Supporting Information

S.1 Literature review methods

We searched the literature on the ISI Web of Science and Google Scholar. The keywords used were: pesticide, insecticide, herbicide, fungicide, concentration, long-term, trend, and streams. Table S.1 provides the total number and relevant search results using different keyword combinations. Also, all cited references within the relevant literature were checked and included if applicable.

Initial search results (i.e., 10,000's) for studies about pesticide monitoring in surface waters were drastically culled after manually filtering for long-term studies (i.e., > 5 years of monitoring). Another search criterion that limited the number of articles was the focus on surface water monitoring. Long-term pesticide studies that exclusively focus on groundwater were not included in our search.

A large number of long-term pesticide monitoring studies were conducted by the United States Geological Survey (USGS) over the last three decades. Our review focused on the most recent peer-reviewed articles by the USGS that spanned the longest observation periods (Ryberg and Gilliom, 2015). However, we also reviewed earlier USGS publications and made note of any additional insights over time.

Another large source for long-term pesticide monitoring studies was The Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences. Some reports were submitted to the Swedish authorities and were only available in Swedish (i.e., Lindström et al., 2015). However, when possible we reviewed English translated abstracts and figure titles or contacted the corresponding author for clarification.

After filtering and combining literature there were twenty studies from ten different countries that fulfilled the criteria of being a long-term study of pesticide monitoring in surface waters. The reviewed case studies have been summarized in Table S.2 and organized by publication date. Sorting the studies chronologically allows us to see the evolution of methods, conclusions and recommendations over time.

Table S.1: Keywords in literature review search as of 08.01.2020

Keyword Combinations	Total Results	Relevant Results
Pesticide insecticide herbicide fungicide concentration trend	432,000	Ryberg and Gilliom (2015); Stone et al. (2014); Sullivan et al. (2011); Vecchia et al. (2008); Johnson et al. (2011); Ryberg et al. (2010); Larson et al. (1998); Power et al. (1999); Richards and Baker (1993); Konstantinou et al. (2006); McMillin and Means (1996)
long-term trends pesticide insecticide herbicide fungicide streams	99,100	Bundschuh et al. (2014); Stenrød (2015); Martin (2009); Boye et al. (2019); Todd and Struger (2014); Lerch et al. (2011); Lerch et al. (2015)

Table S.2: Summary of long-term pesticide studies in surface waters

Country, years of monitoring & reference(s)	Sampling locations, method & analytes	Evaluation metrics & statistical trend analysis/flow adjustment	Implemented mitigation measures	Conclusions	Limitations/ Recommendations
Canada (Ontario) 1981-1990 **Bodo (1991)**	• Thames, Grand, and Saugeen rivers • Grab samples • Atrazine and desethylatrazine	• Flow-weighted mean, mass discharge • Seasonal Mann-Kendall test. • Beale ratio estimator for mean mass transport.	No specific mitigation measure, but significant price drop in corn led to less corn cultivation.	• Significant trends in atrazine concentrations and load occurred in the 1980s in the outlets of southwestern Ontario Great Lake tributaries. • Shifting patterns of atrazine use due to significant decline in corn cultivation in 1986. • Hydrometeorologic variability exerts significant influence on aqueous concentrations, i.e., more atrazine runoff in wet years and vice versa for drought years. • Risks to aquatic organisms in the main channels of the Grand and Thames are confined largely to storm runoff events during the main application period.	• Characterization of pesticide concentration patterns in streams must focus on consistency and storm runoff events, particularly during the pesticide application season. • Continued monitoring is advised because atrazine and other herbicide usage continues at relatively large quantities and ongoing small watershed studies continue to show extreme levels over summer storm runoff following application.
US (Lake Erie) 1983-1991 **Richards and Baker (1993)**	• 5 stations from Lake Erie tributaries • Autosamplers, 3 samples/day between Apr. 15 to Aug. 15 • 13 herbicides and insecticides	• Time- and flow-weighted average concentrations. • Concentration exceedance curves.	None specified	• Pesticide concentrations are strongly skewed and approximately log-normal. • Average concentrations in tributaries are correlated with the amount applied in the basin, but with important secondary effects from chemical properties (i.e., ease of mobilization and half-life). • Chemograph response of pesticides following storm events and PPP application are different from nutrients, major ions, and sediment, indicating different pathways from the fields to surface water. • Smaller tributaries have higher maximum concentrations, more frequent concentration below detection limit, and fewer intermediate concentrations (i.e., are more strongly skewed and much greater temporal variability) compared to larger tributaries. • Toxic effects due to short exposures at high concentrations would be more likely to occur in small tributaries. Conversely, more subtle biotic effects resulting from long-term exposures to moderate concentrations would be more likely in larger rivers.	• Monitoring must be frequent and of long duration in order to detect trends that result from changed management practices. • Drinking water systems that utilize rivers as a source should employ time-proportional composite sampling to obtain a more reliable estimate of the annual PPP exposure, rather than four (quarterly) grab samples annually.
UK 1988-1997 **Power et al. (1999)**	• River Thames Estuary • Varied grab sampling frequency throughout the year, increasing in summer months coincident with seasonal peaks in pesticide use. • Atrazine, lindane, simazine	• Concentration time series. • Linear regression. • Neither atrazine nor simazine showed any correlation with flow.	Atrazine placed on UK Red List in 1993.	• Concentrations of all studied pesticides declined over the period, despite influences of drought induced reductions in freshwater flow from the Thames catchment. • Measures to control pesticide discharges resulted in dramatic reductions (> 90%) of the triazines, atrazine, and simazine, and a 73% reduction in lindane. • Until August 1993 atrazine use exceeded that of simazine in southern England. Since then, simazine has become the most important triazine herbicide owing largely to the UK Red List classification of atrazine. • Measured atrazine continued to decline from 1988-97, while simazine stabilized from late 1993 and showed no further decline from 1994-97.	• More information on possible synergistic effects of pesticide mixtures is needed, while most studies address exposure to a single pesticide. • Future studies should aim to understand risks to biota from long-term pesticide exposure, bioaccumulation, and food chain effects in estuarine environments. • More research required to understand long-term exposure effects on estuarine biota at sublethal levels of pesticides.

