Compilation and analysis of global surface water concentrations for individual insecticide compounds

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HIGHLIGHTS
• Insecticides contaminate agricultural surface waters globally.
• A compilation of global insecticide surface water concentrations is provided.
• The compilation denotes a valuable tool to classify future monitoring results.
• OC and OP insecticides were reported most often and at highest concentrations.
• Most data were available for surface waters in North America, Asia and Europe.

GRAPHICAL ABSTRACT

ABSTRACT
The decades-long agricultural use of insecticides resulted in frequent contamination of surface waters globally regularly posing high risks for the aquatic biodiversity. However, the concentration levels of individual insecticide compounds have by now not been compiled and reported using global scale data, hampering our knowledge on the insecticide exposure of aquatic ecosystems. Here, we specify measured insecticide concentrations (MICs, comprising in total 11,300 water and sediment concentrations taken from a previous publication) for 28 important insecticide compounds covering four major insecticide classes. Results show that organochlorine and organophosphate insecticides, which dominated the global insecticide market for decades, have been detected most often and at highest concentration levels in surface waters globally. In comparison, MICs of the more recent pyrethroids and neonicotinoids were less often reported and generally at lower concentrations as a result of their later market introduction and lower application rates. An online insecticide classification calculator (ICC; available at: https://static.magic.eco/icc/v1) is provided in order to enable the comparison and classification of prospective MICs with available global insecticide concentrations. Spatial analyses of existing data show that most MICs were reported for surface waters in North America, Asia and Europe, whereas highest concentration levels were detected in Africa, Asia and South America. An evaluation of water and sediment MICs showed that theoretical organic carbon-water partition coefficients (KOC) determined in the laboratory overestimated KOC values based on actual field concentrations by up to a factor of more than 20, with highest deviations found for highly sorptive pyrethroids. Overall, the comprehensive compilation of insecticide field concentrations presented here is a valuable tool for the classification of future surface water monitoring results and serves as important input data for more field relevant toxicity testing approaches and pesticide exposure and risk assessment schemes.

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1. Introduction

1.1. Use and developments of insecticides in global agriculture

Pesticides are an important component of current high-intensity agriculture. Besides their benefits in boosting and maintaining global crop yields (Oerke, 2006), the use of pesticides may also result in ecotoxicological effects in non-target environments such as surface waters (Stehle and Schulz, 2015a; Stone et al., 2014). Increasing evidence suggests clear impacts of pesticides, and particularly insecticides, on freshwater biodiversity and ecosystem functioning (e.g. Stehle and Schulz, 2015a; Malaj et al., 2014). Insecticides as a group of pesticides that combine high ecotoxicity potentials with low application rates (Schulz, 2004; Devine and Furlong, 2007) account for 28% of the global crop protection market, with 404,604 t a.i. applied in 2007 to agricultural areas globally (Fishel, 2013a). According to recent projections, the global insecticide market continues to grow at an annual growth rate of 5.27% since 2016, to reach USD 20.82 Billion by 2022 due to increasing global exports and crop losses due to insect infestation (AgroPages, 2017).

Since the 1940s, insect resistance management (Denholm et al., 2002), regulatory restrictions (Werner and Hitzfeld, 2012), and general agrochemical market growth (Lambeth et al., 2013) led to the evolution of four major insecticide classes differing in their mode of actions (Yu, 2008; Table 1). In 1990, before the introduction of neonicotinoids, the agrochemical market was dominated by organophosphates and carbamates with a market share of 59%, as well as pyrethroids (18%; Jeschke et al., 2011). However, in 2008, neonicotinoids already gained a 24% share, mainly at the expense of organophosphates and carbamates (Table 1). Generally, the research and development of the newer generation insecticides such as pyrethroids and neonicotinoids, which steadily replaced the older classes of organochlorine, organophosphate and carbamate insecticides, have focused on higher selectivities and greater intrinsic insecticidal toxicities for invertebrates, which resulted in considerable application rate reductions over the last decades (Table 1); the application rates of contemporary insecticides, which also depends on the method of application (e.g., Jeschke et al., 2011), can be as low as 10 g/ha, i.e., only 1% of that of outdated compound classes such as organochlorine insecticides (Devine and Furlong, 2007; Lambeth et al., 2013). Overall, the development and design of modern pesticides must tackle the challenges of the rapid increase in pest resistance, increasing regulatory requirements, and demands for environmentally benign compounds (Lambeth et al., 2013; Werner and Hitzfeld, 2012).

