

The legacy of pesticide pollution: An overlooked factor in current risk assessments of freshwater systems

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1 The legacy of pesticide pollution: An overlooked factor in current risk

2 assessments of freshwater systems

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23 ABSTRACT

We revealed a history of legacy pesticides in water and sediment samples from 19 small streams 24 25 across an agricultural landscape. Dominant legacy compounds included organochlorine pesticides, such as DDT and lindane, the organophosphate chlorpyrifos and triazine herbicides such as 26 terbutylazine and simazine which have long been banned in the EU. The highest concentrations of 27 28 legacy pesticides were found in streams draining catchments with a large proportion of arable 29 farmland suggesting that they originated from past agricultural applications. The sum of toxic units (SumTU_{D.magna}) based on storm water samples from agriculturally impacted streams was 30 31 significantly higher when legacy pesticides were included compared to when they were omitted. Legacy pesticides did not significantly change the predicted toxicity of water samples to algae or 32 fish. However, pesticide concentrations in bed sediment and suspended sediment samples exceeded 33 safety thresholds in 50 % of the samples and the average contribution of legacy pesticides to the 34 $SumTU_{C.riparius}$ was > 90%. Our results suggest that legacy pesticides can be highly significant 35 36 contributors to the current toxic exposure of stream biota, especially macroinvertebrate 37 communities, and that those communities were primarily exposed to legacy pesticides via the sediment. Additionally, our results suggest that neglecting legacy pesticides in the risk assessment 38 39 of pesticides in streams may severely underestimate the risk of ecological effects. 40

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- 42
- 43

KEYWORDS: Legacy pesticides, Environmental Risk Assessment, Mixture Toxicity, Pesticide
Monitoring, Streams

46 INTRODUCTION

Publication frequency of articles characterising the contamination dynamics of freshwater systems 47 in space and time has increased over the past decade in recognition of the need to increase realism 48 of current exposure and risk assessments to support an informed management of these systems. 49 Pesticides in particular have received increasing attention given their suggested important role in 50 51 the global loss of freshwater biodiversity and ecosystem functioning (Beketov et al. 2013; Malaj et al. 2014; Rasmussen et al. 2012; Schäfer et al. 2012). In this article, we subdivide pesticides into 52 53 those still registered for agricultural use in the European Union and in Denmark (referred to as contemporary pesticides) and those that have been discontinued or banned for usage in conventional 54 agriculture (referred to as legacy pesticides). 55

56

Pesticides applied to agricultural fields may reach surface water through a series of different 57 pathways with surface runoff and tile drains being widely accepted as the most important routes for 58 contemporary pesticides (Schulz 2004). These transport routes are primarily initiated during heavy 59 precipitation events and lead to transient peak concentrations often exceeding current ecological 60 61 quality criteria (Bundschuh et al. 2014; Liess and von der Ohe 2005; Schulz 2004). In contrast, legacy pesticides may enter surface water continuously via groundwater inflow (Barth et al. 2007; 62 Gilliom 2007; McKnight et al. 2015), atmospheric deposition (Konstantinou et al. 2006; Weber et 63 64 al. 2010) or through continuous leaching from agricultural soils and landfills (Aliyeva et al. 2013). 65 Consequently, legacy pesticides may generate a relatively constant exposure regime in surface waters. The yearly flux of legacy pesticides to freshwater ecosystems may comprise up to several 66 67 percent of the historical yearly applied amounts in a catchment (Barth et al. 2007). Importantly, pesticides and their residues may persist and even accumulate in sediments of freshwater 68 ecosystems (Dai et al. 2014; Kuivila et al. 2012; Nowell et al. 2013). 69