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Sweden 2002-2012 (Since 1992 for Skåne) **Kreuger and Nilsson (2001); Supporting references: Kreuger (1998); Bundschuh et al. (2014) Lindström et al. (2015)**	• 4 small catchments (Västergötland, Östergötland, Halland, and Skåne) and 2 rivers (Skivarpsån and Vege å). • Time-integrated weekly samples, with sub-samples every 80 minutes focused to the summer months. • 76 substances in 2002 to 131 substances in 2012.	• Time-weighted mean concentration for the sum of pesticides in stream (Skåne). • No statistical trend analysis specified (Kreuger and Nilsson, 2001).	• Licensing and training program on correct handling and spraying for farmers and salespeople. • Economic compensation to comply with reduction measures.	• A 90% reduction in total pesticide concentrations in streams after farmers and salespeople received information regarding best management practices for pesticides in 1995 (Skåne). • Pesticide use information aimed at minimizing applied quantities (e.g., calibrating spraying equipment and dose adjustment) and avoiding unintentional spills effectively reduced aquatic pesticide pollution (Skåne). • Farmers were more willing to accept advice when given personally and adjusted for site-specific conditions, rather than receiving general letters or pamphlets. • No clear trends were discernible for individual and total pesticides from 2002-2012 in all catchments (time period after mitigation measures were implemented). • 11 years is a relatively short period to discern clear trends due to high interannual variability in use and weather conditions. • Despite some differences between the model catchments regarding climate, soil type, and crop distribution, the total concentration of pesticides in surface water did not differ substantially between the catchments. This was consistent for all pesticide types.	• The existing environmental quality standards for different pesticides have not been updated for several years and are only preliminary for some substances. The exceedance amount and frequency patterns could shift if new studies were conducted that led to adjusted guideline values. • Increased glyphosate use, both in the field and farmyards has more than doubled and is not reflected in the monitoring results since glyphosate was not analyzed (Skåne). Leaving a potential data gap in estimates of total pesticide in surface water.
Portugal 1983-1999 **Cerejeira et al. (2003)**	• 3 river basins (Tejo, Sado, and Guadiana Rivers). • Grab sampling. • 27 pesticides and 1 metabolite	• Concentrations. • No statistical trend analysis method specified	Agricultural interdiction.	• All substances were detected in surface waters except for BHC isomers, cyclodiens, DDT and derivatives, probably due to their agricultural ban.	• Use of multiresidue methods and automated chemical analytics are desirable in the future. • Other pesticides could be present in Portuguese surface waters. Therefore, an extension of both study areas and range of pesticides and metabolites for analysis should be considered in the future.
US (NW) 1993-2003 **Schreder and Dickey (2005)**	• Thornton Creek (King County, Washington) and Fanno Creek (Portland, Oregon) • Obtained from USGS National Water Information System • Diazinon, chlorpyrifos, and carbaryl	• Concentration time-series and box plot. • Mann-Whitney test.	US Environmental Protection Agency phaseout of diazinon and chlorpyrifos.	• Carbaryl sales in King County increased more than tenfold in 2002 while diazinon sales fell by half. • Diazinon concentrations in Thornton creek were significantly lower in 2001 and 2002 (after the phase out) compared to 1996-1998. • Carbaryl concentrations were significantly greater in Thornton Creek in 2001 and 2002 as compared to 1996-1998. • Carbaryl levels increased in Fanno Creek in 2001-2003 as compared to detections from 1993-1995. At the same time, diazinon concentrations decreased substantially. • Pesticide sales and water pollution data strongly suggest that carbaryl is emerging as a major replacement for diazinon and chlorpyrifos in Northwest urban areas.	• A thorough evaluation of the ecological effects of carbaryl products and other pesticides is needed. • Carbaryl use should be eliminated. • Development of alternatives (e.g., Integrated Pest Management) could stop the toxic tradeoff to carbaryl and other pesticides.
Switzerland 1993-2003 **Singer (2005)**	• Lake Greifensee • Monthly concentration profiles and corresponding	• Concentrations. • Loads from catchment area to Greifensee	• Change in agricultural policy to more environmental practices.	• Amount of applied pesticides was greatly reduced in the catchment area (e.g., Atrazine 1100 kg (1990) to 400kg (2003)). • Atrazine load to Greifensee decreased from 30-40 kg (1990) to 5-10 kg (2003).	• Monitoring should begin before the implementation of mitigation measures to establish a baseline and to accurately evaluate the efficacy of measures.

