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

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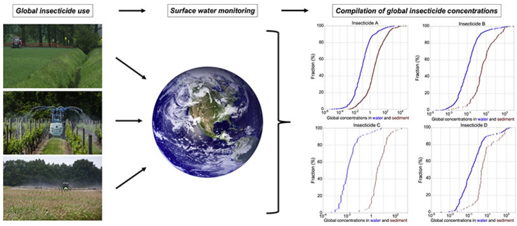
HIGHLIGHTS

- 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



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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 (K_{OC}) determined in the laboratory overestimated K_{OC} 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 suggest 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 (Lamberth 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; Lamberth 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 (Lamberth 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 solubilites and high organic carbon-water partition coefficients (K_{OC}); 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 K_{OC} 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 DT_{50} vales for water in Table S1) via runoff and drainage in the water phase (Morrissey 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 EC_{50} 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 EC_{50} values for *Daphnia magna* (Table S1) are in line with numerous studies (e.g., Morrissey et al., 2015; Sanchez-Bayo et al., 2016), which report that *Daphnia magna* is particularly insensitive towards neonicotinoid exposure, with EC_{50} 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, Morrissey et al. (2015) state that current RTLs often are too high and thus insufficiently protective, specifically

Table 1
Market introduction (Denholm et al., 2002; Elbert et al., 2008), development of insecticide market shares (Jeschke et al., 2011), documentation of first resistance (Denholm et al., 2002), and range of typical application rates (Benbrook, 2003; Racke, 2003) for major insecticide classes.

Insecticide class	Introduction to the market	Insecticide market share (%) 1990/2008	First report of resistance	Typical application rates (g a.i./ha)
Organochlorines	1940	–/–	1946	1000–4000
Organophosphates/carbamates	1950/1962	59/24.4	1965/1972	50–2000
Pyrethroids	1973	18/15.5	1978	10–200
Neonicotinoids	1991	0/23.7	1995	10–100