71	Factors controlling the fate of a pesticide in agricultural landscapes include a variety of chemical
72	and environmental properties of the pesticide (e.g. degradation rate, adsorption to organic carbon
73	and water solubility), climatic factors (e.g. temperature and precipitation), soil characteristics,
74	topography and agricultural practices (Leonard 1990; Wauchope 1978). More than 20,000 pesticide
75	products have entered the market since registration became legislatively required in 1947, and it is
76	therefore not surprising that the combined effect of multiple factors influencing the environmental
77	transport and fate of each pesticide generates highly complex exposure profiles of pesticide
78	mixtures in time and space (Konstantinou et al. 2006; Wauchope 1978). However, pesticides that
79	are currently applied in the highest quantities are also those that occur most often in surface waters
80	with the more water soluble and persistent compounds reaching the highest concentrations
81	(Bundschuh et al. 2014; Kreuger and Tornqvist 1998; Li et al. 2013; Moschet et al. 2014).
82	Therefore, current pesticide usage is often used to guide the prioritisation of active ingredients
83	included in monitoring programmes and research activities. Moschet et al. (2014) showed that a
84	stringent focus on EU priority pollutants or a subset of the active ingredients applied in the highest
85	quantities on the national level may seriously underestimate predicted toxic pressures in streams.
86	Whereas Moschet et al. (2014) aimed to document that an extensive pesticide screening (249 active
87	ingredients) translates into significantly higher predicted mixture toxicities compared to screenings
88	restricted to fewer pesticides (\leq 36), the authors did not distinguish between the toxic contribution
89	of contemporary and legacy pesticides. Based on water samples mainly analysed for herbicides and
90	four sediment samples mainly analysed for insecticides, McKnight et al. (2015) suggested that
91	legacy pesticides could still be prominent players driving observed impairments of freshwater
92	invertebrates, and the authors urged for more extensive studies that allow for quantifying the
93	predicted toxicological potency of legacy pesticides in comparison to current use pesticides. To our

94 knowledge, such an extensive study of the potential toxicity of legacy pesticides to aquatic biota 95 relative to that of contemporary pesticides is still lacking despite a substantial body of literature 96 addressing the occurrence, concentrations and predicted toxicities of selected legacy pesticides (Aliyeva et al., 2013; Gilliom, 2007; McKnight et al., 2015; Weber et al., 2010). The novelty 97 element is therefore to quantify the possible toxicity of legacy pesticides as an integral part of 98 99 current risk assessment. Such an integration has a number of potentially vital implications for the usability of risk assessment, including that i) contemporary regulatory actions are only targeting 100 101 substances that are still in use; ii) it gives an increased explanatory power in river quality assessment by quantifying the impact of current unknowns, which will additionally reduce the 102 potential underestimation of the role of pesticides as stressors in stream ecosystems, which is 103 104 currently most likely the case (Beketov et al., 2013; Malaj et al., 2014), and iii) it provides highly needed insight into pesticide exposure profiles in time and space that may be used as improved 105 benchmarks for the interpretations of ecological response parameters. 106

107

This article aims to compare the toxicity of legacy pesticides and their metabolites to those of 108 contemporary pesticides in 19 Danish 1st and 2nd order streams situated in agricultural landscape 109 covering a range of agricultural intensity, local climate and soil types. Water samples were collected 110 during base flow and peak flow for pesticide analyses, and bulk sediment and suspended sediment 111 112 were sampled to optimize detections of pesticides with low water solubility. In more detail, our objectives were to: i) characterize the occurrence of legacy pesticides in Danish headwater streams, 113 ii) estimate the predicted toxicity of legacy pesticides and their residues using the Toxic Units (TU) 114 115 approach, iii) evaluate the relative contribution of legacy pesticides and their residues to the 116 summed TU of contemporary pesticides, and iv) evaluate which legacy pesticides are of highest ecotoxicological concern. 117

