 regencies including Bandung City, the most densely populated city in West Java. Agricultural activities in the UCRB are quite massive especially for rice fields, considering that West Java is one of the key rice producers in Indonesia (Fulazzaky, 2010).

2.2. Predicted environmental concentrations (PECs)

PECs for 31 pesticides were estimated based on average pesticide use data for single use (agriculture) reported by Utami et al. (2020); multiplied by the agricultural area (ha) of the study location based on data from Statistics Indonesia (2015; Table S.1 of the Supporting information; SI). The use data were based on a survey among 174 farmers across 8 agricultural areas in the UCRB from January to March 2016 during the wet season. The surveyed farmers manage in total an agricultural area of 74.13 ha, with an average of 0.43 ha per farmer. Pesticide use data of 14 crop types were used in this study (Table S.2; the raw data is available in Utami et al., 2020).

Following OECD (1999) and Berenzen et al. (2005) we focused on pesticide runoff as the primary process, while acknowledging that other processes also can transfer pollutants to surface water, such as spray drift, volatilization and transfer with precipitation, drainage or point-source pollution (OECD, 1999). The percentage of the applied pesticide dose transported from land to surface water (Lrunoff) was estimated using Eq. (1) (OECD, 1999; Berenzen et al., 2005):

\[
L_{\text{runoff}} = \frac{Q}{P} \cdot f_1 \cdot f_2 \cdot f_3 \cdot e^{\left(\frac{-\ln 2}{DT_{\text{Soil}}}\right)} \cdot 100 \cdot \frac{1}{1 + K_d}
\]

(1)

where \(Q\) is the amount of runoff (mm/day) based on an empirical relation for the amount of rainfall versus runoff volume in mm as used in OECD (1999) using Scenario III for covered soil with low soil moisture (Table S.3). \(P\) is the amount of precipitation in the rice basin (mm/day). A number of factors are used in Eq. (1), i.e. \(f_1\) as slope factor (\(\sim\)), calculated with \(f_1 = 0.02153\cdot\text{slope} + 0.001423\cdot\text{slope}^2\) if the slope < 20%, and \(f_1 = 1\) if the slope ≥ 20% (modified after Beinat and van den Berg, 1996). \(f_2\) is the plant interception factor (\(\sim\)), calculated with \(f_2 = 1 - \frac{P}{100},\) where \(P\) (in %) is the percentage of plant interception, and \(f_3\) is buffer zone factor (\(\sim\)), calculated with \(f_3 = 0.83^{WBZ},\) where WBZ is width of the buffer zone (m). Variable \(x\) is the average residence time in soil (days), calculated by averaging the number of days between rain events obtained from a rainfall station of PUSAIR (the Research & Development Centre For Water Resources of the Ministry of Public Works in Indonesia). \(DT_{\text{Soil}}\) is the half-life of the pesticide in soil (days) and \(K_d\) is the separation coefficient of the pesticide between soil and water (mL/g), calculated using \(K_d = KOC - fOC,\) where \(KOC\) is the sorption coefficient of the pesticide to organic carbon (mL/g) and \(fOC\) is the fraction organic carbon in soil (\(\sim\)).

The PEC in river water (µg/L) was subsequently predicted using the following equation (OECD, 1999; Berenzen et al., 2005):

\[
PEC = L_{\text{runoff}} \cdot P_{\text{UCRB}} \cdot \frac{1}{Q_{\text{stream}}} \cdot \Delta T
\]

(2)

where \(P_{\text{UCRB}}\) is the total usage of pesticide (active ingredients; a.i.) in UCRB from agriculture activities (µg/year) computed from crop specific pesticide usage (kg/year) taken from Utami et al. (2020); \(Q_{\text{stream}}\) is the average flow stream during the sampling period (L/s) in the Citarum River obtained from discharge stations of PUSAIR, and \(\Delta T\) is the number of seconds in a year (s/year).

2.3. Measured environmental concentrations (passive sampling)

To validate the predicted modelled concentrations (PECs), we deployed passive sampling in the Citarum River. Passive sampling has become a widely used method in the field of environmental monitoring due to its advantages for long-term and cost-efficient on-site monitoring of pollutants (Vrana et al., 2005; Smedes et al., 2010; Kot-wasik et al., 2007; Amato et al., 2018; Gao et al., 2019; Valenzuela et al., 2019; Zillien et al., 2019). The passive sampling technology and its procedures are extensively tested in comparison with traditional sampling (Vrana et al., 2005; Allan et al., 2009; Rusina et al., 2010; Vrana et al., 2016; Rusina et al., 2019). The catchment-oriented monitoring in this study benefits from the passive samplers’ time averaged information, typical sampler deployment time is 15–30 days (Vrana et al., 2005) whereas maximum UCRB catchment water travel time is 2.7 days. Maximum water travel time value is estimated using longest river length to sampling point (48 km; Fig. 1) and lowest flow velocity (0.2 m/s) reported in Muntalif et al. (2016). Passive sampling involves concentration measurement of an analyte as a weighted average over the duration of sampling resulting a better information on the water quality and makes it possible to follow trends in water quality (Amato et al., 2018). Monitoring catchments by passive samplers reduces the number of samples and laboratory analyses needed as compared to grab samples.

The general procedure is that two types of passive samplers (silicon sheets and speedisk) are deployed to cover the hydrophobic/hydrophilic/polar range of substances. Prior to deployment, the silicon sheets and speedisk are deployed to cover the hydrophobic/polar range of substances. Prior to deployment, the silicon sheets are spiked with performance-reference-compounds (PRC) to be able to the sampling rate (L/d) and estimate the aqueous phase concentrations in both the silicon sheets and speedisks (Smedes and Booij, 2012; Hamers et al., 2018). After deployment the samples are cleaned, kept cool and transferred to the laboratory for extraction and substance identification.