1.2. Physicochemical properties, environmental fate and ecotoxicity of insecticides

Physicochemical properties, selected ecotoxicity values and legally accepted regulatory threshold levels (RTLs) defined for pesticide registration (Stehle and Schulz, 2015a) of 28 commonly used insecticide compounds (see below for insecticide compound selection) are shown in Table S1 (Supplementary data). Apart from few organophosphate and carbamate insecticides (i.e., diazinon, parathion-methyl, carbofuran) and the neonicotinoids, insecticides have rather low water solubilities and high organic carbon-water partition coefficients (KOC); this is specifically true for the highly sorptive pyrethroids, which are also characterized by comparably short half-life times in water, suggesting fast dissipation from the water phase and a high affinity for organic matter, e.g. in sediments (Li et al., 2017; Fig. S1a). Importantly, physicochemical properties such as the KOC of pesticides are generally determined under artificial laboratory conditions (Wauchope et al., 2002), although, however, they are used to predict and describe the distribution of pesticides under highly complex real-world conditions. However, due to their high hydrophobicity, pyrethroids are in surface waters more likely to be retained at or close to the entry sites compared to the highly water soluble and environmentally stable neonicotinoids; the latter are prone to enter and persist in surface waters (see DT50 values for water in Table S1) via runoff and drainage in the water phase (Morrisey et al., 2015) and even via plant materials, i.e., senescent foliage falling from treated trees (Englert et al., 2017). However, nonpoint-source pollution entries (i.e., exposure via spray drift, irrigation–or rainfall-induced runoff and drainage, see Reichenberger et al. (2007) and Schulz (2004) for further information on these entry routes) are generally regarded as the major source of insecticide surface water exposure (Schulz, 2004; Stehle and Schulz, 2015a). Insecticide contamination is thus characterized by complex input dynamics driven by meteorological conditions (e.g., wind, rain events) and seasonal application, which results in a discontinuous and complex exposure pattern and brief occurrence of peak concentrations (Götz et al., 2010; Stehle et al., 2013). Resulting insecticide surface water concentrations are additionally determined by the abiotic features of the water body and the respective physicochemical properties of a given compound, which facilitates transport, retention and degradation (Capel et al., 2001). However, due to insecticides’ high intrinsic acute ecotoxicity potentials towards aquatic organisms and their fast modes of action (Devine and Furlong, 2007; Yu, 2008), brief exposure events can already trigger clear ecological effects (Schulz, 2001; Schulz and Liess, 1999).

It follows that insecticides are generally compounds of high ecotoxicological concern (Stehle and Schulz, 2018), with the development of newer insecticide classes from organochlorines via organophosphates and carbamates to pyrethroids accompanied by higher ecotoxicity potentials specifically for aquatic invertebrates and consequently lower RTLs (Table S1; Fig. S1). For example, pyrethroids’ median EC50 for the common model test organism Daphnia magna and RTL values are one and three orders of magnitude lower than those of organophosphate and organochlorine insecticides, which indicates clearly increased ecotoxicological risks for aquatic ecosystems (Spurlock and Lee, 2008; Fig. S1). It is, however, important to note that pyrethroids and neonicotinoids are substantially less toxic to birds and mammals than organophosphate and carbamate insecticides and have lower bioaccumulation potentials than organochlorine insecticides (Werner and Hitzfeld, 2012). However, neonicotinoids’ high EC50 values for Daphnia magna (Table S1) are in line with numerous studies (e.g., Morrisey et al., 2015; Sanchez-Bayo et al., 2016), which report that Daphnia magna is particularly insensitive towards neonicotinoid exposure, with EC50 values of at least two to three orders of magnitude higher than those for many aquatic insect groups. Due to controversies over this insecticide class, the RTLs used here for neonicotinoids have been or currently are under critical review and considerable variation exist between countries. However, Morrisey et al. (2015) state that current RTLs often are too high and thus insufficiently protective, specifically

Table 1

<table>
<thead>
<tr>
<th>Insecticide class</th>
<th>Introduction to the market</th>
<th>Insecticide market share (%) 1990/2008</th>
<th>First report of resistance</th>
<th>Typical application rates (g a.i./ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organochlorines</td>
<td>1940</td>
<td>59/34.4</td>
<td>1946</td>
<td>1000–4000</td>
</tr>
<tr>
<td>Pyrethroids</td>
<td>1973</td>
<td>0/23.7</td>
<td>1978</td>
<td>10–200</td>
</tr>
<tr>
<td>Neonicotinoids</td>
<td>1991</td>
<td>0/23.7</td>
<td>1995</td>
<td>10–100</td>
</tr>
</tbody>
</table>
considering chronic and long-lasting effects for aquatic communities; they thus propose based on species sensitivity distributions considering 173 acute and chronic toxicity tests that neonicotinoid surface water exposure should not exceed 0.2 μg/L (short-term acute) or 0.035 μg/L (long-term chronic) to avoid lasting effects on aquatic invertebrate communities, i.e., threshold levels of up to three orders of magnitude lower than those used here (Table S1).

Despite elaborate regulations enforced to ensure an environmentally safe pesticide use (e.g., European Commission, 2009; FIFRA, 1947), recent studies (Stehle and Schulz, 2015a, 2015b; Knäbel et al., 2012) showed based on field data that current regulatory risk assessment concepts fail to protect surface waters from excessive insecticide contamination. In 2015, Stehle and Schulz (2015a) used for the first time RTLs to evaluate agricultural insecticide concentrations in global surface waters. However, Stehle and Schulz (2015a) presented aggregated global insecticide field data only and a pure risk-based evaluation, i.e., aggregated exceedance frequencies of RTLs. Importantly, this study did neither report or discuss the particular concentration levels of individual insecticide compounds, nor for different geographical regions.

