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Aquatic pesticide exposure in the U.S. as a result of non-agricultural uses

Sebastian Stehle[a,b,*], Abigail Bline[c], Sascha Bub[a], Lara Luisa Petschick[a], Jakob Wolfram[a], Ralf Schulz[a]

[a] iES Landau, Institute for Environmental Sciences, University of Koblenz-Landau, Fortstrasse 7, D-76829 Landau, Germany
[b] Eusserthal Ecosystem Research Station, University of Koblenz-Landau, Birkenthalstrasse 13, 76857 Eusserthal, Germany
[c] Fielding School of Public Health, University of California Los Angeles, 650 Charles E. Young Drive South, Los Angeles, CA 90095, USA

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ABSTRACT

Non-agricultural uses of pesticides are common in the U.S. and may thus lead to exposure of non-target ecosystems such as urban waterways. However, surface water exposure resulting from agricultural pesticide uses has received substantially more attention during the last decades. Here we conducted a literature review and meta-analysis of peer-reviewed studies to identify measured environmental concentrations (MEC) of pesticides in perennial surface water bodies due to non-agricultural uses in the U.S. Acute and chronic Aquatic Life Benchmarks (ALB_{acute}, $ALB_{chronic}$) for water-phase concentrations and regulatory threshold levels (RTL_{SED}) for sediment concentrations were used for risk evaluations. Based on 10,755 MECs retrieved from 70 scientific studies, results show that a multitude of pesticide compounds (approx. 150) have been detected at 609 urban surface water sites. Particularly herbicides and insecticides were among the most frequently detected compounds in the water phase, whereas insecticides dominated detections in sediments. While overall acute (5.64% ALB_{acute} exceedances; n = 9034 MEC) and chronic (9.31% $ALB_{chronic}$ exceedances; n = 9036 MEC) risks were comparably low in the water phase, 35% of sediment concentrations (n = 1621 MEC) exceeded RTL_{SED}. Insecticides and particularly pyrethroids were identified as the main drivers of benchmark exceedances in both the water phase and sediments. In addition to pesticide type, a linear model analysis identified further drivers important for risks such as sampling methods. Overall insecticide risks in non-agricultural surface waters were significantly (by a factor of 1.9) lower than those already known from agricultural surface waters in the U.S. However, substantially higher risks in sediments were identified for urban compared with agricultural waterbodies. The present study provides the first comprehensive assessment of pesticides in urban surface waters in the U.S. with overall results indicating common occurrence and non-negligible risks particularly due to urban insecticide uses.

1. Introduction

The environmental impacts of pesticides are often studied within the context of agricultural uses (e.g., Stehle and Schulz, 2015a; Wolfram et al., 2018), which totaled up to 899 million pounds of pesticide active ingredients applied to cropped areas in the U.S. in 2012 (Atwood and Paisley-Jones, 2017). However, pesticides are also commonly applied in non-agricultural settings to maintain residential and commercial landscaping/turf, prevent structural damage to buildings, eradicate disease vectors, and maintaining open spaces in utility and road right-of-ways (Hoffman et al., 2000; Shamim et al., 2014). In 2012, 107 million pounds of pesticide active ingredients were used in the U.S. in the home and garden, as well as the industrial/commercial/governmental sector (Atwood and Paisley-Jones, 2017). Pesticides expenditures in the non-agricultural sector totaled $4760 million in 2012, amounting to 34% of the total U.S. pesticide expenditures (Atwood and Paisley-Jones, 2017). While agricultural applications of pesticides are limited to specific crops, their use in urban environments is more diverse, with, besides indoor uses, applications to e.g., gardens, lawns, sealed areas, facades and roads. In addition, the rate of pesticide active ingredient applications in non-agricultural settings is often considerably higher than in agriculture, with about 240 and 1300 kg active ingredients of insecticides and 580 and 500 kg active ingredients of herbicides applied per km^2 on lawns and golf courses, respectively (Hoffman et al., 2000); Haith (2010) report pesticide application rates to be three to eight times greater on urban turfgrass areas than on agricultural crops.

After application, pesticides may be transported to urban waterways, with stormwater runoff identified as one of the major transport pathways (Hoffman et al., 2000; Weston and Lydy, 2012). Urban

* Corresponding author at: iES Landau, Institute for Environmental Sciences, University of Koblenz-Landau, Fortstrasse 7, D-76829 Landau, Germany.
E-mail address: stehle@uni-landau.de (S. Stehle).

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stormwater drainage systems are generally designed to collect runoff from adjacent impervious surfaces and channel it to a discharge point, usually a surface water body, with little or no retention (Davis, 2005). Substantial impervious surface cover is a distinct feature of urban landscapes compared to agricultural landscapes, where the presence of vegetation and soil may reduce the velocity and pesticide loads of stormwater runoff through percolation, physical interactions and biological degradation (Hoffman et al., 2000). It follows that during rain events, pesticides deposited on impervious surfaces have a high probability to be transported to urban surface water bodies. This direct transport may lead to particularly high surface water concentrations after accumulation of pesticide residues on impervious surfaces over the course of a summer season due to repeated pesticide applications and lack of rainfall (Jiang et al., 2016). However, since insecticides and non-selective herbicides may be used in urban settings throughout the year (Weston et al., 2009), and because urban runoff may be strongly influenced by irrigation in addition to natural storm events (Miller et al., 2014), as well as due to continuous pesticide releases via wastewater treatment plants, there is potential for aquatic organisms in urban waterways to be exposed continuously throughout the year (Ensminger et al., 2013; Shamim et al., 2014). Nevertheless, depending on the climate, varying seasonal patterns of pesticide concentrations may also exist for different geographic regions of the U.S., although these patterns are generally less pronounced compared with agricultural streams (Hoffman et al., 2000; Gilliom et al., 2006).

Monitoring efforts conducted between 1992 and 2011 within the United States Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program detected pesticides in urban streams throughout the year (greater than 97% of the time) and suggested specifically insecticides to occur more frequently and at higher concentrations in urban than in agricultural streams across the U.S. (Gilliom et al., 2006; Stone et al., 2014). However, the concentrations of individual pesticides used in urban settings varied over these two decades of the NAWQA program in response to changes in use driven by regulatory actions and new pesticide introductions. Risk assessment results indicate that pesticide concentrations in urban streams exceeded benchmark levels in 83% of 30 urban streams in the period 1992–2001 (Gilliom et al., 2006), as well as in 90% of 30 urban stream sites in the period 2002–2011 (Stone et al., 2014), with a higher frequency of benchmark level exceedances in urban than in agricultural streams (1992–2001: 57% of 83 sites; 2002–2011: 61% of 36 sites), mainly driven by insecticide concentrations. However, uncertainties prevail concerning NAWQA program results as it did not consistently evaluate pesticides highly relevant in urban and agricultural uses and focused on legacy organochlorine compounds in sediments only (Gilliom et al., 2006; Stone et al., 2014).

Overall, compared to agricultural surface waters for which Wolfram et al. (2018) reported a regulatory threshold level (RTL) exceedance rate of 49.4% for measured insecticide concentrations (n = 5,817, detected at 644 sites) and thus substantial risks, our knowledge on pesticide surface water exposure and risks due to non-agricultural pesticide uses in the U.S. is still comparably scarce. Nevertheless, there is also a large and growing body of scientific work documenting the exposure and effects of residential pesticide uses on stream ecosystems in the U.S. These studies, however, focused on single or rather few locations (i.e., < 40 sites) only (e.g., Hoffman et al., 2000; Stone et al., 2014; Carpenter et al., 2016; Nowell et al., 2018); yet, available studies often indicate higher exposure levels and risks in urban compared with agricultural streams (e.g., Hoffman et al., 2000; Gilliom et al., 2006; Stone et al., 2014). However, a comprehensive evaluation of urban pesticide risks at the national scale - including the comparison with risks from agricultural use - is still needed to thoroughly assess the risks of pesticides in urban waterways.