In this study, we use the same procedures and analyses were done in the same laboratory as described in detail in Smedes and Booij (2012), Hamers et al. (2018) and Zillien et al. (2019). Two types of passive samplers were employed, i.e. silicone rubber targeting hydrophobic substances with a \(\log K_{oc} > 3\), and speedisk targeting hydrophilic/polar substances with \(\log K_{oc} < 3\) (Smedes et al., 2010; Gao et al., 2019). The
silicone rubber sheets (0.5 mm thick) were cut to a size of 5.5 × 9.5 cm (Fig. 2; right panel). The sheets were pre-extracted for a week to remove impurities and oligomers using ethylacetate (Boom BV, Netherlands). To estimate sampling rate (L/d) the silicone rubber sampler sheets were spiked with performance reference compounds (PRC) biphenyl-D10 and PCB congeners 1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145 and 204 (i.e. all congeners not occurring in technical mixtures). See supplementary materials of Hamers et al. (2018) for all details on the procedure and computations.

The speedisks (diameter 5 cm) consisted of a hard propylene cage containing adsorption material and a glass fiber filter to keep the sorption material in the sampler (Fig. 2; left panel). Details about the deployment are according to Hamers et al. (2018). Before field deployment the speedisk adsorbent was cleaned by elution with 3 times 5 mL dichloromethane, acetone and milli-Q water, respectively. The wet speedisks were immersed in water in a glass jar to keep the sorption material wet and stored at 4 °C until deployment.

We deployed the passive sampler in the wet season (December 16th, 2014 until January 14th, 2015) when rainfall induced runoff occurs most. The pesticide usage data was taken in the same season, although in 2016 (see Section 2.2). For deployment, six silicon sheets and three speedisks were mounted on a metal sample holder and were kept submerged during the entire sampling period of 30 days. The samplers were installed in the downstream part of UCR behind the Cisirung Street of Bandung City (Fig. 1). As the approximation of water-travel time in the catchment is 2.7 days for maximum travel time, we considered that 30 days is sufficient to have a representative sample of average pesticide use as crop-cycles of different farmers are not synchronized in the catchment.

Samplers were extracted in the laboratory and analysed using High-Performance Liquid Chromatographic (HPLC) and Gas Chromatographic (GC) columns, the equipment is detailed in Zillien et al. (2019). Of the 31 surveyed pesticides (see Section 2.2) 14 pesticides were available in the standard analysis package of the laboratory and used in our analysis (Table 1). Despite different hydrophobic-hydrophilic/polar ranges, the uptake of silicon and speedisk samplers might overlap. Whenever the procedure resulted in two measurements, the highest measured concentration was used as input for the validation and prioritization exercise.

2.4. Prioritization approach

A risk-based method was adopted for prioritization of the 31 pesticides (Burns et al., 2018). For each pesticide, a risk indicator was calculated as the ratio between the PEC or MEC and a reference concentration for either human health or ecosystem protection based on open international databases. Risk indicators were subsequently ranked in decreasing order (Kools et al., 2008). In total, four prioritization lists were constructed reflecting each possible combination of predicted and measured exposure concentrations and reference concentration for human health and ecosystem protection.

2.4.1. Ecological risk prioritization

The procedure for ecological risk prioritization is illustrated in Fig. 3. Prioritization was based on a dimensionless ecological risk indicator (RIeco) which was calculated for each substance separately using Eq. (3):

\[ RI_{eco} = \frac{PEC \text{ or } MEC}{PNEC} \]

where PEC is predicted environmental concentration (µg/L) resulting from the model, MEC is measured environmental concentration (µg/L) as determined by passive sampling, and PNEC is predicted no effect concentration (µg/L) for aquatic ecosystems derived from ecotoxicity data.

The Predicted No Effect Concentration (PNEC) was derived for each pesticide based on aquatic ecotoxicity data extracted from five (inter) national databases, i.e. the RIVM substances database (in Dutch), the US-EPA ECOTOX knowledgebase, the Pesticide Properties Database (PPDB) from University of Hertfordshire UK, the Finland database on environmental properties of chemicals: Ymparisto (in Finnish) and the INERIS chemical substances portal (in French). We extracted acute (LC50 and EC50) and chronic (NOEC, EC10, and LC10) ecotoxicity data resulting from freshwater experiments with aquatic organisms representing three different taxonomic levels, i.e. primary producers (plants & algae), invertebrates (crustacean, insects, molluscs & worms) and vertebrates (fish & amphibians). Only ecotoxicity data relating to population relevant effects were included. For example, 6 of the 11 major effect groups included in US-EPA’s ECOTOX database were considered population relevant, i.e. mortality effects (MOR), population effects (POP), reproduction effects (REP), growth effects (GRO), intoxication effect (ITX; as a part of physiology effect), and Multiple effects reported as one result (MULT; as a part of “no group code” effect; US-EPA, 2016). All extracted data were converted into µg/L.

The extracted dataset comprised 4303 records in total (31 substances, 1138 chronic values, 3165 acute values) (Tables S.8 to S.12). The dataset was screened for implausible toxicity values (De Zwart, 2002). Implausible values were traced to their original reference to identify potential errors which were often attributable to errors in unit transformations, typing errors or tests conducted under sub-optimal conditions. Erroneous entries were corrected when possible, and data were removed when original sources could not be checked.