The aim of this study is therefore to specify and provide the surface water concentrations (water and sediment) of 28 important insecticide compounds, including integrating evaluations for the respective insecticide classes and analyses at the continental and country scale. The present analysis is based on the aggregated data reported in Stehle and Schulz (2015a), yet provides for the first time a concentration-based evaluation for individual insecticide compounds, which facilitates new insights into distribution of insecticide exposure levels in surface waters globally. Such information promote the design of realistic effect studies, the classification of future monitoring results, and the calibration and evaluation of current regulatory exposure models and risk assessment concepts for specific compounds of concern. In addition, insecticide water-phase and sediment concentrations are used to calculate KOC values based on actual field data; these KOC values are subsequently compared to theoretical KOC values taken from the Pesticide Properties Database (Lewis et al., 2016) in order to assess the field-relevance of KOC values determined in the laboratory.

2. Materials and methods

2.1. Literature search and global insecticide exposure dataset

We used here the global insecticide exposure dataset provided in Stehle and Schulz (2015a; see this publication for detailed information on the entire literature review process, selection criteria, information retrieval and the complete dataset). In brief, insecticide exposure data were derived by a comprehensive literature research on measured insecticide concentrations (MIC; i.e., insecticide concentrations actually detected above their limit of quantification (LOQ; see Stehle and Schulz (2015a) for details)) in global surface waters considering more than 50 insecticide compounds from four major insecticide classes, i.e., organochlorine insecticides, organophosphates (incl. carbamates), pyrethroids, and neonicotinoids (Table 1). The dataset includes MICs from agricultural nonpoint source pollution only, which excludes concentrations related to, for example, point sources, urban, industrial, and public health activities, forest application, as well as accidental spills and intentional water contamination. The dataset comprises 838 scientific articles published between 1962 and 2012 and field concentrations of a total of 28 insecticide compounds (Table S1). In total, the dataset includes 8166 water-phase concentrations (MICSW) and 3134 sediment concentrations (MICSED) measured between 1960 and 2011 in more than 2500 surface water sites in 73 countries worldwide. 17 and 24 out of the 28 insecticides considered here are currently authorized in the EU and the US, respectively (Table S1).

2.2. Insecticide classification calculator (ICC)

An online tool termed “insecticide classification calculator” (ICC; available at: https://static.magic.eco/icc/v1), which allows scientists to classify additional insecticide concentrations (water and sediment) using the global insecticide exposure dataset described above, is provided. In detail, additional MICs of a given compound can be entered online in an input mask of the ICC and will subsequently be classified using all particular MICs of that compound available in the global insecticide dataset by calculating the percentile of this particular concentration; moreover, the entered MIC will be highlighted graphically in the cumulative frequency distribution curve of this particular compound. Please see also https://static.magic.eco/icc/v1 for instructions.

2.3. Regulatory Threshold Levels (RTLs)

The ecological significance of the insecticide concentrations was evaluated using RTLs (see Table S1) derived from official EU and US pesticide registration documents (see Stehle and Schulz (2015a) for details). In essence, the average values of the US and EU RTL for water-phase concentrations (RTLsw) reported in Stehle and Schulz (2015a) were used here to assess MICSW in global surface waters. Concerning sediment concentrations, the RTLsed reported in Stehle and Schulz (2015a), which were derived either from official EU and US pesticide risk assessment documents or from Crommentuijn et al. (2000), were applied.

2.4. Field data-based organic carbon-water partition coefficient

Insecticide field concentrations were used to calculate field data-based organic carbon-water partition coefficients (KOC(field)). In detail, we first calculated field data-based particle-water distribution coefficients (Kd(field), values) by dividing the median sediment concentrations by the median water-phase concentrations of all substances with more than 100 MICSW and more than 100 MICSED available:

\[ K_{d\ (\text{field})} = \frac{C_s}{C_w} \text{ (kg L}^{-1}) \]

where \(C_s\) and \(C_w\) are the median sediment and water-phase concentrations, respectively, of a given insecticide compound.

Next, field data-based KOC values (KOC(field)) were calculated by dividing Kd(field) values by a typical fraction of organic carbon (fOC) of 0.01 in order to normalize Kd values for the organic content of the sediments:

\[ K_{\text{OC\ (field)}} = \frac{K_{d\ (\text{field})}}{f_{\text{OC}}} \text{ (L kg}^{-1}) \]

The KOC(field) values were subsequently compared with the respective theoretical, laboratory-based KOC values listed in the Pesticide Properties Database (Lewis et al., 2016). These freely available KOC values for the respective insecticide compounds are the geometric mean values determined for different soils and pH values.

2.5. Global insecticide exposure dataset evaluation

The global insecticide exposure dataset was evaluated as follows:

(i) distribution, key statistics and comparative analyses of MICSW and MICSED for each insecticide class in order to compare the environmental occurrence and exposure levels among different insecticide generations;

(ii) distribution, key statistics and comparative analyses of MICSW and MICSED for all 28 individual insecticide compounds (including ecotoxicological evaluation of MICs using RTLs) in order to provide a comprehensive compilation of global insecticide
2.6. Data representation

Boxplots are used here to depict MIC\textsubscript{SW} and MIC\textsubscript{SED}, with each box enclosing 50% of the data and the median value of the concentrations displayed as a line. The top and bottom of the box mark the limits of ±25% of the concentration population. The lines extending from the top and bottom of each box mark the minimum and maximum values within the dataset that fall within a maximum of 1.5 of the interquartile distance (i.e., the distance between the upper and lower quartiles). Any value outside this range denotes an outlier and is displayed as an individual point.