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	water volumes used to calculate loads • 50 Substances	• Loss rate (load/applied amounts) as function of discharge during application period. (only possible for atrazine)	• Atrazine ban on railway tracks.	• Pesticide losses to the lake are mainly driven by the coincidence of pesticide application and rain events (timing and intensity). • Little evidence of the influence of substance properties between different corn herbicides because losses were governed by fast transport processes. • Measures on restricting the quantity of pesticides used led to detectable trend in load reduction. • Eco-measures (e.g., buffer strips, crop rotation) showed no significant change in percentage of atrazine removal.	• Financial support should be available to upgrade spray equipment (e.g., fresh water tanks to enable in-field cleaning). • Fields at risk of erosion should be converted to pesticide-free areas. • Training courses and professional licenses should be issued for pesticide-users.
US (NE & Mid-W) 1992-2004 **Phillips et al. (2007)**	• 20 sites within northeast and midwest US • Standard width- and depth-integrated samples at least 6 samples per year collected bimonthly • Diazinon, chlorpyrifos, and carbaryl	• Concentration time-series and box plots before and after 2001 phaseout. • Seasonal step-trend analysis, a nonparametric rank-sum test. • No flow adjustment.	Federally mandated phaseout of diazonin and chlorpyrifos insecticide use in outdoor urban settings.	• Temporal insecticide trends showed significant step decreases in diazinon concentrations occurred at 90% of the sites after the phaseout. • Concentrations generally decreased by > 50% in summer samples. • Decreases in diazinon and chlorpyrifos concentration were greatest in highly urbanized watersheds (i.e., population densities > 400/km2 & agricultural land use < 40%. They did not decrease as much at the two agricultural sites. • Lack of a carbaryl increase should not be extrapolated to other insecticides, and the use of pyrethroid insecticides may have expanded in response to the phaseout.	• Data on other insecticides used to replace diazinon and chlorpyrifos (e.g., imidacloprid, fipronil, and pyrethroids) is required to fully assess the effect of the phaseout.
Greece 1999-2007 **Vryzas et al. (2009)**	• 8 sampling points along the rivers Ardas, Evros and Erythropotamos • Grab sampling • 147 compounds	• Computed 'Quantity factor applied' which is the product of number of crops, application frequency, % of crop acreage applied, and dose applied. • Quantity factor applied correlated with highest concentrations of most frequently detected pesticides.	None specified	• Soil applied pesticides were the most frequently detected of the 28 compounds (pesticides, metabolites and caffeine) detected in surface waters of northeastern Greece. • High pesticide concentrations were detected within 2 months of their application. • Extreme pesticide concentrations were detected in the beginning of the irrigation season or just after high rainfall events. Increased loading seemed to be a consequence of application (timing, rate, frequency) and intense rainfall during the application period. • Low levels of pesticide residues were found in the 1st sampling point (Greek/Bulgarian boarders) of all rivers, however o', p' DDT, o', p', DDE and γ-HCH were mainly detected in this sampling point regarded as cross-boundary contamination. • Most commonly encountered compounds in the river waters were atrazine, DEA, alachlor, trifluralin, prometryne, molinate, carbofuran, carbaryl, and diazinon. • Aquatic risk assessment revealed that from the 28 compounds that were constantly detected 12 (mostly insecticides) showed non-acceptable risk when median concentrations were used as predicted environmental concentration (PEC) and 18 when extreme concentrations were used as PEC values.	• Establishment of an integrated monitoring system in the surface water of Evros basin would identify specific areas susceptible to contamination. • It is necessary to extend the monitoring program at the Bulgarian and Turkish part of the Evros basin and implement an ecotoxicological testing with inhabitant species.
US (Lake Erie) 1983-2004 and	• Four Lake Erie catchments from	Fast flow index (FFI): Long-term	None specified	• Empirical data analysis showed that fast flow is important in determining the extent of herbicide losses and the combined	• FFI-FFV proxy is a promising catchment vulnerability screening tool for moderately persistent, pre-emergent,