The PNEC value was derived from the extracted ecotoxicity data, loosely following the EU assessment factor method (ECHA, 2008; EC.
According to this method, an assessment factor (AF) is applied to the lowest available ecotoxicity value. The value of the AF depends on the nature and number of available ecotoxicity data. A factor of 10 was applied when chronic ecotoxicity data were available covering 3 taxonomic groups (i.e., primary producers, invertebrates and vertebrates), a factor of 50 if covering 2 taxonomic groups and a factor of 100 if covering only 1 taxonomic group. If chronic toxicity were lacking and acute toxicity data were available covering the 3 taxonomic groups, a factor of 1000 was applied to the lowest acute value. If acute toxicity values were available for >3 taxonomic groups, no PNEC was derived. When the lowest chronic toxicity value was higher than the lowest acute value, the latter value was used to derive the PNEC in combination with the AF for chronic data. This can happen if the most sensitive species was tested in an acute test, but not chronically.

Data allowing, a separate PNEC was derived for each substance and database combination. This was done because quality assurance procedures differ between databases. We ultimately selected one PNEC per pesticide applying the following preferential order: (1) PNEC derived from RIVM reports (because of strict quality control criteria such as using the Klimisch codes); (2) Lowest PNEC resulting from the four other databases. The resulting PNECs from all databases are listed in Table S.6 of the SI.

### 2.4.2. Health risk prioritization

The procedure for human health-based risk prioritization is illustrated in Fig. 4. Prioritization was based on a dimensionless human health-based risk indicator ($R_{\text{Him}}$) which was calculated for each substance separately using Eq. (4):

$$R_{\text{Him}} = \frac{\text{MEC}}{\text{PNEC}}$$

<table>
<thead>
<tr>
<th>Pesticide Name</th>
<th>CAS Number</th>
<th>Type</th>
<th>Use (kg/year)</th>
<th>$L_{\text{runoff}}$ (%)</th>
<th>PEC (ng/L)</th>
<th>MEC (ng/L)</th>
<th>LOD (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nitrophenol sodium salt</td>
<td>824-39-5</td>
<td>PGR</td>
<td>2.9E+01</td>
<td>1.0E-02</td>
<td>6.2E-02</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>4-Nitrophenol sodium salt</td>
<td>824-78-2</td>
<td>PGR</td>
<td>4.4E+01</td>
<td>6.4E-03</td>
<td>6.0E-02</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Abamectin</td>
<td>71751-41-2</td>
<td>I</td>
<td>2.3E+03</td>
<td>6.0E-04</td>
<td>2.9E-01</td>
<td>3.0E-01</td>
<td>3.0E-01</td>
</tr>
<tr>
<td>Alpha-cypermethrin</td>
<td>67735-30-8</td>
<td>I</td>
<td>3.1E+03</td>
<td>1.2E-05</td>
<td>8.0E-03</td>
<td>&lt;LOD</td>
<td>1.6E-02</td>
</tr>
<tr>
<td>Aoxystrobin</td>
<td>131860-33-8</td>
<td>F</td>
<td>2.5E+04</td>
<td>5.9E-03</td>
<td>3.1E+01</td>
<td>1.6E+00</td>
<td>1.2E-01</td>
</tr>
<tr>
<td>Beta-cyfluthrin</td>
<td>224-81-6</td>
<td>I</td>
<td>2.7E+03</td>
<td>7.9E-05</td>
<td>4.4E-02</td>
<td>2.0E+00</td>
<td>1.0E+00</td>
</tr>
<tr>
<td>Brodifacoum</td>
<td>50703-10-0</td>
<td>R</td>
<td>4.8E+00</td>
<td>1.3E-03</td>
<td>1.3E-03</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>1565-66-2</td>
<td>I</td>
<td>4.4E+04</td>
<td>2.9E-02</td>
<td>2.7E+02</td>
<td>2.6E+01</td>
<td>9.0E+00</td>
</tr>
<tr>
<td>Chlorantraniliprole</td>
<td>500008-45-7</td>
<td>I</td>
<td>2.0E+04</td>
<td>9.5E-03</td>
<td>4.0E+01</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Chlorfenapy</td>
<td>122453-73-0</td>
<td>I</td>
<td>3.3E+03</td>
<td>2.0E-04</td>
<td>1.4E-01</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>1897-45-6</td>
<td>F</td>
<td>2.0E+05</td>
<td>1.3E-03</td>
<td>5.4E+01</td>
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<td>NA</td>
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<tr>
<td>Chlorpyrifos</td>
<td>2921-88-2</td>
<td>I</td>
<td>8.9E+04</td>
<td>6.5E-04</td>
<td>1.2E+01</td>
<td>1.0E+00</td>
<td>6.0E-03</td>
</tr>
<tr>
<td>Cypemethrin</td>
<td>52315-07-8</td>
<td>I</td>
<td>4.7E+04</td>
<td>1.1E-05</td>
<td>1.1E-01</td>
<td>7.0E-02</td>
<td>1.6E-02</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>52918-63-5</td>
<td>I</td>
<td>4.1E+03</td>
<td>3.5E-07</td>
<td>3.0E-04</td>
<td>&lt;LOD</td>
<td>1.3E-02</td>
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<tr>
<td>Difenoconazole</td>
<td>119446-68-3</td>
<td>F</td>
<td>1.1E+04</td>
<td>9.5E-04</td>
<td>2.2E+00</td>
<td>1.0E+00</td>
<td>5.0E-01</td>
</tr>
<tr>
<td>Dimehopro (Thiosultap disodium)</td>
<td>52207-48-4</td>
<td>F</td>
<td>5.1E+04</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Emamectin benzoate</td>
<td>155569-91-8</td>
<td>I</td>
<td>4.6E+03</td>
<td>9.4E-06</td>
<td>9.1E-03</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>115-29-7</td>
<td>I</td>
<td>1.9E+04</td>
<td>3.0E-04</td>
<td>1.2E+00</td>
<td>5.9E-01</td>
<td>5.0E-03</td>
</tr>
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<td>Imidacloprid</td>
<td>138261-41-3</td>
<td>I</td>
<td>7.1E+03</td>
<td>1.5E-02</td>
<td>2.3E+01</td>
<td>3.0E-01</td>
<td>3.0E-01</td>
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<tr>
<td>Lufenuron</td>
<td>103055-07-8</td>
<td>I</td>
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<td>8.6E-05</td>
<td>1.8E-04</td>
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<td>NA</td>
</tr>
<tr>
<td>Mancozeb</td>
<td>8018-01-7</td>
<td>F</td>
<td>3.2E+05</td>
<td>3.4E-08</td>
<td>2.3E-03</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Maneb</td>
<td>12427-38-2</td>
<td>F</td>
<td>7.4E+04</td>
<td>9.3E-04</td>
<td>1.5E-01</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Mefenoxam (Metalaxyl-M)</td>
<td>70630-17-0</td>
<td>F</td>
<td>8.4E+02</td>
<td>5.0E-03</td>
<td>8.9E-01</td>
<td>3.7E+00</td>
<td>1.3E+00</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>16752-77-5</td>
<td>I</td>
<td>1.7E+04</td>
<td>6.8E-02</td>
<td>2.4E+02</td>
<td>&lt;LOD</td>
<td>5.4E+02</td>
</tr>
<tr>
<td>Metiram</td>
<td>9006-42-2</td>
<td>F</td>
<td>2.0E+04</td>
<td>2.6E-06</td>
<td>1.1E-02</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Metsulfuron-methyl</td>
<td>74223-64-6</td>
<td>H</td>
<td>1.8E+02</td>
<td>2.1E-01</td>
<td>7.8E-01</td>
<td>&lt;LOD</td>
<td>1.5E+01</td>
</tr>
<tr>
<td>MIPC (Isoperox)</td>
<td>2631-40-5</td>
<td>I</td>
<td>3.9E+04</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Paraquat dichloride</td>
<td>1910-42-3</td>
<td>H</td>
<td>4.6E+03</td>
<td>1.2E-04</td>
<td>1.2E-01</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Profenofos</td>
<td>41198-08-7</td>
<td>I</td>
<td>1.3E+05</td>
<td>1.6E-03</td>
<td>4.2E+01</td>
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<td>NA</td>
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<tr>
<td>Propineb</td>
<td>12071-83-9</td>
<td>F</td>
<td>1.8E+05</td>
<td>9.7E-02</td>
<td>3.6E+03</td>
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<td>NA</td>
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<td>Spinetoram</td>
<td>187166-40-1</td>
<td>I</td>
<td>2.4E+02</td>
<td>1.5E-04</td>
<td>7.4E-03</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of the 31 pesticides considered in the present study, i.e. pesticide name, CAS number, type of pesticide (PGR = Plant Growth Regulator, I = Insecticide, F = Fungicide, R = Rodenticide, H = Herbicide), estimated use in the study location (kg/year), calculated runoff percentage ($L_{\text{runoff}}$; %), predicted environmental concentration (PEC; ng/L), measured environmental concentration (MEC; ng/L) and limit of detection (LOD; ng/L); <LOD = measurements below the limit of detection; NAv = not available; NA = not analysed.