3. Results and discussion

3.1. Number and distribution of MICs per insecticide class

The numbers, statistics and distributions of MICs for each insecticide class are shown in Table 2 and Fig. 1. Generally, large differences exist in the amount of water-phase concentrations irrespective of the number of compounds considered per class (Table 2). In detail, substantially more MIC\textsubscript{SW} were available for organochlorine and organophosphate insecticides (n = eight compounds) compared with pyrethroids and neonicotinoids (n = 20 compounds). The longer time span of organochlorine and organophosphate insecticide usage in global agriculture, as well as their dominating market shares in the 20th century (see Table 1) reasons their high numbers of MICs documented in the scientific literature. In contrast, neonicotinoids gained importance in the recent years and have thus not been analyzed in the vast majority of field studies discussed here. However, neonicotinoid water concentrations were increasingly reported in the scientific literature particularly during the last five years (e.g., Morrissey et al., 2015; Sanchez-Bayo et al., 2016). Concerning sediments, hardly any difference exists between the insecticide classes concerning the number of MIC\textsubscript{SED} apart from neonicotinoids, for which no MIC\textsubscript{SED} have been documented in the scientific literature till 2012. The hydrophobicity of pyrethroids and concerns related to effects on benthic organisms (e.g., Li et al., 2017) led to most detections of this substance class in sediments, whereas MIC\textsubscript{SW} prevail in case of the other insecticide classes (Table 2).

The field concentrations of all insecticide classes span several orders of magnitude, with maximum MICs detected for organochlorine (6344 μg/L; 52,400 μg/kg) and organophosphate insecticides (9000 μg/L; 20,400 μg/kg) (Fig. 1; Table 2). The general distribution pattern of water- and sediment-phase MICs is comparable among all classes, with, however, median neonicotinoid MIC\textsubscript{SW} exceeding those of pyrethroids by one order of magnitude and those of organochlorine and organophosphate insecticides by approximately a factor of three (Fig. 1a). It is thus interesting to note that the distribution pattern of field concentrations does not reflect typical application rates, which differ by up to three orders of magnitude between the four insecticide classes (Table 1). However, it is important to note that the restricted number of neonicotinoid concentrations available (n = 131 MIC\textsubscript{SW}) restricts here final conclusions for this insecticide class. Nevertheless, specific physicochemical properties such as the high water solubility and longer environmental half-life times of neonicotinoids (Table S1) potentially foster elevated water-phase concentrations, and thus counteract the effects of low application rates (Table 1). In this context, the high hydrophobicity of the other insecticide classes led to generally higher insecticide concentrations detected in sediments, i.e., MIC\textsubscript{SED} of organochlorine and organophosphate insecticides exceeded respective MIC\textsubscript{SW} by on average 1.5 orders of magnitude, whereas sediment concentrations of pyrethroids exceeded water-phase concentrations by two orders of magnitude (Fig. 1).

3.2. Number and distribution of MICs reported for individual insecticide compounds

Boxplots of the concentrations and key statistics for the individual insecticide compounds are shown in Fig. 2 and Tables S2 and S3. The cumulative frequency distribution curves of MICs for all compounds with more than three field concentrations (n = 24) are shown in Fig. S2. These key statistical numbers and concentration distribution curves comprise all MICs reported in the scientific literature in global agricultural surface waters between 1962 and 2012 and thus denote a reference work to (i) classify and compare, among other, field concentrations detected in future sampling campaigns (using, e.g., the ICC, which enables an exact classification of a given field concentration using the global exposure data presented here), (ii) select field-relevant and realistic test concentrations for laboratory or higher tier toxicity