The aim of the present study is therefore to provide a comprehensive meta-analysis of peer-reviewed field studies reporting measured environmental concentrations (MEC) of pesticides in urban surface waters across the U.S. The present meta-analysis covers 147 compounds and includes particularly current-use substance classes such as neonicotinoids, and a substantially larger number of stream sites compared with previous monitoring programs. Pesticide field concentrations were compared to benchmark levels to determine overall risks for urban surface waters considering here also different pesticide types and individual compounds, to reveal spatial and temporal trends, as well as potential differences between risks arising from agricultural (Wolfram et al., 2018) and urban pesticide applications on a national scale. Based on the available literature on use, entry pathways and monitoring results, we expect that aquatic risks from urban pesticide use strongly exceed those from agricultural use. Spatial regression analyses were used to identify drivers of risks. Overall, this study aims to comprehensively assess for the first time the exposure and ecological risks for U.S. surface waters arising from non-agricultural pesticide uses.

2. Materials and methods

2.1. Literature search and data extraction

Potentially relevant peer-reviewed articles reporting pesticide or pesticide degradation product (subsumed apart from specific analyses also under “pesticide”) water-phase and sediment concentrations in urban surface waters were identified using Clarivate Analytics’ Web of Science citation indexing service. Web of Science searches were conducted on September 12th and 23rd 2016 and included the years 1975–2016 and all pesticide compounds, as well as pesticide degradation products. The terms used in the searches are provided in the supporting information (Methods, Supporting Information). In a first step, the titles and abstracts from the resulting citation returns (n = 404) were reviewed and obviously irrelevant entries were removed from further consideration. Next, the texts of potentially relevant articles were screened to determine if they contained relevant pesticide concentration measurements (i.e., pesticide concentrations in urban surface waters of the U.S.) based upon the criteria provided in the supporting information (Methods, Supporting Information); this resulted in the identification of 89 articles. Beyond the articles identified by the Web of Science searches, additional articles were identified by consulting the reference lists of empirical and review papers (White, 2009). Overall, a total of 70 scientific articles were finally included in this meta-analysis. For each pesticide surface water concentration, additional information such as the sample date, exact location, sampling interval, or catchment area information was also recorded (Methods, Supporting Information). A full list of references used to compile the database is provided online (https://static.magic.eco/urban).

Prior to further analyses, the data were cleaned-up to remove redundant samples, consolidate sample data reported in separate studies, and increase uniformity (Methods, Supporting Information).

2.2. Specification of sampling locations and land use in catchment

If reported, geographic coordinates of sampling locations were taken from the scientific articles. For sample locations described in articles by USGS station numbers without reported geographic coordinates, this information was obtained online from the USGS National Water Information System (NWIS) web-based interface (USGS, 2019). For other sample locations where no geographic coordinates were reported in a given article, an attempt was made to approximate geographic coordinates using the article’s figures and/or text descriptions combined with aerial photographs and the stream feature shape file layer provided by the USGS StreamStats web-based geographic information system application (USGS, 2016). Using the reported or estimated geographic coordinates, the contributing catchment area was identified for each location in StreamStats if it was not available from the data source article. Depending on data availability, the percent urban land, percent agricultural land, percent impervious surface,

percent forested land, mean slope, and mean annual precipitation in the contributing catchment area provided by StreamStats were recorded in the database. No StreamStats data were available for Michigan, Wyoming, Nebraska, Kansas, Missouri, Nevada, West Virginia, Texas, Louisiana, or Florida.

2.3. Aquatic life toxicity metrics

Pesticide concentrations reported in the water phase were assessed using acute and chronic Aquatic Life Benchmarks (ALBs) defined in United States Environmental Protection Agencys' (USEPA) most recent ecological risk assessment for pesticide registration (USEPA, 2019a). ALBs are based on the most sensitive acute and chronic aquatic toxicity data for different taxa (i.e., fish, invertebrates, nonvascular plants, vascular plants) and denote effect threshold concentrations, below which no harm for aquatic life is expected to occur (USEPA, 2019a). We used the lowest acute ALB (ALB_{acute}) across all taxa to assess acute exposure and the lowest chronic ALB ($ALB_{chronic}$) from any taxon to assess prolonged exposure. In cases in which the ALB_{acute} for a given pesticide was lower than the $ALB_{chronic}$ (e.g., due to the restricted availability of chronic toxicity data) or no chronic endpoint was available (five compounds), we also used the acute benchmark value instead of the $ALB_{chronic}$ for the chronic risk assessment. Because some pesticides recorded in the database are no longer registered for use in products marketed within the US, they do not have ALBs established by USEPA. In these cases, due to their comparability to ALBs, the acute and chronic Aquatic Life Criteria (ALC) established by the USEPA (USEPA, 2019b) were used (referred to here also as ALBs). In general, acute and chronic endpoints were available for 93 and 94 compounds, respectively. No ALB could be derived for 25 out of 119 compounds; however, this concerns outdated compounds or degradates with less than ten reported concentrations only (0.8% of all water-phase concentrations).

Pesticide ALBs for sediment have not been established by USEPA. Therefore, we used either regulatory threshold levels (RTLs) for benthic organisms defined by USEPA for pesticide registration, threshold effect benchmarks (TEBs) taken from Nowell et al. (2016), or maximum permissible concentrations (MPCs) from Crommentuijn et al. (2000), with the latter two normalized for 4% organic carbon (see Wolfram et al., 2018) as acute and chronic benchmark levels (termed here RTL_{SED}) for the risk assessment for benthic organisms. No sediment benchmarks could be derived for twelve outdated pesticides or degradates, which however, affects only 2% of all sediment concentrations.

All threshold levels (ALB_{acute}, $ALB_{chronic}$, RTL_{SED}) used in this meta-analysis are provided online (https://static.magic.eco/urban).

2.4. Data analysis and risk assessment

The top 10% most frequently detected pesticides in water-phase and sediment samples by site were calculated for all years and the latest five years of data within the dataset. In addition, frequency analyses were performed based upon the number of locations at which each pesticide was detected multiplied by the frequency of locations at which the pesticide was detected relative to the number of locations at which it was analyzed (Methods, Supporting Information). The occurrence of mixtures was determined for water-phase and sediment concentrations on a sample and site-specific base.

To assess overall risks for urban surface waters, water-phase MECs (MEC_{SW}) were compared to acute and chronic ALBs, whereas sediment concentrations (MEC_{SED}) were compared to RTL_{SED}, respectively. In addition, risks were depicted for the top ten compounds with highest threshold level exceedance frequencies, as well as within a spatial (i.e., highest threshold level exceedance per site across the U.S. for water-phase and sediment concentrations) and temporal context considering the whole exposure dataset. We further on differentiated risks for major pesticide types (i.e., herbicides, fungicides, insecticides) and degradation products, as well as specifically for the different insecticide classes.