119 METHODS

120 *Study streams*

Nineteen Danish 1st and 2nd order streams (Fig. S1) were sampled for pesticide occurrences. Nine 121 streams with < 50% agricultural land-use in a two-sided buffer extending 2,000 m upstream of the 122 sampling site were selected in addition to 10 streams with expected high impact of pesticides 123 (conventional agriculture > 60% in the two-sided 100 m buffer). Furthermore, all study sites 124 125 complied with the following selection criteria: i) forest should occupy < 50% of a two-sided 50m buffer extending from the study site and 2,000 m upstream, ii) proportional coverage of silt and 126 mud in stream substrates (indicative of drainage ditches) should be < 50%, and iii) no influence 127 128 from waste water treatment plants, but scattered settlements may influence the chemical water quality. Detailed information on the study streams and catchments is provided in Table S1). In this 129 article, we refer to the nine streams with expected low agricultural impact as controls and the ten 130 streams with expected high agricultural impact as agricultural streams. All catchments are 131 characterised by loam or sandy loam, low elevation and precipitation ranges from ca. 800-850 mm 132 year⁻¹ for central Jutland and on Funen and 700-750 mm year⁻¹ on Zealand. 133

134

Base flow discharge was calculated as the product of the mean stream width, mean depth and mean water velocity, based on measurements at ten transects along a 100 m stream reach extending upstream from the sampling point (depth and velocity measured at 0, 25, 50 and 75% of the width of each transect). Moreover, yearly mean discharge was estimated as the product of yearly mean discharge coefficients (L s⁻¹ km⁻²), calculated for national hydrological monitoring stream sites geographically/geologically selected as representative for the study streams, and catchment area for the study streams (km²). In a few cases national monitoring sites could not be regarded as truly representative, and yearly mean discharge was designated as > base flow (Table S1). The
proportion of conventional agriculture was quantified for the catchments of each study stream and
for a two-sided 100 m buffer extending 2,000 m upstream of the sampling site were quantified in
ArcGis 10.1 for windows.

146

147 *Pesticide sampling*

Sampling was conducted during May – August in 2012 coinciding with the main pesticide 148 149 application season in this part of Europe. Dissolved phase pesticides were sampled with: i) manual grab samples in August during low flow conditions to optimize detections of pesticides originating 150 from groundwater inflow (one sample per stream) and ii) event-triggered water samplers designed 151 152 to capture water during storm flow (Liess et al. 1999). Manual collection of water samples during low-flow conditions were consistently preceded by one week without precipitation. Event-triggered 153 water samplers were checked every week during May, June and July and collected if full, resulting 154 in 64 storm flow water samples. The event-triggered water samplers strategically collect water 155 representing a temporal point measurement during the first hours of a heavy rain incident (Liess et 156 157 al. 1999).

158

Sediment associated pesticides were sampled with two different methods. Bed sediment was
collected (top 1 cm) in depositional areas using Kajak corers (8 cm in diameter). Each bed sediment
sample was comprised of 20-30 subsamples to obtain samples representative for the stream reach.
Bed sediment was collected in all streams in mid-August reflecting newly deposited material during
the summer period. Suspended sediment was additionally collected since the mobile sediment
fraction may provide a stronger estimate for worst case scenarios (Liess et al. 1996). The Suspended
Particle Samplers (SPS) used in this study are described in detail elsewhere (Laubel et al. 2001).

167 *Chemical analyses*

Water samples were screened for 70 pesticides and metabolites comprising 42 contemporary
pesticides, 26 legacy pesticides and 2 metabolites (Table S2). The 68 active ingredients included 35
herbicides, 16 fungicides and 17 insecticides. Bed sediment and suspended sediment samples were
screened for 38 pesticides and residues comprising 16 contemporary pesticides, 18 legacy pesticides
and 4 metabolites (Table S3). The 34 active ingredients included in the screening included 12
herbicides, 5 fungicides and 17 insecticides.