Fig. 3. Flowchart of the ecological risk prioritization approach.
where CDI is the estimated chronic daily intake (mg/kg/day), as explained below; and HRV is the health-based reference value (mg/kg/day) (Table S.7).

The Chronic Daily Intake (CDI; mg/kg/day) was estimated assuming the direct ingestion of surface water as drinking water and by applying the following equation:

$$CDI = \frac{C \times IR}{BW}$$  (5)

where C is the concentration of the substance (mg/L) in ingested water, i.e. the MEC or PEC; IR is the water ingestion rate, assumed to equal 2 L/day for adults and BW is the body weight, i.e. 60 kg for adults (Gordon et al., 2008).

Health-based reference values (HRVs) for chronic oral exposure such as the Acceptable Daily Intake (ADI), the Tolerable Daily Intake (TDI) and Reference Dose (RfD) were extracted from six databases, i.e. the EU Pesticides Database from European Commission (EC), the RIVM substances database (in Dutch), the Joint Meeting on Pesticide Residues (JMPR) Database, the US-EPA Integrated Risk Information System (IRIS), the Federal Institute for Risk Assessment of Germany (BfR, 2007), and the ATSDR Toxic Substances Portal: Minimal Risk Levels (MRLs) List. All HRVs extracted are listed in Table S.7 of the SI. For each HRV database, substances were ranked based on the RIhealth calculated with the HRV originating from that particular database, resulting in six different health-based rankings. The ultimate prioritization was based on the average rank of each substance over the six health-based rankings.

3. Results

3.1. Predicted versus measured concentrations

Table 1 lists the most important results for the 31 pesticides included in the present study, i.e. the total annual use data estimated based on the farmer’s survey (Utami et al., 2020), the calculated runoff fraction, the calculated PECs and the MECs resulting from the passive sampling campaign.