Lastly, a linear model analysis was conducted to determine and quantify the influence of different drivers on the outcome variable maximum logarithmic MEC_{SW} to ALB_{acute} ratio per location for the individual sampling days (Methods, Supporting Information). All data analyses were performed with the open source software R (version 3.5.3) including the R packages data.table and ggplot2.

2.5. Comparison of risks from agricultural and urban insecticide uses

We compared the risks from agricultural insecticide use for U.S. surface waters reported for 39 insecticides and degradates in a meta-analysis of the scientific literature by Wolfram et al. (2018) to those derived here for urban insecticide uses. In order to facilitate a direct and unbiased comparison, we considered only compounds (n = 25; Methods, Supporting Information) common to both the agricultural (Wolfram et al., 2018) and urban (present study) datasets and applied the same acute threshold levels. In detail, the ALB_{acute} from eight insecticide compounds (i.e., chlorpyrifos, cypermethrin, esfenvalerate, lambda-cyhalothrin, malathion and permethrin) differed from the respective acute water-phase RTLs used by Wolfram et al. (2018); in these cases, we also applied the acute water-phase RTL (RTL_{SW}) to urban insecticide water-phase concentrations for the comparison of acute risks for urban and agricultural surface waters in the U.S. Wolfram et al. (2018) did not assess chronic risks for water-phase concentrations so that this comparison is omitted here. The RTL_{SED} did not differ between both evaluations.

3. Results

3.1. Pesticide occurrence in urban surface waters of the U.S.

The overall dataset comprised 10,755 MECs (9100 MEC_{SW} and 1655 MEC_{SED}; see https://static.magic.eco/urban for a complete list of MECs for all compounds) resulting from 3043 unique samples (i.e. unique sample location/sample date combinations) taken between 1987 and 2014; more than 50% of all MECs were measured from the year 2000 onwards. Among all samples, a total of 147 different pesticides (n = 119; n = 9841 MECs) and degradates (n = 28; n = 914 MECs) were detected; the 119 pesticide compounds comprised 55 herbicides (n = 5698 MECs), seven fungicides (n = 35 MECs), and 57 insecticides (n = 4108 MECs). The samples were collected from 609 different sampling sites across 39 states plus Washington, DC (see Fig. S1), with 377 locations with only one sample with measured pesticide concentrations.

3.1.1. Water-phase concentrations

Concerning water-phase concentrations, a total of 9100 MEC_{SW} resulting from analysis of 2630 unique samples collected between 1987 and 2014 were recorded. The samples were collected from 325 different locations across 34 states plus Washington, DC (see Fig. S1a), with 131 locations with only one sample with measured pesticide concentrations and 149 locations with two to ten samples with pesticide detections. In the water-phase samples, a total of 119 different pesticides (n = 97, comprising 52 herbicides (n = 5681 MEC_{SW}), 38 insecticides (n = 2807 MEC_{SW}), seven fungicides (n = 31 MEC_{SW})), and degradates (n = 22, comprising twelve herbicide degradates and ten insecticide degradates with overall 581 MEC_{SW}) were detected.

Table 1 presents the most frequently detected pesticides in water-phase samples by site and by site relative to the frequency of analysis, as well as in terms of absolute detections and summary statistics calculated from all unique samples in which each pesticide was detected in the dataset. Specifically, herbicides (seven compounds) and insecticides (four compounds) were among the most frequently detected pesticides, with atrazine, diazinon and simazine detected at > 100 sites and in

Table 1
Summary and site-based statistics for top 10% most frequently detected pesticides by site for water-phase samples (all years).

Pesticide	Pesticide type	Number of sites with detections (number of overall detections)	Frequency of analysis by site[a]	Frequency of detection relative to analysis by site[b]	Median (maximum) concentration (ng/L)	$ALB_{acute}/ALB_{chronic}$ (ng/L) (number of exceedances of $ALB_{acute}/ALB_{chronic}$)
Atrazine	Triazine herbicide	166 (1311)	0.76	0.69	18 (14,000)	1000/1000 (31/31)
Diazinon	Organophosphorus insecticide	158 (1413)	0.74	0.67	27 (6900)	105/105 (253/253)
Simazine	Triazine herbicide	118 (1259)	0.73	0.51	36 (158,000)	2240/2240 (41/41)
Prometon	Triazine herbicide	89 (913)	0.59	0.47	34 (4200)	98,000/98,000 (0/0)
Metolachlor	Chloroacetanilide herbicide	64 (599)	0.62	0.32	15 (2420)	21,000/1000 (0/8)
Fipronil	Phenylpyrazole insecticide	59 (142)	0.63	0.29	20 (275)	110/11 (8/90)
Chlorpyrifos	Organophosphorus insecticide	58 (370)	0.78	0.23	11 (340)	50/40 (32/46)
Tebuthiuron	Urea herbicide	52 (345)	0.52	0.31	22 (2830)	50,000/50,000 (0/0)
Bifenthrin	Pyrethroid insecticide	52 (130)	0.25	0.64	8 (106)	75/1.3 (4/133)
Fipronil desulfinyl	Breakdown product of fipronil	46 (126)	0.58	0.25	7 (101)	10,000/590 (0/0)
2,4-D	Phenoxy herbicide	36 (138)	0.19	0.59	322 (35,600)	299,200/299,200 (0/0)
Diuron	Urea herbicide	35 (119)	0.15	0.73	180 (10,900)	2400/2400 (9/9)

[a] : Number of sites at which a pesticide was analyzed relative to the overall number of sampling sites.
[b] : Number of sites with detections for the respective compound multiplied by the frequency of sites at which the pesticide was detected relative to the number of locations at which it was analyzed.

more than 1000 samples. Together with chlorpyrifos, these three substances were also analyzed most often (i.e., at most sites), whereas the herbicides diuron and atrazine, as well as the insecticides diazinon and bifenthrin were detected most often when also considering the overall frequency of analysis per compound and site (Table 1). In terms of water-phase exposure levels, high concentrations of up to 1.58×10^5 ng/L were detected particularly for herbicides whereas those of insecticides were generally substantially lower, i.e., below 1000 ng/L. However, median concentrations were comparable across all pesticide types, with only those of 2,4-D and diuron exceeding 100 ng/L (Table 1).

Since 2010, which comprised the latest five years of data within the dataset, 354 unique surface water samples with pesticide detections were collected from 97 different locations across 12 different states. From these samples, there were 813 individual concentration measurements for 49 different pesticides. Three insecticides and two herbicides are among the most frequently detected pesticides in water-phase samples since 2010 (Table S1), with specifically the insecticides bifenthrin and imidacloprid analyzed more frequently compared with the overall dataset (cf. Table 1).

3.1.2. Sediment concentrations

The database compiled here contained 1655 individual MEC_{SED} resulting from analysis of 413 unique samples collected from the years 1991–2013. The samples were collected from 352 different locations across 33 states plus Washington, DC (see Fig. S1b); out of all the 352 locations, 308 had only one sample with measured pesticide concentrations. Among the sediment samples, a total of 53 different pesticides (n = 42, comprising eight herbicides (n = 17 MEC_{SED}), 32 insecticides (n = 1301 MEC_{SED}, two fungicides (n = four MEC_{SED})) and degradates (n = 11, comprising insecticide degradates only, with 335 MEC_{SED}) were detected.

Table 2 presents the most frequently detected pesticides in sediment samples for all years in the dataset, which comprise insecticide compounds (i.e., organochlorine insecticides or their degradates, one pyrethroid insecticide) only. All five compounds have been detected at > 100 sites and in > 100 samples, respectively. A maximum concentration of 6950 μg/kg has been detected for DDT, whereas those of the other four compounds were at least one order of magnitude lower. However, the median concentrations were comparable for all of the compounds detected most frequently (Table 2).