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Switzerland 1990-2003 **Leu et al., (2010)**	Richards and Baker (1993) and Two Swiss lakes from Singer et al. (2005) • Acetochlor, Alachlor, Atrazine, Metolachlor	average proportion of fast flow to total discharge and the fast flow volume (FFV): Stormflow component of the hydrograph during the spring flush period.		proxy of FFI and FFVs explained the interannual and spatial variability of atrazine and metolachlor losses as a percentage of use. • Percentages of applied amounts of 3 out of 4 herbicides lost to surface water was positively correlated with FFV, and the slope of the correlation was positively correlated with FFI. • Dependency between FFI and herbicides losses seems reasonable because as FFI increases, less rain is needed to trigger fast flow and more herbicide is available in the topsoil. • FFI and FFV represent the integral influence of intrinsic catchment characteristics on herbicide losses like climate, topography, soil, and geology. • Application of the FFI-FFVs proxy on 65 European catchments shows low predicted loss rates in many catchments due to a low FFI or low FFV values, suggesting that point sources are expected to dominate contributions in many parts of Europe due to a limited vulnerability for diffuse losses.	single-application herbicides, which can guide researchers and authorities in selecting monitoring areas, setting monitoring results into context, and prioritizing mitigation strategies according to catchment vulnerability. • Measured herbicide losses was restricted to areas with fairly high FFI values that were above the average of European catchments because no long-term time series of herbicide use and monitoring data were available for catchments with a low FFI. Therefore, there is a need to confirm conclusions based on long-term data on diffuse herbicide losses from catchments with little fast flow generation.
US (Missouri) 1991-20010 **Lerch et al. (2011a, 2011b, 2015)**	• Goodwater Creek Experimental Watershed, northeastern Missouri • Weekly grab samples under baseflow conditions and flow-weighted composite samples from autosampler for events up to 150 mm of runoff. • 13 herbicides and metabolites (e.g., acetochlor, alachlor, atrazine, cyanazine, metolachlor, and metribuzin, simazine).	• 14-, 30-, 60-, and 90-day maximum running average. • Cumulative frequency distributions (CFD) for flow-weighted concentration, load and stream discharge. • Cumulative vulnerability index (CVI) • Linear regression analysis.	Grassed waterways, Conservation Reserve Program	• Relative annual atrazine loads varied from 0.56 to 14% of applied, with a median of 5.9%. This median relative load is amongst the highest in the reported literature, indicating that this claypan watershed is extremely vulnerable to herbicide transport. • Running average atrazine concentrations exceeded the USEPA screening criteria for days to weeks, 10 years out of 15. • CFD and linear regression analysis showed no significant atrazine concentration time trends. • Observed trends in daily load were mainly a function of stream discharge trends. • 25% increase in atrazine use over the course of this study was too small to affect trends in atrazine concentration or load. • CVI based on crop planting progress (surrogate for spraying progress), atrazine degradation kinetics, and occurrence of runoff events was shown to correlate to annual atrazine loads, suggesting they are key factors in controlling annual variation in atrazine transport at the catchment scale. • Acetochlor, alachlor, metolachlor ,and metribuzin use and annual variation in second quarter stream discharge are the primary factors affecting trends in flow-weighted concentrations and loads. • 15-year trend analysis (1992-2006) of herbicides concentrations and loads showed that changes of 50% or more in herbicide usage were required for significant trends to be observed at the outlet. • Near-surface restrictive soil layers result in greater herbicide transport than soils with high percolation and low clay content. Thus, streams in claypan soil watershed of northeastern Missouri	• Atrazine registrants (i.e., manufacturer, distributors, sellers) are required to work with farmers to implement atrazine transport reduction measures. • Management challenges for restrictive layer soils include development and validation of metrics (e.g., depth to restrictive layer, clay content, slope, saturated hydraulic conductivity) for identification of vulnerable areas within watersheds that can provide the basis for targeting conservation practices and development of practices that can simultaneously manage for erosion control and reductions in soil-applied herbicide transport.