### Table 2

<table>
<thead>
<tr>
<th>Insecticide class (number of compounds)</th>
<th>Number</th>
<th>Minimum</th>
<th>10th Percentile</th>
<th>25th Percentile</th>
<th>Median</th>
<th>75th Percentile</th>
<th>90th Percentile</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (μg/L)</td>
<td>2021</td>
<td>0.000005</td>
<td>0.0015</td>
<td>0.015</td>
<td>0.083</td>
<td>0.44</td>
<td>3.6</td>
<td>6344</td>
</tr>
<tr>
<td>Organochlorines (1)</td>
<td>5095</td>
<td>0.00001</td>
<td>0.005</td>
<td>0.02</td>
<td>0.1</td>
<td>0.59</td>
<td>4</td>
<td>9000</td>
</tr>
<tr>
<td>Organophosphates (7)</td>
<td>919</td>
<td>0.000133</td>
<td>0.0027</td>
<td>0.008</td>
<td>0.0381</td>
<td>0.5135</td>
<td>2.8482</td>
<td>250</td>
</tr>
<tr>
<td>Neonicotinoids (5)</td>
<td>131</td>
<td>0.005</td>
<td>0.019</td>
<td>0.1</td>
<td>0.353</td>
<td>0.91</td>
<td>2.09</td>
<td>320</td>
</tr>
<tr>
<td>Sediment (μg/kg)</td>
<td>1033</td>
<td>0.00144</td>
<td>0.0732</td>
<td>0.79</td>
<td>3.75</td>
<td>24.9</td>
<td>218</td>
<td>52,400</td>
</tr>
<tr>
<td>Organochlorines (1)</td>
<td>1156</td>
<td>0.001</td>
<td>0.3</td>
<td>1.2</td>
<td>4.8</td>
<td>21.1</td>
<td>138.3</td>
<td>20,400</td>
</tr>
<tr>
<td>Organophosphates (7)</td>
<td>945</td>
<td>0.004</td>
<td>0.6</td>
<td>1.62</td>
<td>5.08</td>
<td>16.4</td>
<td>70.5</td>
<td>10,640</td>
</tr>
<tr>
<td>Neonicotinoids (4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Please note that all pyrethroid and neonicotinoid compounds were considered in the literature research but MICs could only be derived for 16 pyrethroids and four neonicotinoids.*
testing (e.g., assessment of effects triggered by the median or 95th percentile field concentration of a given compound), and (iii) provide input data for a more field-relevant pesticide exposure and risk assessment (i.e., distribution of MICs can be used to evaluate the protectiveness of exposure model outcomes (cf. Knabel et al., 2012)). However, we acknowledge that MICs reported in the last five years (i.e., from 2013 onwards) are not included in the insecticide field data presented here and that future work is thus needed to compile and add current and future field concentrations to the dataset. However, we intend to update the ICC on a regular basis using insecticide concentration data from the scientific literature as well as from governmental monitoring programs.

Considerable differences exist in the scientific literature concerning the number of MICs reported for individual substances, i.e., far less MICs were available for compounds of newer insecticide classes (i.e., neonicotinoids and pyrethroids) compared with those of classes available since several decades on the global crop protection market (i.e., organochlorine and organophosphate insecticides). In addition to market introduction and share, physicochemical properties like hydrophobicity (i.e., few or no MICs available for hydrophilic compounds such as carbofuran or neonicotinoids), insecticide application patterns, as well as specific environmental concerns or scientific interests potentially influence the sampling and thus reporting frequencies. Moreover, the low field application rates of modern insecticide compounds (Table 1) pose challenges for their analytical detection in the environment (Werner and Hitzfeld, 2012; Akerblom et al., 2008). Within this context it is, however, important to note that these low field application rates are accompanied by particularly high invertebrate toxicities of contemporary insecticides (i.e., pyrethroids and neonicotinoids). These high toxicity potentials trigger acute toxic effects already at concentrations hard to detect in surface waters, complicating to link ecological effects to insecticide exposure in the field (Akerblom et al., 2008). Notwithstanding, the low application rates of contemporary insecticides are often appraised as substantial progress towards more environmental benign pesticide compounds (Lamberth et al., 2013; Housset and Dickmann, 2009).

All maximum MICs of organochlorine and organophosphate insecticides exceed $10^3$ μg/L, whereas those of pyrethroids and neonicotinoids vary in the range of $6 \times 10^{-2}$ and $3.2 \times 10^2$ μg/L (Fig. 2; Table S2). A similar pattern can be observed for sediments, i.e., maximum MICs of all organochlorine and organophosphate insecticides exceeded $10^3$ μg/kg, whereas those of pyrethroids generally were one to two orders of magnitude lower (Fig. 2; Table S3). These findings can be attributed to the substantially higher application rates for organochlorine and organophosphate insecticides (Table 1), as well as to the higher number of concentrations detected, making the detection of higher concentrations more likely. For example and based on additional field studies available only in the past five years, recent reviews of neonicotinoid water concentrations reported higher maximum concentrations (e.g., 44.1 μg/L acetamiprid; 225 μg/L thiamethoxam (Morrissy et al., 2015; Sanchez-Bayo et al., 2016)) than those available from the dataset included in the present study (Table S2).

The general distribution of the MICs of individual organophosphate compounds are rather even and similar to each other (i.e., most concentrations lie the range of $10^{-2}$ and 1 μg/L and 1 and 100 μg/kg), whereas the distribution of pyrethroids MICs is rather uneven and more diverse (Fig. 2). This pattern can be attributed to the restricted availability of MICs for particular pyrethroid compounds (e.g., five pyrethroids (i.e., acrinathrin, β-cyfluthrin, α-cypermethrin, tau-fluvalinate, tralomethrin) with less than ten MICs in Table S2), which partly originated from one field study only; it is important to note that this restricts the representativeness of these five compounds’ concentrations for global agricultural surface waters. Within this context, less than ten MICs were available for three out of four neonicotinoid insecticides (Table S2), which hinders a thorough statement on the environmental distribution of these particular compounds. Although heavily used in global agricultural, no surface water concentrations of clothianidin could be retrieved from the scientific literature evaluated for our dataset; however, since 2012, clothianidin concentrations of up to 3.1 μg/L (Morrissy et al., 2015) and 3.5 μg/L (Sanchez-Bayo et al., 2016) have been reported.