174

Analysis of water samples for the non-polar compounds was done by liquid/liquid extraction 175 176 followed by gas chromatography mass spectrometry (GC-MS). For the polar and semi-polar compounds online solid-phase extraction followed by liquid chromatography tandem mass 177 spectrometry (LC-MS/MS) was performed as described by Jansson & Kreuger (2010). 178 Wet sediment sample (20 g) was mixed with a drying agent (10 g). A sub-sample of the mixture (9 179 g, corresponding to 6 g sediment) was placed in pre-cleaned (400 °C) glass fibre cartridges and 180 181 extracted together with the internal standards ethion and terbuthylazin-D5 by a Soxtec Avanti 2050 Auto System using dichloromethane and acetone (1:1). The extract was evaporated and diluted in 182 cyclohexane and dichloromethane (1:1) before purification by Gel Permeation Chromatography 183 184 (GPC), followed by evaporation and dilution in cyclohexane and acetone (9:1). The volume was adjusted to 1 ml. The extract was injected on two separate GC-MS systems, one in negative 185 chemical ionization (NCI) mode (Agilent Technologies GC 7890, MS 5975C) and one in electron 186 187 impact (EI) mode (Agilent Technologies GC 6890, MS 5973), quantifying against an external 188 standard calibration. In order to enhance the sensitivity of the DDTs, a part of the initial extract was purified with sulphuric acid and with the internal standards added once again before injection. The 189

standards used were obtained from Dr Ehrenstorfer GmbH. Dry-weight measurements of sediment were performed in a dry oven (105 °C) during ca. 16 hours, with analytical results presented as μg per kg of dry weight.

193

Values between the limit of detection (LOD) and the limit of quantification (LOQ) were given as trace
concentrations. At this level, the uncertainty of the concentration might be higher than stipulated (i.e. above
30 %), but the identity of the compound has been confirmed and was therefore considered appropriate to be
included in the subsequent data analysis.

198

199 Data analysis

All pesticide properties including effect concentrations (Tables S1 and S2) were acquired from the 200 Pesticide Properties Database (http://sitem.herts.ac.uk/aeru/ppdb/en/ accessed 18.08.2014) and from 201 the US EPA Ecotox Database (http://cfpub.epa.gov/ecotox/ accessed on 25.08.2014). In the cases 202 where more than one effect concentration was available for a pesticide, the lowest value was 203 selected. Legal status of the pesticides in Denmark and the EU was acquired from the Danish 204 205 Pesticide Database (http://middeldatabasen.dk/Middelvalg.asp_accessed on 04.09.2014) and the EU Pesticides Database (http://ec.europa.eu/sanco_pesticides/public/?event=homepage accessed on 206 04.09.2014), respectively (Tables S1 and S2). 207

208

For all water samples and sediment samples with pesticide detections above the LOD, the sum of toxic units (SumTU) was calculated to standardise exposure concentrations according to a benchmark organism. For water samples we used 96h growth inhibition tests on the green algae *Pseudokirchneriella subcapitata* to benchmark sample toxicity to primary producers. In the cases where no data existed, we used data for *Scenedesmus subspicatus* as an alternative. Acute 48h mortality tests on *Daphnia magna* were used to benchmark the toxicity to invertebrates and 96h mortality tests on *Oncorhynchus mykiss* were used to benchmark sample toxicity to fish. *Lepomis macrochirus* was used as an alternative species in the few cases where no data was available for *O*.
 mykiss.

218 The sum of toxic units (SumTU) is calculated as:

219
$$\operatorname{SumTU} = \sum_{i=1}^{n} \frac{C_i}{\text{EC50}_i}$$
(1)

where C_i is the concentration of pesticide *i* in the sample, and EC50_{*i*} is the concentration of chemical *i* causing a 50% effect to the benchmark organisms.

222

Bed sediment and suspended sediment pesticide concentrations were converted to TU using 96h 223 acute mortality tests for the sediment dwelling non-biting midge Chironomus riparius 224 supplemented with 28d chronic exposure tests on emergence success for C. riparius in the cases 225 where no 96h acute mortality test data existed. Often, only one of the tests was available for a 226 227 pesticide, but in the few cases where data for both acute and chronic tests existed, we selected the lowest effect concentration. Effect concentrations in the C. riparius tests were based on measured 228 229 pore water concentrations. In the cases where no sediment test data existed for a pesticide, we used 230 the 48h LC50 for D. magna as surrogate measure for sediment toxicity. Plotting the C. riparius toxicity data as a function of 48h LC50 for D. magna for the pesticide compounds having both sets 231 of toxicity data revealed that the deviation from the 1:1 line rarely exceeded one order of magnitude 232 233 (Fig. S2).