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				have exceptionally high herbicide concentrations and relative loads compared with other areas of the Corn Belt.	
Spain 2002-2010 **Hermosin et al. (2013)**	• Guadalquivir river basin (10 surface water locations) • No sampling method specified. Fixed time intervals for sampling (i.e., Aug, Nov–Dec, and Mar–Apr). • 4 to 6 herbicides and 2 metabolites	• Sum of mean annual concentrations and mean percentage of samples above drinking water limit. • Principal component analysis.	Changes in herbicide registration and actions (e.g., courses and technical workshops on best pesticide practices) in 2002.	• Individual herbicide concentrations had a very large variability throughout the year and across the locations. • Herbicide concentrations were related to field doses, soil runoff processes in surface waters, and chemical properties (e.g., solubility and half-life). • The mean % of samples above the limits for dinking water improved from 2002 to 2010. For surface waters, values decreased from 72% (diuron) to 33% (terbuthylazine). • The coincidence of the highest concentration measured in the final 3 years for terbuthylazine, in both surface and groundwater, indicates the danger of focusing on a few herbicide products. • Mean herbicide level in surface water showed a decreasing trend over the study period due to regulations (changes in authorized herbicides) and actions (courses and technical workshops) starting in 2002 by regional and national government.	• High concentrations in groundwater suggests the need for recommendations on limiting groundwater for human consumption. • Annual mean concentration of olive herbicides in groundwater and the presence of simazine (banned in 2002) in surface water suggests that more effort from the authorities is needed. • Engaging farmers and local pesticide distributers regarding herbicide management in olive crop fields of southern Spain should be maintained.
Canada (Ontario) 2003-2012 **Todd and Struger (2014)**	• 10 urban streams. • Grab sampling during low and high flow conditions from May to October. • Acid herbicides 2,4-D, dicamba and mecoprop.	• Concentration time-series and box plot for pre- and post-ban. • Linear regression, Mann-Whitney rank-sum test, Hodges-Lehmann estimator. • No flow adjustment.	Cosmetic (non-essential) pesticide ban.	• Following the cosmetic pesticide ban in Apr 2009, the average concentration decrease was 64%, 74%, and 69% for 2,4-D, dicamba, and mecoprop, respectively. • Concentrations were significantly related to population density or urban land cover, and the relative proportion of the 3 herbicides observed in urban stream water approximated the ratios found in pesticide products for urban use. • Longer-term trends indicate that decreases in surface water herbicide concentrations may have preceded the ban and may be related to increased public awareness of pesticide issues and voluntary reductions in urban pesticide use.	• Further study is needed to understand the potential sublethal effects of environmental pesticide mixtures on aquatic life.
US (National) 1992-2010 **Ryberg and Gilliom (2015); Supporting references: Gilliom et al. (2006); Sullivan et al. (2009); Vecchia et al. (2009); Johnson et al. (2011); Stone**	• 212 stream sites within 38 major US rivers. • Varied by sites and years. Fixed-interval and high-flow sampling. Flow-weighted, depth- and width-integrated using isokinetic samplers. • 11 pesticides.	• Concentration trend vs. use trend (%/year) analysis. • Seasonal Wave and Adjustment for Streamflow (Q), SEAWAVE-Q (Ryberg and Vecchia, 2013).	Regulatory actions/phase-outs and market forces.	• Widespread agreement between agricultural pesticide use (e.g., cyanazine, alachlor, atrazine, metolachlor, and carbofuran) trends and concentrations in rivers trends. • Pesticides with substantial use in both agricultural and nonagricultural uses (e.g., simazine, chlorpyrifos, malathion, diazinon, and carbaryl) had concentration trends that were mostly explained by a combination of agricultural- and urban-use changes. • Reductions in concentrations due to improved management practices (unrelated to use reduction) is difficult to discern given the uncertainty in the concentration and use trends, or there may have been little or no change in management practices.	• Potential adverse effects is likely underestimated because a wide range of potentially important pesticide compounds were not included in the assessment. • Use trends were for agricultural use only, while concentration trends integrate all pesticide sources (i.e., nonagricultural uses). • Changes in agricultural management practices (e.g., increased tile drainage) may change pesticide losses, independent of use trends. • Improved basin-specific watershed-scale data on agricultural and nonagricultural pesticide uses and on the timing of specific management practices (e.g., conservation tillage and implementation of buffer strips)