Since 2009, i.e., the latest five years of data within our dataset, 80 unique sediment samples were collected from 66 different locations across 19 different states. From these samples, there were 196 individual concentration measurements for 27 different pesticides. Pyrethroid insecticides were analyzed and detected in sediment samples most frequently, with particularly bifenthrin spearheading detection frequencies by both sites and absolute numbers of detections (Table S2).

3.1.3. Occurrence of pesticide mixtures in urban surface waters

Out of the 3022 individual water-phase and sediment samples, 2239 (74.1%) contained mixtures of pesticides (i.e., a minimum of two pesticides or degradates were present in a given sample), with a mean of 4.45 (median 4) compounds per sample and a maximum of 17 compounds per sample. Accordingly, mixtures were present at 510 (83.7%) out of the 609 individual sampling sites.

In 72.6% of all unique water-phase samples (n = 2622), pesticides were detected in mixtures of two or more compounds. Similarly, two or more pesticides were recorded at approximately 81% of all water-phase sample locations (n = 325), with 44 (median) and 138 (maximum) compounds analyzed per sampling site. The mean number of pesticides detected per water-phase sample was 4.4 (median = 4) with a maximum of 17 pesticides detected in one sample.

Concerning sediments, pesticide mixtures were detected in approximately 82% of all samples (n = 413) and at approximately 85% of

Table 2
Summary and site-based statistics for top 10% most frequently detected pesticides by site for sediment concentrations (all years).

Pesticide	Pesticide Class	Number of sites with detections (number of overall detections)	Frequency of analysis by site[a]	Frequency of detection relative to analysis by site[b]	Median (maximum) concentration (µg/kg)	RTL_{SED} (µg/kg) (number of exceedances of RTL_{SED})
Chlordane	Organochlorine insecticide	188 (195)	0.74	0.72	9 (619)	2080 (0)
DDT	Organochlorine insecticide	166 (176)	0.81	0.58	9 (6950)	1320 (1)
Bifenthrin	Pyrethroid insecticide	160 (188)	0.55	0.82	7 (437)	0.25 (188)
DDE	Breakdown product of DDT	140 (149)	0.73	0.54	4 (150)	2200 (0)
Nonachlor	Organochlorine insecticide	105 (112)	0.50	0.59	4 (421)	2080 (0)

[a] : Number of sites at which a pesticide was analyzed relative to the total number of sampling sites.
[b] : Number of sites with detections for the respective compound multiplied by the frequency of sites at which the pesticide was detected relative to the number of locations at which it was analyzed.

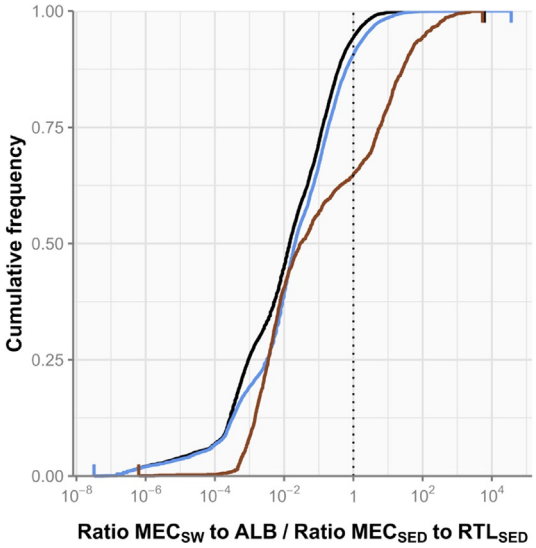

Fig. 1. Cumulative frequency distributions of measured environmental concentrations in the water phase (MEC_{SW}) and sediments (MEC_{SED}) in relation to respective threshold levels (ALB_{acute}, $ALB_{chronic}$, RTL_{SED}; vertical dotted line), with cumulative frequency distributions of MEC_{SW} to ALB_{acute} ratio (black curve; n = 9034 MEC_{SW}), MEC_{SW} to $ALB_{chronic}$ ratio (blue curve; n = 9036 MEC_{SW}), and MEC_{SED} to RTL_{SED} ratio (brown curve; n = 1621 MEC_{SED}). MEC to threshold level ratios larger than one represent threshold exceedances and the small vertical bars denote minimum and maximum ratios of each curve.

all sediment sample locations (n = 352); 12 (median) and 118 (maximum) pesticide compounds were analyzed per site. The mean number of pesticides detected per sediment sample was 4.7 (median = 4) with a maximum of 17 pesticides detected in one sample.

3.2. Risk assessment for pesticide concentrations in urban surface waters

3.2.1. Overall risks for water-phase and sediment concentrations

Overall, 1077 (10.1%; 268 of 609 sites) of all (n = 10,655) water-phase and sediment MEC exceeded either ALB_{acute} or RTL_{SED}, whereas $ALB_{chronic}$ and RTL_{SED} were exceeded for 1408 (13.21%; 299 of 609 sites) of all MECs (n = 10,657). Concerning MEC_{SW}, 510 out of 9034 (5.64%; 91 of 325 sites) water-phase concentrations of 93 pesticide compounds exceeded ALB_{acute} up to a factor of 6000, whereas 841 out of 9036 (9.31%; 138 of 325 sites) MEC_{SW} (n = 94 compounds) exceeded $ALB_{chronic}$ up to a factor of 36,206 (Fig. 1). RTL_{SED} were available for 42 compounds and 1621 MEC_{SED}, with 567 (35%; 200 of 352 sites) of these exceeding their RTL_{SED} up to a factor of 5375 (Fig. 1); importantly, 80% (n = 1297) of these 1621 MEC_{SED} were insecticide concentrations.

3.2.2. Spatial distribution and temporal development of pesticide risks for urban surface waters in the U.S.

The spatial distribution of risks depicted as the highest ALB exceedance at each site indicates no clear pattern for acute risks related to pesticide water-phase concentrations, but particularly higher chronic risks in urban surface waters located in the West Pacific States California, Oregon and Washington (Fig. S2a and S2b). This pattern is even more pronounced for sediment concentrations, i.e. substantially higher RTL_{SED} exceedances were observed for urban surface water sites located in these three western U.S. states, with particularly highest risks in sediments identified for urban surface waters located in California (Fig. S2c).