The most widely used pesticide in the UCRB was mancozeb with a total use of 3.2.E+05 kg/year, closely followed by chlorothalonil with 2.0.E+05 kg/year, propineb with 1.8.E+05 kg/year and profenofos with 1.3.E+05 kg/year. These pesticides were mostly used for growing chili/pepper, tomato, potato, cabbage, and rice (Table S.2). The highest runoff fraction was calculated for metsulfuron-methyl (0.21%), followed by propineb (0.097%), and closely followed by methomyl (0.088%). The lowest runoff was calculated for mancozeb (3.4.E-08%), followed by deltametrin (3.5.E-07%) and metiram (2.6.E-06%). The highest PEC was calculated for propineb with 3.6.E+03 ng/L followed by carbofuran with 2.7.E+02 ng/L and methomyl with 2.4.E+02 ng/L (Table 1).

To assess the performance of our emission estimation and fate model, the PECs were plotted against the MECs (Fig. 5). The plot contains only 10 dots, representing pesticides for which the MEC was above the limit of detection (LOD) and for which a PEC could be calculated. Of the 21 remaining pesticides, 4 had a MEC below the LOD and 17 were not included in the standard monitoring package. Our model correctly predicted a concentration below the LOD for 4 of these 21 pesticides. For 2 pesticides (dimethyhy & MIPC), no PEC could be calculated because of lacking chemical properties data, i.e. DT50 or Koc, values.

The solid line in Fig. 5 indicates a perfect match between predicted and measured values and the dashed lines indicate a factor of 10 difference. The model performs relatively well from the comparison between PEC and MEC (see Fig. 5), particularly for difenconazole, endosulfan, abamectin, and cypermethrin. The PECs of these 4 resulting close values with their MECs. Predicted concentrations are substantially higher than measured for carbofuran, azoxystrobin, chlorpyrifos, and imidacloprid. Predicted concentrations (PECs) are substantially lower than measured (MECs) for mefenoxam and beta-cyfluthrin. Overall, from 10 PECs, 5 are

Fig. 5. Comparison of measured (MEC; x-axis) and predicted (PEC; y-axis) concentration of pesticides in river water of Upper Citarum River Basin. The solid line indicates a 1:1 match between MEC and PEC; the dashed lines indicate a ten-fold difference.
within a factor of 10.2 are slightly above a factor of 10 and 3 are within a factor of 100.

3.2. Prioritization

Table 2 lists the results of the prioritization based on ecological risks for pesticides for which PEC, MEC and PNEC values were available, i.e. 10 out of the 31 pesticides. Using the MECs, the highest risk was calculated for beta-cyfluthrin with a RIhum-MEC of 1.0.E+01, followed by chlorpyrifos with a RIhum-MEC of 2.2.E+00 and carbofuran with a RIhum-MEC of 1.6.E+00. Using the PEC, the highest risk was calculated for chlorpyrifos with a RIeco-PEC of 2.6.E+01, followed by carbofuran with a RIeco-PEC of 1.7.E+01, and imidacloprid with a RIeco-PEC of 9.4.E+00. All other pesticides had a risk indicator value below unity, implying the PNEC was not exceeded. The rankings based on MECs and PECs were quite similar. The most important differences were the ranking of beta-cyfluthrin (1st based on MEC, 8th based on PEC) and imidacloprid (7th based on MEC, 3rd based on PEC).

Table 3 lists the ecological prioritization results for all pesticides for which PEC and PNEC values are available, i.e. 29 of the 31 pesticides. Several pesticides that were not detected by the passive sampler (i.e., for which a MEC is lacking) are now predicted to cause a substantial risk for beta-cyfluthrin (1st based on MEC, 8th based on PEC) and imidacloprid (7th based on MEC, 3rd based on PEC).

Table 4 lists the results of the prioritization based on human risks for pesticides for which PEC, MEC and HRV values were available, i.e. 10 out of the 31 pesticides. The HRVs used in this prioritization can be found in Table 5.7 of the SI. Using the MECs, the highest risk was calculated for carbofuran with a geometric mean RIhum-MEC of 7.8.E-04, followed by chlorpyrifos with a geometric mean RIhum-MEC of 8.4.E-06 and abamectin with a geometric mean RIhum-MEC of 8.0.E-06. Using the PECs, the highest risk was calculated for carbofuran with a geometric mean RIhum-PEC of 8.2.E-03, followed by chlorpyrifos with a geometric mean RIhum-PEC of 1.0.E-04 and imidacloprid with a geometric mean RIhum-PEC of 1.3.E-05. The rankings based on MECs and PECs show substantial differences for abamectin (rank 3 versus 6), beta-cyfluthrin (rank 6 versus 10) and imidacloprid (rank 10 versus 3). All calculated individual risk indicator values were more than two orders of magnitude below unity, indicating negligible human health risks.

Table 5 lists the health-based prioritization results for all pesticides for which PEC and HRV values are available, i.e. 28 of the 31 pesticides. Some of the pesticides that were not detected by the passive sampler (i.e., for which a MEC is lacking) rank relatively high, i.e. propineb (rank 2), methomyl (rank 3), chlorothalonil (rank 5), profenofos (rank 6) and maneb (rank 7). However, the highest mean of predicted risk indicator value is still far below unity (i.e., RIhum-MEC = 1.7.E-02 for propineb), indicating negligible health-based risks for all individual pesticides.

4. Discussion

We developed a novel method to prioritize pesticides in a river basin based on usage data, emission estimation, fate prediction and comparison of modelled water concentrations with reference values for ecological and human health effects. The method was applied to prioritize 31 pesticides used in the Upper Citarum River Basin (URCB) in West Java, Indonesia. The results indicate that the current application of some pesticides in the UCRB involves substantial risks for the aquatic ecosystem, while the human health-based risks after intake of river water are negligible. Before we discuss the practical implications of our study, we first discuss the uncertainties involved in our methodology.