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et al. (2014); Ryberg et al. (2014); Oelsner et al. (2017)				• Deethylatrazine (DEA), a degradant of atrazine, was frequently observed to have concentration trends in the opposite direction of (atrazine) use trends. • Environmentally persistent pesticides and degradants may have concentration trends that lag use trends. • Nested analysis for the Mississippi River indicates that most trends observed in the largest rivers are consistent with streamflow contributions and concentration trends observed at tributary sites.	are needed to reliably evaluate their influence on pesticide concentrations in surface water. • Complex mixtures of multiple pesticides are the most common mode of occurrence. Thus, tracking co-occurrence and assessing the potential toxicity of mixtures to humans and aquatic biota is vital to future assessments. • Pesticides and degradants targeted for analysis need to be reevaluated regularly as use changes over time and new pesticides are introduced.
Norway 1991- 2012, 1995-2012 [4x], 1996-2015 **Stenrød (2015)**	• 6 small agricultural catchments. • Flow proportional composite sample averaged over 14-days of the spraying season (May-Sep). • 96 pesticide active ingredients and 19 metabolites.	• Detection frequency, measured concentration, and summed monthly relative cumulative risk. • Pearson correlation (r) and linear regression for pesticide use. • Quantile regression and Kendall's Tau for cumulative risk.	Lowering of recommended dose (metribuzin)	• In-stream pesticides can be mainly explained by pesticide use on nearby land areas and the prevailing weather conditions. • Environmental load of pesticide used in Norwegian agriculture decreased from 1995 to 2012 in the monitored catchments. • Vegetable & potato cropping areas showed the highest level of total environmental risk, but also a statistically significant decreasing trend over the monitoring period. • Cereal cropping areas exhibited no statistically significant time-dependent trends, but did show an increase in fungicide use. • Multiple stressors and mixture toxicity of pesticides in streams is equally relevant in cold climatic conditions.	• Continued attention should focus on herbicides metribuzin and aclonifen. • Emerging concerns regarding the fungicide prothioconazole and the insecticide imidacloprid. • Need for more complete coverage of pesticides and metabolites (e.g., sufonylurea herbicides and herbicides with glyphosate as active ingredient). • Need for more sufficient sampling techniques that consider short-term peak concentrations, • Need for data outside of spraying season (May-Sep) since there are indications of delayed degradation of pesticides in colder climates. • Need for risk assessment of mixture toxicity effects.
US (California) 2008-2013 **Budd et al. (2015)**	• 16 watersheds in seven counties of California. • Grab samples and automated time-proportional composite samples for a few storm events. • Fipronil	• Akritas-Theil-Sen line for trend analysis with associated Kendall's tau correlation coefficient.	None specified	• Data collected at long-term monitoring stations indicate that higher concentrations in southern California correspond to higher use patterns in the region. • Clear pattern of increased transport of fipronil with higher flow associated with rain events. • Lack of seasonality effects on degradants' concentrations, which suggests a constant source of fipronil with a corresponding lag time of transport to surface waters during the dry season (from Apr. to Nov.). • Fipronil application is predominantly made during the dryer periods with offsite transport driven by lower-velocity irrigation waters. • Longer lag periods between application and transport allows more time for photolytic and hydrolysis process increasing the ratio of degradants contributions during the dry season. • Parent material accumulated during the dry season applications is transported by rainfall events. The first rainfall event has the	• Although fipronil was the focus of this analysis, the transport mechanisms discussed will likely hold true for other urban surface water contaminants with similar physiochemical properties. • Fipronil has been previously detected in sediment originating from urban landscapes, thus future monitoring efforts should include sediments as a long-term source of fipronil.