The comparison of the last ten years with available water-phase exposure data (i.e., 2005–2014; ALB_{acute} exceedance rate: 4.2%; n = 2192 MEC_{SW}) with those of the timespan from 1987 − 2004 (ALB_{acute} exceedance rate: 6.1%; n = 6842 MEC_{SW}) shows decreasing

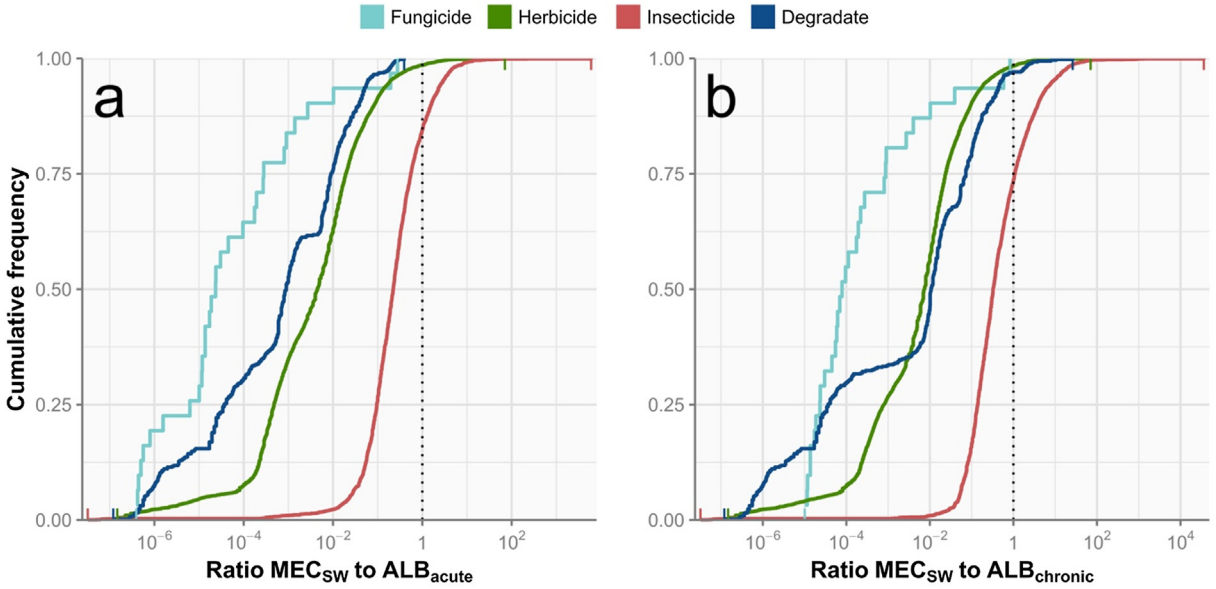

Fig. 2. Cumulative frequency distributions of (a) MEC_{SW} to ALB_{acute} ratios and (b) MEC_{SW} to $ALB_{chronic}$ ratios of the different pesticide types (insecticides (acute and chronic): n = 2783, 31 compounds; herbicides (acute): n = 5670, 45 compounds; chronic: n = 5672, 46 compounds; fungicides (acute and chronic): n = 31, seven compounds; degradates (acute and chronic): n = 550, ten compounds). The vertical dotted lines indicate the ALB_{acute} (a) and $ALB_{chronic}$ (b) and small vertical bars denote minimum and maximum ratios of each curve.

acute risks for urban surface waters in the U.S. This is in line with results from the linear model analysis (Results, Supporting Information; Table S3). However, chronic risks increased when comparing these periods, with $ALB_{chronic}$ exceedance rates increasing from 6.9% (n = 6842 MEC_{SW}) for the timespan 1987–2004 to 16.9% (n = 2194 MEC_{SW}) for the timespan 2005–2014 (Fig. S3a and S3b). Concerning sediments, a significant ($p < 0.001$; $R^2 = 0.20$; n = 1569 MEC_{SED}) increase in risks were observed over time (Fig. S3c); RTL_{SED} exceedance rates for the last ten years with available exposure data (2004–2013) were substantially higher (56.9%; n = 937 MEC_{SED}) when compared with the exposure data available for the years 1991–2003 (4.27%; n = 632 MEC_{SED}).

3.2.3. Risk assessment for pesticide types, insecticide classes and individual compounds

The comparison of risks for water-phase concentrations of the different pesticide types (Fig. 2) shows highest risks for insecticides, with 15.4% and 26.3% (n = 2783) acute and chronic ALB exceedances, respectively. In contrast, no ALB exceedances were found for fungicides (n = 31) and only 1.45% (n = 5670) and 1.62% (n = 5672) of herbicide concentrations exceeded acute and chronic ALBs, respectively. Moreover, 2.91% (n = 550) of degradate MEC_{SW} exceeded $ALB_{chronic}$, whereas no ALB_{acute} exceedances were found for these compounds. The linear model analysis also identified higher acute risks for water-phase concentrations of insecticides compared with those of herbicides and degradates, respectively (Results, Supporting Information; Table S3).

In terms of sediment concentrations, insecticides showed by far highest RTL_{SED} exceedances (41.8%; n = 1297), whereas only 7.7% (n = 309) of degradates MEC_{SED} exceeded RTL_{SED} (Fig. S4). Only ten and three sediment concentrations were available for herbicides and fungicides, respectively, with no and one of these concentrations exceeding RTL_{SED}.

As insecticide concentrations showed highest risks in both the water phase and sediments, this pesticide type was analyzed in greater detail concerning the risks of different insecticide classes. Highest ALB_{acute} exceedance rates were found for organophosphates (18.5%; n = 2059) and pyrethroids (10.1%; n = 217), whereas highest $ALB_{chronic}$ exceedance rates stemmed from pyrethroid (79.7%; n = 217) and neonicotinoid insecticides (46.6%; n = 88) (Table 3). At least 19.4% of the water-phase concentrations from five out of the seven insecticide classes analyzed here exceeded the $ALB_{chronic}$ values.

Table 3
Acute and chronic ALB exceedance rates for water-phase concentrations and RTL_{SED} exceedance rates for sediment concentrations of the individual insecticide classes.

Insecticide class	Number of compounds with MEC_{SW}/MEC_{SED}	Number of MEC_{SW}/MEC_{SED}	$ALB_{acute}/ALB_{chronic}/RTL_{SED}$ exceedances (%)
Carbamate	4/-	208/-	4.3/7.2/-
Neonicotinoid	3/-	88/-	5.7/46.6/-
Organochlorine	3/13	65/701	5.9/25/7.6
Organophosphate	12/4	2059/39	18.5/19.4/7.7
Phenylpyrazole	1/1	463/1	1.7/22.3/0
Pyrazole	-/1	-/1	-/-/0
Pyrethroid	7/9	217/555	10.1/79.7/89.9
Sulphite ester	1/-	3/-	0/0

Concerning sediments, particularly pyrethroid concentrations exceeded their RTL_{SED} (89.9%; n = 555), whereas less than 8% RTL_{SED} exceedances were found for the other insecticide classes (Table 3).

3.2.4. Risks of individual compounds

Concerning the environmental significance of individual compounds, Tables S4-S6 show summary and site-based statistics for the top ten pesticides detected most frequently above acute and chronic ALBs or RTL_{SED} in the available dataset. Concerning the water phase, nine and ten out of ten pesticides with highest acute and chronic ALB exceedance frequencies were insecticide compounds (Tables S4 and S5). In particular, the insecticides dichlorvos and permethrin showed highest acute (94% and 37% of the MEC_{SW} and 89% and 57% of the sites with detection) and chronic ALB (both 100% of the MEC_{SW} and sites with detection) exceedance frequencies in the water phase, with dichlorvos also accounting for absolute highest acute and chronic ALB exceedances (Tables S4 and S5). Malathion (35% acute and chronic ALB exceedance frequencies) showed acute and chronic ALB exceedances at 76% of the sites with detections. MEC_{SW} of the insecticides bifenthrin, fipronil and imidacloprid exceeded their $ALB_{chronic}$ in more than 50% of the cases and at least at 50% of the sites with detection (Table S5).