4.1. Methodological issues

The prediction of pesticide concentrations in the UCRB necessarily involves uncertainties, e.g. in estimated usage, runoff, sorption and environmental persistence. As such, it is hardly surprising that we find substantial differences in predicted and measured pesticide concentrations in the UCRB. For the 10 pesticides for which PEC and MEC values were available, 5 are within a factor of 10, 2 are slightly above a factor of 10 and 3 are within a factor of 100 of the measured concentration (Table 1). Additionally, for the 4 pesticides that were analysed but not detected, the LOD was consistently higher than the predicted concentration (Table 1).
We adopted passive sampling as our approach to validate PEC values as its ability to measure concentration as a weighted average over the duration of sampling fits with the application to prioritize more or less chronic exposure risks and it is a well-tested method (see Section 2.3). The time-averaged nature of the sampling makes it difficult to compare statistically to traditional sampling as it samples a much larger water volume (in 30 days), averaging the concentration, which leads to lower detectable concentrations and lower variability (Vrana et al., 2005; Allan et al., 2009). Even an inter-laboratory study showed that the variation between (all highly qualified laboratories) is greater than the variation between the passive samplers in one laboratory (Vrana et al., 2016). But, the accuracy of passive sampling depends on substance and matrix characteristics. The speedisks are not spiked and the sampling volume was estimated, and calibrated against substances that behave similarly on speedisks and the silicon samplers, but for the speedisk there could be factor of 2 uncertainty in this estimate, implying that the true MEC is within a factor of 2 of the reported MEC (Smedes and Booij, 2012; Hamers et al., 2018).

Regarding the sampling time, we assumed the 30 days sampling period is sufficient to monitor the catchment in the rainy season. Maximum water travel time in the UCRB is 2.7 days, so clearly the whole catchment can reach the sampler. As for capturing actual pesticide emissions, we assumed continuous pesticide use on average due to the large area and unsynchronized crops cycles in the catchment. If, however, this is not the case, then longer-term averages of pesticide concentrations could be lower (in case of peak use in the sampling period) or higher (in case of lower than average use). As the PEC is based on mean yearly use, this can influence the comparison. Furthermore, we monitored one downstream location, but comparing MECs of sub-catchments with different land use with PECs of these sub-catchments can provide insight in model sensitivities. Recommendations for a follow-up study would be a longer monitoring period, simultaneous monitoring of main and sub-catchments differing in land use and monitoring at least all the surveyed pesticides.

One of the sources of uncertainty in the PEC is the estimated usage. Usage was estimated based on a survey among 174 farmers across 8 agricultural areas in the UCRB from January to March 2016 (wet season; Utami et al., 2020). The survey was conducted one year after the passive sampling campaign. The survey and the passive sampling campaign were both performed in the wet season (Dec-Jan and Jan-March, respectively), but the months did not fully overlap. Since pesticide usage tends to vary between years and seasons (Oosterhuis et al., 2013; Celle-Jeanton et al., 2014; Rahman, 2003; Wiese et al., 2018; Mariyono et al., 2018), the estimated emission may differ from the actual emission in the sampling period. Other sources of uncertainty include a potential selection bias towards farmers with high usage (overestimation), underreporting by farmers (underestimation), non-agricultural use (underestimation) and random variability due to the limited number of farmers involved in the study, particularly for pesticides that are used incidentally (Utami et al., 2020). A similar study of pesticide ecological risk assessment was done by Iturburu et al. (2019) in Pampas region (Argentina) where the risk assessment was based on a concentration addition model. The model input was gathered from available reported measured environmental concentrations of Argentina. This kind of approach make the uncertainty factor of potential selection bias of emission concentrations towards farmers usage is negligible. However, we cannot expect this kind of data in low- and middle- income countries where concentrations data were limited or even nonexistent, that makes our study is more applicable on this particular situation. Overall, we expect our pesticide estimates to be within a factor of 2 of the true agricultural usage for common used pesticides in UCRB, such as mancozeb, profenofos, carbofuran, deltamethrin, abamectin, chlorpyrifos, and maneb, up to
a factor of 5 for incidentally used pesticides such as 2- and 4-nitrophenol sodium salt, beta-cyfluthrin, brodifacoum, dimehypo, imidacloprid, lufenuron, methomyl, metiram, metsulfuron-methyl, paraquat dichloride and spinetoram (Utami et al., 2020). For pesticides extensively used in non-agricultural settings, usage may be much higher than estimated in the current study; the extent of underestimation depending on the ratio between agricultural and non-agricultural usage.

The estimation of the runoff fraction (Urunge) is another important source of uncertainty in the PEC (Dubus et al., 2003; Gassmann et al., 2014). Runoff is influenced by many different factors, including pesticide application method and timing, wet and dry agriculture (rice), environmental characteristics such as rainfall intensity, slope, distance to the river, vegetation cover, soil composition and organic carbon content, and substance-specific characteristics such as water solubility, degradability, sorption behavior and vapor pressure. Some of these factors vary in space and time (e.g. pesticide application, rainfall, slope, vegetation cover, soil composition and organic carbon content), while others are inherently uncertain (e.g., degradability and sorption properties). Studies by Tsaboula et al. (2019a, 2019b), about assessment and management of pesticide pollution at a river basin level, indicated that environmental quality factors of the surface water should be generalized with caution in time and in space. Since the ecosystem is a vivid and dynamic entity, its structure is complicated and the interactions of biotic and abiotic factors are multidimensional, a degree of uncertainty in the risk assessment is unavoidable.