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				highest associated runoff potential, but residual amounts on the hardscape are available to runoff months later.	
US (California) 1992-2014 **Wang et al. (2017) Supporting references: Wang et al. (2016); Hall and Anderson (2014); Hall (2003)**	• Data compiled from three databases covering 150 total sites in Sacramento Valley (52 sites), Westside San Joaquin (28 sites), East San Joaquin (37 sites) and Delta (33 sites). • Grab sampling and depth or width integrated sampling. • Diazinon (Chlorpyrifos 2005-2013, see Hall and Anderson, 2014; Wang et al., 2016)	• Diazinon use rate and exceedance frequency of water quality objectives. • Temporal trend in diazinon concentrations in surface water used censored regression. • Akritas-Theil-Sen line for trend analysis with associated Kendall's tau correlation coefficient.	• Agricultural and non-agricultural diazinon use restrictions and bans from 2000-2010	• The use of diazinon had reduced in accordance with regulatory developments and actions taken by United States Environmental Protection Agency, California Department of Pesticide Regulation (CDPR), and The State of California Central Valley Regional Water Quality Control Board (CVRWQCB). • Reduced diazinon use had led to a downward trend in concentrations and exceedance frequencies in surface waters. • The current level of diazinon concentrations in California's surface water (water years 2012-2014) pose a negligible risk to aquatic organisms. • If the use remains at the current or lower levels, the aquatic risk posed by diazinon alone should be negligible. • The higher explanatory power of the previous year's use may be a result of delayed transport of diazinon from the use sites to the water ways. • A significant downward trend in chlorpyrifos concentrations was observed with a low aquatic risk. • Historical values of chlorpyrifos use, precipitation, and irrigation demand influenced the exceedance frequency of chlorpyrifos over water quality criteria.	• Agricultural use of diazinon peaked in water year (WY) 1993 and 1994. Since then, there has been a general decreasing trend, with a significant decreasing trend before the implementation of mitigation measures from WY 1994-1998. • There is no clear regulatory stimulus behind the reduction in WY 1994-1998; the reduction in use could be a result of changing pest pressures, economy, and market forces.
Costa Rica 2007-2012 **Carazo-Rojas et al. (2018)**	• 17 sampling sites in La Mula micro-catchment. • Grab sampling. • 80 active ingredients.	• No correlation between Quantity factor applied (product of application dose, frequency, area, number of crops) and max. concentration detected in water.	None specified	• Dimethoate (61.2 μg/L), propanil (30.6 μg/L), diuron (22.8 μg/L) and terbutryn (4.8 μg/L) were detected at the highest concentrations in water samples. • Pesticides carbendazim, diuron, endosulfan, epoxyconazole, propanil, triazophos and terbutryn showed non-acceptable risk even when a conservative scenario was considered. • Pesticide use patterns followed in the crops near La Mula (high application dose and frequency of some pesticides) did not directly correlate with higher detection frequencies or higher concentrations, suggesting that factors related to the fate of pesticides (e.g., rainfall events, soil properties, adsorption, runoff, leaching, and degradation) may be more crucial to determine pesticide occurrence in the area. • Exceptional ecological conditions of the tropical agro-ecosystem affect the fate of pesticides in water and sediment environment differently than the temperate one.	• Pesticide properties combined with environmental fate, monitoring and ecotoxicological data, as well as agricultural activities in a tropical agro-ecosystem, may provide useful inputs to support the pesticide registration process in Costa Rica and other Latin American countries.
Switzerland 2008-2015 (Charmilles) 2005-2016 (Boiron)	• Charmilles and Boiron river basins in western Switzerland • One-week flow-proportional	• Sum of concentrations and biological indicators (e.g., SPEAR)	• Wash station and biobeds. • Problematic pesticides replaced by less harmful	• ~50% decrease in pesticide load with concentrations staying about the same (Charmilles). Reduced peak flow and runoff from pesticide application sites, likely due to installing grass strips between the vine rows.	• Need for improved coordination between sampling strategy, the selection of substances for analysis, and pesticide applications. • Close cooperation between the farmers, food industry, and water protection authorities should be established as early as possible.