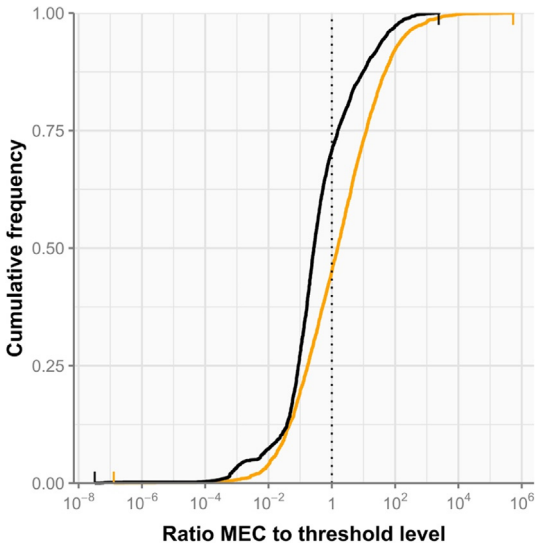

Fig. 3. Cumulative frequency distributions of MEC to threshold level ratios (combined water-phase and sediment data) reported for urban (black curve; 29% threshold level exceedance; n = 3605 MECs) and agricultural (orange curve; 54.7% threshold level exceedance; n = 4601 MECs) surface waters in the U.S. The comparison is based on 25 insecticide compounds common to both datasets. The vertical dotted line indicates the respective threshold levels (ALB_{acute}/RTL_{SW}; RTL_{SED}) and small vertical bars denote minimum and maximum ratios of each curve.

Concerning sediments, the three pyrethroids bifenthrin, cyfluthrin and cypermethrin, as well as the insecticide degradate heptachlor epoxide exceeded RTL_{SED} in 100% of the samples, as well as at 100% of the sites with detections (Table S6). In addition, MEC_{SED} of the three insecticides deltamethrin, lambda-cyhalothrin and heptachlor, as well as of the fungicide hexachlorobenzene exceeded RTL_{SED} in at least 90% of the samples and at a minimum of 90% of the sites with detections. Overall, eight out of the ten pesticides with highest RTL_{SED} exceedance frequencies were insecticide compounds.

3.3. Comparison of risks for U.S. Surface waters from agricultural and urban insecticide uses

The comparison of risks from urban (present study) and agricultural (Wolfram et al., 2018) insecticide uses based on compounds considered in both studies (n = 25) and harmonized threshold levels indicates an overall significantly higher (Welch two sample *t*-test; $p < 0.001$) risk for agricultural (54.7% threshold level exceedance; n = 4601 MECs) compared with urban surface waters (29% threshold level exceedance; n = 3605 MECs) (Fig. 3). In the water phase (20 compounds), insecticides' MEC_{SW} in urban surface waters (n = 2986) led to 18.1% ALB_{acute}/RTL_{SW} exceedance, whereas 55% of all MEC_{SW} (n = 2961) exceeded the RTL_{SW} in agricultural surface waters (Fig. S5a). In this context, the maximum water-phase concentrations and associated risks reported for the 20 insecticides were also consistently higher in agricultural than in urban surface waters, with eleven compounds showing at least two orders of magnitude higher maximum concentrations (Fig. S6a). However, the comparison of sediment risks for 17 insecticide compounds common to both datasets clearly shows higher risks for urban (81.9% RTL_{SED} exceedance; n = 619 MEC_{SED}) compared with agricultural (54.21% RTL_{SED} exceedance; n = 1640 MEC_{SED}) surface waters (Fig. S5b). In contrast, twelve out of 17 compounds showed up to 2.5 orders of magnitude higher maximum sediment concentrations and thus risks in agricultural compared with urban surface waters (Fig. S6b).

4. Discussion

4.1. Pesticide occurrence in urban surface waters of the U.S.

Based on the findings of the present study, pesticides are widely distributed in urban-dominated surface water bodies across the U.S. A multitude of non-agricultural pesticide application scenarios such as lawn care, structural pest control, indoor uses, vector control, etc. and a high percentage of impervious surfaces in developed areas facilitates the pesticide transport to urban surface waters. In the water phase, both insecticides and particularly herbicides were among the most frequently detected pesticides, while fungicide concentrations were substantially less reported. Although this pattern reflects the pesticide usage statistics, with overall 54, 26 and 12 million pounds of herbicides, insecticides and fungicides, respectively, applied in non-agricultural settings (Atwood and Paisley-Jones, 2017), the lack of fungicide concentrations is also likely due to the less intensive sampling efforts and a stronger focus on herbicide and insecticide environmental concentrations (Stone et al., 2014); particularly chlorothalonil was one of the most used pesticides in the industry/commercial/government sector but only two MEC_{SW} have been reported. Nevertheless, Nowell et al. (2018) recently provided the first regional-scale characterization of fungicides in urban Midwestern streams and reported particularly carbendazim, azoxystrobin, metconazole and tebuconazole to occur frequently in urban surface waters; the majority of fungicide compounds showed higher occurrences at urban compared with agricultural sites indicating the need for increased monitoring efforts of these compounds in urban surface waters. However, there are further issues where the present database does not reflect pesticide use pattern in the U.S. Although the herbicides 2,4-D and glyphosate are the two most commonly used pesticides in non-agricultural settings in the U.S. (Atwood and Paisley-Jones, 2017), they have been analyzed at 19% and 4% of all sampling locations only. However, the triazine herbicides atrazine, simazine and prometon, as well as the organophosphate insecticides diazinon and chlorpyrifos were frequently analyzed and frequently detected in urban surface water samples (Table 1), as also shown in previous studies across the U.S. (Hoffman et al., 2000; Gilliom et al., 2006; Stone et al., 2014). Triazine herbicides target broadleaf weeds and are in urban environments most commonly applied to golf courses, lawns, and other turf grass areas, whereas diazinon and chlorpyrifos prior to their federally mandated phase-out in 2001 (USEPA, 2006a; USEPA, 2006b) have been heavily used in urban settings including dormant sprays, building pest control and animal-care products. In this context, the registration changes and phase-out of organophosphate and organochlorine insecticides and the resulting shifts in urban insecticide uses led to considerably more frequent detections of bifenthrin, fipronil and imidacloprid and less frequent detections of diazinon and chlorpyrifos in the water phase since 2010 (Table S1). This is in line with Ryberg et al. (2011) who also found significant downward trends in organophosphate insecticide concentrations in 27 urban streams between 1992 and 2008 and significant upward trends for fipronil. Frequent detections of new types of insecticides (particularly bifenthrin, fipronil and imidacloprid) in urban streams during the last decade have also been reported for urban streams in the U.S. Midwest (Nowell et al., 2018), California (Weston et al., 2009; Ensminger et al., 2013) and Oregon (Carpenter et al., 2016). Concerning water-phase exposure levels, the overall higher concentrations detected for herbicides compared with those of insecticides (Table 1) are reasoned by herbicides' higher application rates and their specific physicochemical properties (e.g., higher water solubilities), as both aspects foster surface water exposure (Gilliom et al., 2006; Stehle et al., 2013).

Sediment exposure was dominated by insecticides, with their high hydrophobicity (particularly pyrethroids and organochlorine insecticides) and high environmental persistence (particularly organochlorine insecticides and bifenthrin), resulting in the accumulation of

these compounds in benthic layers (Gilliom et al., 2006; Carpenter et al., 2016). Accordingly, organochlorine insecticides (including the DDT degradation product DDE) – each of which had all non-agricultural uses cancelled by 1988 or earlier (Gilliom et al., 2006) - and the pyrethroid bifenthrin constitute the most frequently detected compounds in sediments (Table 2), which corroborates findings from Gilliom et al. (2006) and Ding et al. (2010). However, as shown particularly for urban sediments in California (Weston et al., 2009; Phillips et al., 2010) but also other regions of the U.S. (Ding et al., 2010; Kuivila et al., 2012; Carpenter et al., 2016), the increasing urban uses of pyrethroids results in frequent detections of these compounds in recent years (Table S2).