Concerning neonicotinoids in general, recent compilations of neonicotinoid concentrations found these compounds to be present in surface waters worldwide with geometric mean concentrations in the range of 0.1 μg/L and 1 μg/L (Sanchez-Bayo et al., 2016; Morrissy et al., 2015). In addition, a recent worldwide assessment of neonicotinoids reports widespread and frequent (i.e., detection frequencies of up to 100%) surface water exposure in many countries, with maximum concentrations of up to 83 μg/L imidacloprid detected in agricultural streams (Giorio et al., 2017). Importantly, neonicotinoid water concentrations increased over the past 15 years (Sanchez-Bayo et al., 2016) reflecting the worldwide trend in increasing neonicotinoid usage in global agriculture (Table 1).

Generally, the distribution of field concentrations reported here is controlled by the analytical LOQ at the lower end, as well as the interplay of various factors such as the application rates and methods, the physicochemical properties of the individual compounds, the specific agri-environmental settings including meteorological and hydrological...
Fig. 2. Boxplots of the water-phase and sediment concentrations of the 24 insecticide compounds: (a) organochlorine MICSW; (b) organochlorine MICSED; (c) organophosphate MICSW; (d) organophosphate MICSED; (e) pyrethroid MICSW; (f) pyrethroid MICSED; (g) neonicotinoid MICSW (no MICSED were available for neonicotinoids). Acrinathrin, β-cyfluthrin, tefluthrin, and tralomethrin are not displayed since less than three water-phase and sediment concentrations were available.
conditions, as well as the sampling strategy at the upper end. Concerning the first point, Stehle and Schulz (2015a) reported for the present dataset that mean LOQs did not differ substantially between the substance classes, i.e., the lower concentration limits for the different insecticide classes are generally comparable. In addition, no clear trend exists for the LOQs employed in the studies over time (Fig. S3). Nevertheless, few individual studies focusing specifically on analytical methods achieved particularly low LOQs for some insecticide compounds (e.g., Kampioti et al., 2005; Iwafuna et al., 2011). However, concerning the upper concentration limits it is important to note that in many cases actual maximum concentrations in the field are most likely higher than those reported here as it is extremely hard to capture the highly transient, short-term insecticide concentration peaks (see Stehle et al., 2013 for details).

The compliance and exceedance of water and sediment RTLs are shown for each individual compound in Table S4 and Table S5, as well as by the vertical dashed lines in Fig. S2. As reported in Stehle and Schulz (2015a), RTL exceedances in global agricultural surface waters are common (overall 40.8% exceedance frequency) and are generally higher for compounds of newer insecticide classes (except neonicotinoids) reasoned by increasing toxicity potentials of newer generation insecticides (Table S1; Fig. S1). The application of the acute ecological threshold level (0.2 μg/L) for neonicotinoid water-phase concentrations proposed by Morrissey et al. (2015) instead of RTL exceedances indicates also high ecological risks for neonicotinoid surface water concentrations, i.e., 62.6% of all (n = 131) neonicotinoid MIC exceed this threshold level. These findings are in contradiction to perceptions by regulators (Fishel, 2013b), industry (ECFA, 2013) and the scientific community (Devine and Furlong, 2007; Lambeth et al., 2013) claiming that the development and application of newer insecticide classes such as pyrethroids and neonicotinoids led to reduced risks for aquatic ecosystems. At the individual compound level, 19, 14, nine and seven out of the 28 compounds showed RTL exceedances of 30%, 50%, 70%, and 90%, respectively (Table S4). Concerning sediments, high exceedance frequencies of up to 100% could be observed across 30%, 50, 70%, and 90%, respectively (Table S4). The application of the acute ecological threshold level (0.2 μg/L) for neonicotinoid water-phase concentrations proposed by Morrissey et al. (2015) instead of RTL SW exceedances indicates also high ecological risks for neonicotinoid surface water concentrations, i.e., 62.6% of all (n = 131) neonicotinoid MIC exceed this threshold level. These findings are in contradiction to perceptions by regulators (Fishel, 2013b), industry (ECFA, 2013) and the scientific community (Devine and Furlong, 2007; Lambeth et al., 2013) claiming that the development and application of newer insecticide classes such as pyrethroids and neonicotinoids led to reduced risks for aquatic ecosystems. At the individual compound level, 19, 14, nine and seven out of the 28 compounds showed RTL exceedances of 30%, 50%, 70%, and 90%, respectively (Table S4). Concerning sediments, high exceedance frequencies of up to 100% could be observed across all compounds with detections in sediments, indicating high risks for benthic organisms due to the high hydrophobicity of many insecticides; out of the 20 compounds, for which MIC exceedable, 15 and seven showed RTL exceedance frequencies of 70% and 90%, respectively (Table S5). In conclusion, these risk assessment results prove that the agricultural use of insecticides pose large ecological risks for aquatic ecosystem worldwide (see Stehle and Schulz (2015a) for further information).