Country, years of monitoring & reference(s)	Sampling locations, method & analytes	Evaluation metrics & statistical trend analysis/flow adjustment	Implemented mitigation measures	Conclusions	Limitations/ Recommendations
Daouk et al. (2019)	composite samples from Mar. to Oct. (Charmilles). 24 hour time-proportional samples taken once per month for a total of 8 from Mar. to Oct. (Boiron) • 76 to 147 pesticides Charmilles. 36 to 80 pesticides in Boiron.	• Fischer test (Boiron)	active substances. • Grass/ Buffer strips	• Increase in observed sum of concentrations (Boiron) may be due to increase in substances analyzed rather than increased pesticide losses. • Glyphosate concentrations decrease over time despite relatively constant use, suggesting that measures to control runoff and wash stations reduced pesticide losses (Boiron). • Sampling strategy (e.g., flow-proportional sampling to calculate loads) and substance selection (e.g., nicosulfuron) determine the conclusions drawn from data. • Certain biological indicators point to long-term improvement, however it was difficult to establish a direct link between the implemented mitigation measures and the monitoring results because several measures were implemented simultaneously.	• All exotoxicological data and chemical properties (volatilization, sorption, degradation) should be gathered to properly assess the benefit of substance substitution for aquatic organisms. • Additional data (e.g., application, discharge, precipitation) are crucial to draw cause-and-effect relationships of mitigation measures.
US (California) 2009-2018 **Budd et al. (2020)**	• 22 watersheds in 8 California counties. • Composite storm runoff samples at select sites using autosamplers. Flow-weighed storm runoff samples at two sites. Samples collected evenly over the course of the storm. • Pyrethroids (e.g., bifenthrin, cypermethrin, deltamethrin).	• Detection frequency and frequency of benchmark exceedance. • Mann-Whitney test and Akritas-Theil-Sen line with associated Kendall's tau correlation coefficient.	• Regulations requiring professional applicators to hold a license to make structural or landscape pesticide applications.	• In Northern California, decreasing trends in bifenthrin and cypermethrin concentrations may be counterbalanced by a potential switch to deltamethrin-containing products. • Few observed concentration trends in Southern California could be a result of regional hydrological and pest pressure differences. • Results from a pyrethroid tracer experiment highlight the potential for contaminant laden sediment to serve as a long-term (observed half-lives >514 days) source of pyrethroids within surface waters. • Chemistry and observed toxicity data indicate that storm water runoff as a primary transport mechanism. • Presence of pyrethroids in dry-weather runoff suggests that significant loading can occur under various hydrologic conditions.	• Regulations only apply to professional applications, it is likely that consumer use patterns serve as a covariate for observed concentration trends. • Caution must be taken when interpreting future trend evaluations, as sediment bound contaminants may serve as a potential source of pyrethroids for years to come due to the very slow decay rate of sediment-bound pyrethroids. • This study relies on results from a targeted-monitoring design program; and is therefore, biased toward a dataset consisting of higher concentrations among Californian water bodies.

References

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P. and Wolock, D.M., 2006. Pesticides in the nation's streams and ground water, 1992-2001 (No. 1291). US Geological Survey.

Hall, L.W.J., 2003. Analysis of diazinon monitoring data from the Sacramento and Feather River watersheds: 1991–2001. Environmental monitoring and assessment, 86(3), pp.233-253.

Hall, L.W.J. and Anderson, R.D., 2014. Temporal trends analysis of 2004 to 2012 toxicity and pesticide data for California's Central Valley water quality coalitions. Journal of Environmental Science and Health, Part A, 49(3), pp.313-326.Johnson, H.M., Domagalski, J.L. and Saleh, D.K., 2011. Trends in pesticide concentrations in streams of the western United States, 1993-2005. Journal of the American Water Resources Association, 47(2), p.265.

Ryberg, K.R., Vecchia, A.V., Gilliom, R.J. and Martin, J.D., 2014. Pesticide trends in major rivers of the United States, 1992–2010. US Geological Survey Scientific Investigations Report, 5135, p.63.

Singer, H., H.-G. Anfang, A. Lück, A. Peter, and S. Müller. 2005. Pestizidbelastung von Oberflächengewässern. Auswirkungen der ökologischen Massnahmen in der Landwirtschaft (in German). Gas-Wasser-Abwasser (gwa) 2005:879–886.