In both the water phase and sediments, pesticides occurred more frequently in mixtures of two or more (up to 17 compounds) rather than individually. This common occurrence of pesticide mixtures has also been shown for urban surface waters by Gilliom et al. (2006), i.e., two or more pesticides were detected more than 90% of the time and ten or more compounds more than 20% of the time, as well as by Nowell et al. (2018) for urban midwestern U.S. streams. As demonstrated also for agricultural streams (Stehle and Schulz, 2015a), complex mixtures of multiple pesticides are thus the most common mode of occurrence in urban surface waters. Importantly, urban surface waters may have been exposed simultaneously towards even higher numbers of pesticides than were recorded here; Moschet et al. (2014) showed that expanding the number of pesticide compounds analyzed in surface water samples from the 15–40 compounds typically covered by routine monitoring programs to over 200 compounds, increased the number of pesticide compounds detected on average by a factor of two. However, the analytical scope of water quality monitoring programs is often driven primarily by cost and technical feasibility (Stone et al., 2014), which hinders measurements of all compounds potentially present. In essence, the presence of pesticide mixtures in urban surface waters and sediments is the general rule and the data presented here represents the lower limit of pesticide mixture occurrence as by far not all compounds potentially present were analyzed in the respective samples.

4.2. Overall risk assessment

According to the overall data, pesticides in the water phase of urban surface waters often comply with ALBs, indicating tolerable risks for aquatic ecosystems. Nevertheless, when considering the fact that pesticides in urban waterways frequently occur in mixtures not only with other pesticides but also with other toxic chemicals, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and heavy metals (Nowell et al., 2013), as well as that the hydromorphology of urban surface waters is often heavily impaired (Hall et al., 2009), the potential risk is compounded. In addition, although acute risks slightly decreased over time (Results, Supporting Information; Table S3; Fig. S3a), chronic risks increased over time (Fig. S3b) and more than doubled within the last ten years of available data, presumably due to more frequent use and detection of pesticides with high chronic toxicity such as bifenthrin, fipronil and imidacloprid (Table S1 and Table S5). Although the present dataset does not prove exposure to be prolonged, year-round uses of pesticides in non-agricultural settings and continuous releases due to recurring rain events, irrigation, and wastewater treatment plant discharges indicate the potential for chronic risks in urban surface waters (Weston et al., 2009; Ensminger et al., 2013; Shamim et al., 2014).

Particularly insecticides trigger the comparably high threshold level exceedances found for sediments, which prove benthic communities to be at risk in urban surface waters. Increasing detections of pyrethroids (Table S2) thereby amplify risks in recent years, with more than 10-fold increases of RTL_{SED} exceedance frequencies when comparing the timespan of 1991–2003 and 2004–2013 (Fig. S3 and Fig. S7).

A site-specific evaluation shows that benchmark level exceedances are distributed throughout the U.S. and vary widely among sites, with particularly high risks for urban streams in California (Fig. S2). “Hot spots” of pesticide contamination of urban surface waters and particularly sediments in California have previously been reported (Amweg et al., 2006; Kuivila et al., 2012). Concerning the water phase, 28% and 42.5% of the sites with water-phase samples (n = 325) exceeded acute and chronic ALBs, which is less than the 83% water-quality benchmark exceedances for the period 1992–2001 (Gilliom et al., 2006) and 90% chronic ALB exceedances for the period 2002–2011 (Stone et al., 2014) reported by the USGS for 30 urban streams sites across the US. Possible reasons are a higher focus on insecticides, on event-based sampling (Results, Supporting Information; Table S3; Crawford, 2004; Stehle et al., 2013), and a higher number of compounds analyzed (Results, Supporting Information; Table S3; Moschet et al., 2014). However, benchmark level exceedances for bed sediment concentrations in the present dataset (56.8% of all sites; n = 352) and those reported for the time period 1991–2002 in the national USGS study (70% of all sites; n = 30) were rather similar; this is in accordance with the fact that both sediment datasets were dominated by organochlorine insecticides (Table 2; Gilliom et al., 2006) and differences in sampling design are of less importance for pesticide concentrations in sediments due to prolonged exposure durations.

4.3. Risk assessment for pesticide types, insecticide classes and individual compounds

Insecticides appear to be the most problematic pesticide type in urban surface waters (Fig. 2; Results, Supporting Information; Table S3) and acute and chronic ALB exceedances of more than 15% and 25% indicate a clear potential for adverse ecotoxicological effects (Beketov et al., 2013; Stehle and Schulz, 2015a). In contrast, herbicides, fungicides and degradates all showed ALB exceedances below 3% indicating negligible aquatic risks of these compounds. Higher threshold level exceedance rates for insecticides compared with other pesticide types have also been reported for urban surface waters in the U.S. (Stone et al., 2014; Carpenter et al., 2016; Nowell et al., 2018), 4000 freshwater monitoring sites across the EU (Malaj et al., 2014), as well as in agricultural surface waters in EU (Stehle and Schulz, 2015b). Despite the fact that herbicide usage is twice as high than insecticide usage by mass in urban settings of the U.S. (Atwood and Paisley-Jones, 2017), the high ecotoxicities particularly towards invertebrates substantiates insecticides‘ higher risk potentials (Devine and Furlong, 2007; Stehle and Schulz, 2015). Specifically, the use of more recent insecticide classes such as pyrethroid, neonicotinoid and phenylpyrazole insecticides resulted in high chronic risks for urban surface waters (Table 3).

The organophosphate fumigant insecticide dichlorvos, which is both an insecticide registered for domestic indoor and outdoor uses and a major degradate of the organophosphate insecticide naled, showed highest ALB exceedances frequencies, with exceedances up to 6000 and 36,207 times the respective acute and chronic ALBs (Table S4 and S5). However, although a recent synoptic study in Midwestern streams also found dichlorvos substantially contributing to toxicity in urban streams (Nowell et al., 2018), only 18 MEC_{SW} detected in three studies at eight sites were available here, restricting large-scale risk evaluation conclusions. The pyrethroids permethrin and bifenthrin showed particularly high $ALB_{chronic}$ exceedances of 100% and 90% which is reasoned by their extremely low $ALB_{chronic}$ values (1.4 ng/L and 1.3 ng/L) and frequent uses in non-agricultural settings (USEPA, 2006c; Carpenter et al., 2016). Concerning further insecticide compounds with highest ALB_{acute} and $ALB_{chronic}$ exceedance rates, no clear pattern exists as representatives of five different insecticide classes contribute to the top 10 of compounds exceeding ALBs (Tables S4 and S5); this finding differs from results presented by Wolfram et al. (2018) showing that in agricultural surface waters only pyrethroids and organophosphate insecticides comprise the top 10 insecticides with water-phase RTL exceedances. More diverse use patterns and application scenarios of insecticides in non-agricultural settings may be the cause (Shamim

et al., 2014).