3.3. Geographical distribution of MICs per insecticide class

The number and distribution of MICs classified per continent is shown in Fig. 3. Across all insecticide classes, by far most MICs were reported for North America, followed by Asia and Europe; in contrast, information on insecticide surface water exposure in Africa and South America are scarce, although, however, agricultural land use also dominates large areas of these continents. In detail, Stehle and Schulz (2015a) reported that, although extensive, the present database does only contain MICs for surface waters located in approximately 10% of global cropped areas. Further evaluations made here (Table S6) show for the 73 countries considered here that on average only one MIC is reported for 353,366 ha of croplands (arable and permanent crops). However, substantial differences between individual countries exist ranging from one MIC per 200 ha up to one MIC per 3,778,000 ha of cropped area (Table S6), with no apparent relationship between the number of MICs and the size of the cropped area per country or a difference between developed and developing countries. Overall, these evaluations in concert with the fact that MICs were available for 73 countries only show that further monitoring studies are needed globally in order to complement our knowledge on insecticide surface water exposure. Such a request is in line with other studies (e.g., Schwarzenbach et al., 2006; Rockström et al., 2009) also postulating an increase in monitoring efforts of synthetic chemicals in the environment. However, it is important to note that our global analysis presented here is based only on the peer-reviewed scientific literature and that further MICs are available from non-peer-reviewed studies such as governmental reports; nevertheless, such reports were intentionally excluded here in order to ensure that scientific standards were met. In addition, although comprehensive database searches in eight important languages have been performed (see Stehle and Schulz, 2015a), it is probable that low numbers of MICs, or even no MICs at all, result from the fact that scientific studies on insecticide exposure of surface waters have only infrequently or not at all been performed in some countries; this potentially limits the representativeness of the global insecticide exposure information presented here.

Generally, insecticide water-phase concentration levels reported for surface waters in Africa, Asia and South America exceed those detected in North America and Europe, most likely due to less stringent pesticide regulations, farmers’ limited knowledge of appropriate pesticide application and overall higher insecticide use in warmer climates (Fig. 3; Ecobichon, 2001; Schreinemachers and Tipraqs, 2012). However, this pattern is less distinct for sediment concentrations, presumably due to small numbers of MIC available for some regions, which hinder a thorough comparison. The global insecticide market is forecasted to continue to grow worldwide at a rate of 5.3% between 2016 and 2021, with specifically the Asia-Pacific region projected to be the fastest-growing market for insecticides globally in the next five years (AgroPages, 2017) due to the ongoing agricultural intensification including increasing pesticide inputs and growing demand for crops in this region. This will put global surface waters in general, and those located in Asia-Pacific particularly, at increasing risks of high insecticide exposure.

In order to provide more detailed information on the risks posed by insecticide contamination of surface waters, Table S7 lists the number of concentrations and RTL exceedances of the four insecticide classes for individual countries. The number of MICs, as well as the RTL exceedance rates differ substantially between countries, with more than 500 MICs reported for surface waters located in the USA, Canada, India, and Australia; RTL exceedance rates vary between 0% and 100% for individual countries and insecticide classes (Table S7). However, small numbers of MICs available for some countries (e.g., 26 countries with less than ten MICs) prevent here an effective comparison and a conclusive evaluation of RTL exceedances across all countries. Nevertheless, RTL exceedances are common across all countries and insecticide classes (Table S7), with in total 52.4% of the 11,300 MICs exceeded respective RTLs globally.

3.4. Field data-based organic carbon-water partition coefficient (KOC (field))

The Kd (field) and KOC (field) values and the respective median water and sediment field concentrations are shown in Table S8 along with the theoretical KOC values taken from the Pesticide Properties Database (Lewis et al., 2016). Although a general relationship between the KOC (field) and theoretical KOC values exist, most (i.e., 7 out of 9) field database-based partition coefficients underestimated the theoretical KOC values by up to a factor of more than 20 (Fig. 4a; Table S8); assuming a fOC of 0.05 instead of 0.01 increases the deviations by a factor of five (Table S8). These results suggest that under field conditions, the directly bioavailable insecticide water-phase concentrations are generally higher than predicted by the available laboratory-based KOC values. This finding has critical implications as the KOC denotes an important input parameter for exposure models used in the regulatory risk assessment conducted for pesticide authorization (e.g., EFSA, 2013; USEPA, 2017). Deviations of laboratory and field data-based KOC values increase with increasing KOC values, i.e., particularly the KOC (field) values of highly sorptive pyrethroids are substantially lower when compared with their theoretical KOC values (Fig. 4b; Table S8); this indicates that under...
actual field conditions, pyrethroid water concentrations are particularly high and partitioning into sediments does not occur to the extents predicted by their theoretical KOC values. Overall, these findings question the results of exposure and fate modeling concepts, specifically when predicting the environmental fate of highly sorptive compounds (see, also, Knäbel et al., 2012); this overestimation of pyrethroids sorption to soils and sediments in exposure modeling may thus be one further explanation for the high RTLSW exceedances determined for pyrethroids by Stehle and Schulz (2015a). The soil-water-pesticide interaction is highly complex in field ecosystems and potentially not well reflected by the artificial KOC determination in laboratory studies (Wauchope et al., 2002). In addition, reported KOC values often vary by a factor of two to three (Lyman, 1990) and specifically the laboratory KOC determination for highly sorptive compounds are prone to error due to sorption to glassware and small test systems (Spurlock et al., 2005). It is also important to note that the theoretical KOC values from the Pesticide Properties Database (Lewis et al., 2016) are geometric mean values across different soils, which might have different attributes (e.g., type of organic matter) when compared with field sediments; this might also result in slight deviations between theoretical KOC values and KOC (field) values.