Several studies have shown that modelling pesticide runoff can be a challenge (Dubus et al., 2003; Köhne et al., 2009; Zhang et al., 2018), with location-specific models of well-characterized systems performing better than large-scale models of poorly characterized systems, and models calibrated on location-specific data outperforming non-calibrated models parameterized with literature data only. We used a relatively simply model covering a large catchment for which calibrating data were lacking. We focus on rainfall-runoff and ignore other routes to surface water, e.g. spray drift, volatilization and transfer with precipitation, drainage (also of wet rice fields), or point-source pollution. Such models currently allow at best an approximate (order-of-magnitude) estimation of concentrations (Köhne et al., 2009; van Gils et al., 2020).

A final source of uncertainty in the PEC is the dilution by river water. However, this source is considered of minor importance since river flow was measured on a daily basis, matching the sampling period and flow measurements generally are relatively reliable.

When looking at the substance-specific PECs (Fig. 5), four pesticides (imidacloprid, azoxystrobin, chlorpyrifos and carbofuran) were overestimated by more than a factor of 10, and one pesticide (beta-cyfluthrin) was underestimated by more than a factor of 10. The latter is probably caused by the fact that beta-cyfluthrin is also widely used for domestic purposes, not included in our model (Vodeb and Petanovska-Ilievska, 2006; Nakagawa et al., 2017; Palmquist et al., 2012). The overestimation of imidacloprid, azoxystrobin, chlorpyrifos and carbofuran is more difficult to explain. Assuming that the use estimate is reasonable, the most probable explanation is that the retention of these pesticides in crops and soil is higher than predicted, e.g. due to application methods, soil infiltration and sorption or degradation processes not included in our model (Koskinen and Harper, 1990; OECD, 1999; Luo and Zhang, 2009).

The ranking of pesticides is not only influenced by uncertainties in the PEC and MEC, but also by uncertainties in the PNEC. These uncertainties can be substantial. This is illustrated by the substantial variation in PNECs derived from different data sources (Table 5.6). The level of uncertainty depends on the representativeness of the tested species, quality assurance procedures, the number of taxonomic groups tested and the associated assessment factor. For PNEC values involving much uncertainty, exceeding the PNEC does not necessarily imply a high risk. In these cases, a risk manager may consider to commission extra ecoexotoxicity testing to improve the robustness of the PNEC. Out of the 7 pesticides with a RPEC above one (Table 3), two PNECs (i.e., propineb and chlorantraniliprole) had an assessment factor (AF) of 100 or more, indicating substantial room for improvement.

4.2. Ranking of risks

A comparison of the PEC- and MEC-based rankings (Tables 2 and 4) shows considerable consistency, indicating that our prediction-based ranking method is reasonably robust. One exception is beta-cyfluthrin which ranked substantially higher in the MEC-based than in the PEC-based rankings. This is explained by the fact that we did not include domestic use in our estimations, stressing the importance of a comprehensive and accurate assessment of usage when applying our method. Another exception is imidacloprid, ranking considerably higher in the PEC-based rankings than in the MEC-based rankings, possibly due to overestimation of the runoff fraction. Such overestimations can be considered less problematic than underestimations since a screening tool should preferably be conservative.

In terms of absolute aquatic risks, our prioritization method predicted two out of the three pesticides with a risk indicator above unity correctly, i.e. chlorpyrifos and carbofuran (Table 2). The exception is again beta-cyfluthrin for the reasons outlined above. More importantly, the PEC-based ranking for substances with PECs and PNECs data (Table 3) shows an additional strong point of our method, i.e. the option to prioritize pesticides that were not detected using passive sampling. Profenofos, propineb, methomyl and chlorantraniliprole are all predicted to exceed their PNEC although these substances were not detected. Most of the high risk pesticides have a reliable PNEC (i.e., assessment factor < 100), but the robustness of the PNECs of profenofos and chlorantraniliprole could be improved by additional ecotoxicity testing.

For human health, consumption of river water is predicted to cause negligible risk for all individual pesticides considered. However, it should be kept in mind that we did not include other exposure routes such as inhalation, dermal exposure, spray drift or the consumption of polluted fish, nor potential interaction effects in our assessments. Also, interactions between pesticides may generate effects which do not present when there is only an individual pesticide in the water (Thompson, 1996; Mukono, 2005). For example, study on interactions between chlorpyrifos, profenofos, and endosulfan showed that particular combinations of these pesticides resulted in completely different environmental toxicity response compared to individual component (Woods et al., 2002). Another study showed that combination between diazinon and esfenvalerate gave an acute toxicity on Pimephales promelas larvae, while there is no acute effect reported esfenvalerate are exposed (Denton et al., 2003). Therefore, caution needs to be taken when predicting combination toxicity on specific pesticide in the water for further study.