Most likely as a consequence of their low water solubility, high toxicity and their increasing use as a replacement for organophosphate insecticides, pyrethroids, such as bifenthrin, cyfluthrin, and cypermethrin showed highest RTL_{SED} exceedance frequencies (Table S6). Their presence (Weston et al., 2009; Kuivila et al., 2012; Weston and Lydy, 2012; Nowell et al., 2018) and toxicity (Amweg et al., 2006; Ding et al., 2010; Phillips et al., 2010; Carpenter et al., 2016) in urban sediments corroborates previous studies. According to the present dataset, the detection of organochlorine insecticides in sediments of urban surface waters in the U.S. decreased in the last two decades (Fig. S7) and their overall RTL_{SED} exceedance frequencies is substantially lower compared with that of pyrethroids (Table 3).

Pesticide degradates were also of ecotoxicological importance particularly in sediments with RTL_{SED} exceedances of approximately 8% (Fig. S4). Degradates are often more persistent than their parent compounds and often have similar or lower toxicity potentials (Sinclair and Boxall, 2003; Gilliom et al., 2006). However, uncertainty remains regarding the toxicity potential of degradates (Sinclair and Boxall, 2003; Weston and Lydy, 2014) and their slow degradation provides opportunity for long-term exposure that may affect stream life (Carpenter et al., 2016).

4.4. Comparison of risks for U.S. Surface waters from agricultural and urban insecticide uses

The present study showed for a subset of 25 insecticides a 1.9-fold, significantly lower threshold level exceedance in urban compared to data from Wolfram et al. (2018) for the same compounds from agricultural surface waters (29.1% vs. 54.7% threshold level exceedances; Fig. 3) in the U.S. This is a new insight, since virtually all studies reported higher insecticide levels and threshold levels exceedances in urban than in agricultural surface waters in the U.S. (e.g., Brown et al., 2009; Ding et al., 2010; Stone et al., 2014; Nowell et al., 2018); yet, these studies have been restricted to individual regions or a limited number of sites (< 40). The synoptic nature of exposure data of both agricultural (Wolfram et al., 2018) and urban (present study) insecticides in surface waters enables for the first time a large scale (644 and 609 sites, respectively) and comprehensive comparison of risks across the U.S. The extent of cropland areas in the U.S. (1,186,919 km^2) is nearly three times that of urban areas (430,076 km^2) implying that more surface water bodies are threatened by threshold level exceedances from agricultural insecticide use. In contrast, the theoretical insecticide use intensity (i.e., overall insecticide usage divided by area) is more than two times higher in urban (insecticide usage: 26×10^6 lbs (Atwood and Paisley-Jones, 2017); developed area: 430,076 km^2 = 60.5 lbs/km^2) compared with agricultural areas (insecticide usage: 34×10^6 lbs (Atwood and Paisley-Jones, 2017); cropped area: 1,186,919 km^2 = 28.6 lbs/km^2). However, indoor uses without environmental releases in residential areas, more targeted insecticide sampling in agricultural studies, closer proximities of pesticide applications and surface waters in agricultural settings, as well as smaller surface waters in agricultural compared to urban areas are potential explanations for lower overall threshold level exceedances in urban compared with those derived for agricultural surface waters.

In addition, a more complex situation of insecticides‘ risks arises when evaluating the different surface water compartments. In the water phase, threshold level exceedances of agricultural surface waters were more than three times higher compared with those in urban surface waters, with also maximum concentrations consistently and up to several orders of magnitude higher due to agricultural insecticide uses (Fig. S6a). Differences in sampling approaches, i.e., more frequent event sampling and shorter sampling intervals (Table S7) fostered the detection of higher insecticide concentrations in the agricultural dataset (Crawford, 2004; Stehle et al., 2013; Table S3). However, although catchment sizes of urban surface waters with insecticide detections generally (i.e., 50th percentile) were smaller compared with agricultural surface waters (Table S8), more than 25% of the agricultural waterbodies had catchment sizes below 10 km^2 (urban surface waters: 7.6%), which are often highly exposed towards pesticides in agricultural landscapes (Wolfram et al., 2018). It overall follows that in the agricultural dataset, more targeted sampling has been employed, which is one reason for the higher threshold level exceedances detected. Yet, this likely is not sufficient to explain why the present large dataset indicates such a substantially lower threshold level exceedance for urban surface waters.

A reason for the higher RTL_{SED} exceedances in urban sediments (Fig. S5), which has also been shown in previous studies (e.g., Ding et al., 2010), is that catchment sizes of urban surface waters with insecticide detections in sediments were smaller than those in agricultural areas (Table S9), which in turn leads to higher sediment insecticide concentrations (Stehle and Schulz, 2015a; Wolfram et al., 2018). In addition, the frequent detection of pyrethroid concentrations above RTL_{SED} in urban surface waters (Table 3; Table S6), particularly in recent years (Fig. S7), may serve as an explanation. From an ecotoxicological perspective, insecticides in sediments of urban surface waters appear to be of more concern than in agricultural surface waters, which corroborates findings from previous studies (Ding et al., 2010; Hladik and Kuivila, 2012).

5. Conclusions

The extent of developed areas including cities are increasing in the U.S. (Alig, 2010), which puts freshwater ecosystems in these areas under increasing pressure resulting from physical stream habitat alterations (Roy et al., 2003; Chin, 2006), changes in hydrology (Poff et al., 2006) and pollution (Gilliom et al., 2006; Stone et al., 2014). The present meta-analysis highlights widespread exposure of urban waterbodies towards a multitude of pesticides and particularly high threshold level exceedances in sediments. Based upon these findings, the development of standardized scenarios for aquatic risk assessment exposure models that specifically represent urban applications of pesticides may be warranted. By now, the USEPA faces many challenges in conducting a national scale aquatic risk assessment for urban pesticide uses, many of which are related to limitations in quantifying exposure from the wide array of application scenarios available for residential pesticide use (Shamim et al., 2014). In the absence of modelled exposure data, large-scale pesticide monitoring data may support USEPA in conducting ecological risk assessment for urban pesticide applications. Importantly, future monitoring efforts should be adapted to changing pesticide use patterns in urban areas including the consideration of newly introduced pesticide compounds.

However, it should be noted that the present study has some limitations that should be considered: (i) the lack of a nationwide monitoring may result in a regional bias of pesticide detections in urban waterbodies, with also higher risks indicated here for regions with higher monitoring efforts (e.g., California); (ii) the detection frequency of individual compounds depends on the monitoring efforts, i.e., there may be a bias in the literature towards more frequently analyzed pesticides; (iii) although well-established, ALBs and RTLs may in certain situations denote conservative risk predictors for aquatic organisms considering recent findings of genetically-induced resistance to pesticide exposure in the field (Weston et al. 2013).

Generally, threshold level exceedances of pesticides in urban surface waters warrant the necessity for risk management measures. Absent outright bans, which have been shown to effectively reduce pesticide concentrations in urban aquatic systems (Phillips et al., 2007; Ryberg et al., 2011), risk mitigation tools aiming at reducing urban stormwater discharge, such as installing areas for the infiltration of runoff or detention basins may provide some benefit (Davis, 2005). This strategy could also be effective at reducing loads of other toxic urban pollutants in stormwater as well as reducing flood risk (Konrad, 2003). Moreover,

revised application practices such as spot treatments have been proven to be an effective management practice for reducing pyrethroid loss in runoff water from urban areas (Davidson et al., 2014).

Overall, the results of our study show that pesticide exposure of urban streams, the significance of which has also been proven in other areas globally (e.g., Wittmer et al., 2010; Allinson et al., 2015; López-Doval et al., 2017) is common in the U.S. and may – in concert with additional stressors – contribute to degradation and biodiversity losses of these aquatic ecosystems.

Declaration of Competing Interest

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105234.

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