It is important to note that due to data availability restrictions (i.e., lack of paired water and sediment samples; but see below) the field data-based partition coefficients were calculated based on median values integrating water and sediment concentrations from different sampling sites globally. In addition, we assumed a sediment fOC of 0.01 across all sites for KOC (field) calculations. However, to overcome the potential implications of these generalizations and to analyze the large deviations specifically of the highly sorptive pyrethroids, the available pyrethroid studies for field surveys that collected paired surface water and sediment samples simultaneously at a given sampling site were screened. KOC (field) values were then recalculated using paired water and sediment concentrations of pyrethroids and actual fOC values reported for the sampling sites. Results show that the distributions of these KOC (field) values (Fig. S4) are highly variable by comprising up to six orders of magnitude for individual pyrethroids and field studies (only three were available) and that KOC (field) values are still generally lower than theoretical KOC values. However, the ratios of the median field data-based and theoretical KOC values generally are smaller than those derived from the overall dataset (Fig. S4; Table S8). This indicates that KOC (field) values based on paired water and sediment samples and actual fOC values coincide better with theoretical KOC values. Nevertheless, these pyrethroids’ KOC (field) values based on paired water and sediment samples still substantially underestimate up to one order of magnitude those derived.

Fig. 3. Distribution of MICs (water and sediment) per insecticide class ((a) organochlorine; (b) organophosphate; (c) pyrethroid; (d) neonicotinoid) and continent.
in the laboratory, confirming the results obtained from the overall dataset.

Another factor potentially explaining the rather low $K_{OC\ (l田野)}$ values of pyrethroids might be that water-phase concentrations determined without appropriate pre-filtration procedures (e.g., 0.45 μm filtration) potentially not only comprise dissolved pyrethroid concentrations but also particle-associated pyrethroid concentrations (Stehle and Schulz, 2015a; Spurlock et al., 2005), thereby overestimating pyrethroid water-phase concentrations used for calculation of $K_{OC\ (l田野)}$. The calculation of $K_{OC\ (l田野)}$ using filtered cypermethrin water-phase concentrations ($n = 46$; median water-phase concentration of 0.01775 μg/L) indeed resulted in a value of 52.394 at a $f_{OC}$ of 0.01, i.e. approximately a factor of five higher compared with the $K_{OC\ (l田野)}$ value calculated using all cypermethrin water-phase concentrations (Table S8). This $K_{OC\ (l田野)}$ value is, however, still approximately a factor of three lower than the laboratory-based, theoretical $K_{OC}$ value. Restricted availability of filtered water-phase concentrations of the other pyrethroids hindered the recalculation of their $K_{OC\ (l田野)}$ Values. Overall we conclude that the fate and the distribution specifically of highly hydrophobic insecticides such as pyrethroids in real world surface water systems does not match those predicted by laboratory based $K_{OC}$ values indicating the need for further research on potential reasons and implications.

4. Conclusion

Aquatic ecosystems are exposed towards agricultural insecticides at a global scale. Application rates and patterns, physicochemical properties and local environmental conditions determine the occurrence, duration and heights of insecticide concentrations in water and sediments of surface waters. Organochlorine and organophosphate insecticides, which dominated the global insecticide market for decades, have been detected most often and at highest concentrations in surface waters globally. However, although exposure levels of recent insecticide classes such as pyrethroids and neonicotinoids are generally lower, these compounds are of high ecotoxicological concerns due to their extremely high toxicity potentials towards aquatic organisms. Compilations and comparative analyses of global insecticide field concentrations are important for realistic and field-relevant toxicity testing procedures, to compare actual environmental levels and thus risks across individual insecticide compounds and classes, to evaluate insecticides’ physicochemical properties and behavior in the field, as well as to evaluate and adapt current regulatory exposure models and risk assessment concepts. Such a reference work is moreover helpful to identify compounds and geographical areas with limited information on surface water exposure; more studies are currently needed to gain a more complete picture of the global contamination levels for individual insecticides.

Despite the ongoing advances in agricultural technology, risk assessment concepts and strict regulation of pesticides in many developing countries, recent data for surface waters in the European Union (Malaj et al., 2014), the US (Stone et al., 2014) and globally (Stehle and Schulz, 2015a; Morrissey et al., 2015) evidence substantial and ongoing risks for the aquatic biodiversity due to insecticide exposure. It follows that effective risk mitigation measures are needed to reduce insecticide concentrations levels in global agricultural surface waters.

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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.2018.05.158. The insecticide classification calculator (ICC) is available at: https://static.magic.eco/icc/v1.

References


Fig. 4. (a) Relationship ($R^2 = 0.551$) between field data-based organic carbon-water partition coefficients ($K_{OC\ (l田野)}$) and theoretical $K_{OC}$ values taken from the Pesticide Properties Database (Lewis et al., 2016), as well as (b) relationship ($R^2 = 0.735$) between the theoretical $K_{OC}$ and the theoretical $K_{OC}$ to $K_{OC\ (l田野)}$ ratio.