The ranking results of pesticides agree with some previous prioritization studies. A human health risk-based prioritization pesticide study in Taiwan showed that endosulfan, carbofuran, chlorpyrifos, cypermethrin and difenoconazole were among the five highest ranking pesticides of 103 in total, ranking 2nd, 3rd, 4th, 4th (chlorpyrifos and cypermethrin scored equally), and 5th, respectively (Chou et al., 2019). A study in South Africa showed that carbofuran ranked 5th in an environmental hazard prioritization of 69 pesticides, while endosulfan ranked high (2nd) in a health-based prioritization (Dabrowski et al., 2014). Another study prioritized pesticides according to hazard-adjusted use in Yuma County, Arizona, USA, Endosulfan (4th) and chlorpyrifos (5th) were included the top 5 out of the 32 pesticides that were assessed based on endocrine disruption hazard (Sugeng et al., 2013). A study in Costa Rica surface water during 2007–2012 also showed that endosulfan was one of the seven non-acceptable risk that suggesting high acute toxicity for the ecosystem (Carazo-Rojas et al., 2018). A number of the pesticides we identified as high priority are receiving increasing regulatory scrutiny. For example, the Stockholm Convention has
banned the usage of endosulfan, although this pesticide still appears in our list. The usage of chlorpyrifos (Top 3 of our lists) has been restricted by Ministry of Agriculture Republic of Indonesia (Ministry of Agriculture Republic of Indonesia, 2011, 2015). The usage of carbofuran has not been prohibited or restricted by any regulation in Indonesia. However, the prioritization results of our study show that this pesticide appears in the top 3 of the ecological and health-based risk ranking, making it a candidate for future regulation.

Summarizing, our study indicates substantial risks for the aquatic ecosystem in the UCRB due to agricultural pesticide use. In order to protect the aquatic environment, water managers should consider implementing measures reducing pesticide use and runoff in the UCRB, particularly targeted towards profenofos, propineb, chlorpyrifos, carbofuran, imidacloprid, methomyl, and chlorantraniliprole. Further refinement of the current assessment is possible by commissioning extra ecotoxicity tests for propineb and chlorantraniliprole, and also gathering MEC data on profenofos, propineb, methomyl and chlorantraniliprole.

4.3. Practical implications

Our results show that the PECs are reasonably similar compared to the MECs, even the 4 pesticides (alpha cypermethrin, deltametrin, chlorantraniliprole). These results lead to similar risk prioritizations.

Regarding the application of our proposed method for the water quality management, we consider that a method consisting of gathering usage data, modelling emissions and prioritization would be beneficial, moreover, with passive sampling as field validation on the catchment level. Relying less on laboratory analysis can save costs, especially important for low- and middle-income countries. Risk prioritization is proven to be effective, for example, an environmental risk prioritization study by Griffero et al. (2019) in surface waters at basin scale of two Atlantic coastal lagoons of Uruguay, South America revealed that only 8 of 16 highest risks were caused by a pesticide group that exceeded their PNECs (RI >1). Most risk prioritization study indicate that only a limited number of contaminants cause the major part of the risk (Guo et al., 2016; Al-Khazrajy and Boxall, 2016; Saunders et al., 2016; Griffero et al., 2019; Lyu et al., 2019).

The advantage of combining risk prioritization with emission modelling is that the model can be applied to predict resulting concentrations from modelled measures or interventions. Being able to test the potential effectiveness of pesticide use policies is a huge advantage. However, emission modelling and risk prioritization are depended on available data. For the modelling we used data that are open data or likely available with authorities in every country (Tables S.4 and S.5), except for the pesticide usage data. Gathering usage data has many more purposes than to feed a model and is highly recommended for adequate and informed pesticide governance (PAN Germany, 2003; Eurostat, 2008; Zhang et al., 2015). We would suggest to also gather usage data from other sources than agriculture only, for example the domestic and industrial use of pesticides that was not included in our study.

The data from databases needed to perform a risk prioritization can be limiting in some cases. In the prioritization procedure we detailed how to work with incomplete databases. But chemical property data was lacking for two pesticides (dimehypo & MIPC) of in total 31 pesticides, i.e. DT50 or Koc values. This situation may produce an involuntary bias in the results because the assessed risk refers to the substances that do have the complete information. It is important to be aware that pesticides without the complete data should not be considered un-risky.

Validation of the results by passive sampling is recommended, which could include banned pesticides or pesticides suspected to be underreported in use surveys. The advantages of passive sampling are its simple deployment and the time-averaged nature, reducing the number of grab-samples and subsequent laboratory analyses needed, while the amount of sampled water volume is increased leading to the detection of lower concentrations and lower variability (Allan et al., 2009). The main downside is losing the temporal resolution, so peak levels are not detected (Vrana et al., 2005).

5. Conclusions

A novel screening method to prioritize aquatic and human health risks of pesticides based on usage data, runoff modelling and effect prediction was successfully developed, and applied to prioritize 31 agricultural pesticides used in the Upper Citarum River Basin in West Java, Indonesia. The method involves considerable uncertainties in terms of use estimates, runoff modelling and effect prediction, but the ranking of 10 pesticides based on predicted concentrations generally showed good agreement with ranking based on concentrations measured by passive sampling. Human health risks resulting from the oral intake of individual pesticides with river water were predicted to be negligible based on “non-mixture” toxicity, but significant aquatic risks were predicted for profenofos, propineb, chlorpyrifos, carbofuran, imidacloprid, methomyl and chlorantraniliprole. In order to protect the aquatic environment, water managers are advised to take measures to reduce the use and runoff of these pesticides in the UCRB.

The screening method could be a valuable tool in countries where pesticides are not monitored on a regular basis, and the fact that many low- and middle-income countries have limited resources to do pesticides measurement. A prerequisite for applying the method is the accurate registration of pesticide use data. The screening method could be further refined by more realistic modelling of runoff processes and improving availability of ecotoxicity data on pesticides. This methodology can help the managers and authorities, to identify contaminants with highest risk in catchments and can optimize the effectiveness of water quality monitoring programs.

Declaration of competing interest

The authors declare that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject materials discussed in this study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140130.

References