234

- 235 Measured sediment-associated pesticide concentrations were converted to pore-water
- concentrations according to the equilibrium-partitioning approach to comply with the sediment
- 237 benchmark toxicity tests that are based on dissolved phase pesticides in pore water. Moreover, pore

water concentrations are superior predictors of sediment toxicity to invertebrates compared to
pesticides adsorbed to sediment particles (Xu et al. 2007).

240 Pore water concentrations from bed sediment and suspended sediment were calculated according to241 Ditoro et al. (1991) as:

$$242 C_{PW} = \frac{C_s}{K_d} (2)$$

where K_d is the partitioning coefficient, C_S is the sediment concentration and C_{PW} the pore water concentration of the pesticide. K_d was calculated as:

$$K_d = K_{OC} \times f_{OC} \tag{3}$$

where K_{OC} is the dimensionless organic carbon-water partitioning coefficient for the pesticide and f_{OC} is the fraction of total organic carbon measured in the sediment sample. Kronvang et al. (2003) found the fraction of total organic carbon in bed sediments from 27 Danish agricultural streams to range from 5.5 to 16.1% with an average of 8.5%. Hence, the f_{OC} was set to 0.085 in our study. The K_{OC} was calculated as:

$$251 \quad \log K_{\rm OC} = a \times \log K_{\rm OW} + b \tag{4}$$

where K_{OW} is the octanol-water partitioning coefficient. The constants a and b were set to 0.72 and 0.49, respectively, according to Schwarzenbach and Westall (1981).

254

We tested correlations between pesticide concentrations (ppm) among sample types (n = 19) using Spearman-Rank analysis. Stream specific (arithmetic) mean concentrations of storm flow samples were used. The number of storm flow samples ranged between two and five among streams (Table S4). Moreover, we tested correlations between sumTU of legacy pesticides and sum TU of contemporary pesticides within base flow, storm flow and sediment samples. For water samples, the correlations were based on data for all benchmark organisms. All data used in the Pearson 261 correlation analyses were log-transformed to obtain normal distribution. The Spearman Rank262 correction analyses were conducted in JMP 11.1.1 for Windows.

263

We tested if the addition of legacy compounds significantly increased the sumTU of water and sediment samples in control and agricultural streams, respectively, by comparing the sumTU of contemporary pesticides to the sumTU of all pesticides using Mann-Whitney tests in JMP 11.1.1 for Windows.

268

269 RESULTS AND DISCUSSION

270 *Pesticide occurrence and toxicity patterns*

271 We found a significant positive relationship among pesticide concentrations in all combinations of sample types (P < 0.05) (Table 1, Fig. S3). The strongest correlations were obtained between 272 suspended sediment and bed sediment samples, between storm flow water and suspended sediment 273 and between storm flow water and bed sediment (Table 1). Thus, streams with high pesticide 274 concentrations in especially storm flow samples also had a high probability of having high pesticide 275 276 concentrations in sediments and to a lesser extent during base flow. Importantly, SumTU based on contemporary pesticides was additionally a strong indicator for SumTU based on legacy pesticides 277 in base flow samples (daphnia: r = 0.724, P < 0.001; fish: r = 0.578, P = 0.009; algae: r = 0.460, P = 0.009278 279 0.046), storm flow samples (daphnia: r = 0.603, P < 0.001; fish: 0.468, P < 0.001; algae: r = 0.359, P = 0.009), suspended sediment samples (chironomids: r = 0.563, P = 0.012) and sediment samples 280 (chironomids: r = 0.696, P < 0.001) (Fig. 1). This indicates that streams which are currently the 281 282 most impacted by contemporary pesticide pollution, have probably also been so in the past. This is perhaps not surprising as areas with productive conventional agriculture rarely are converted into 283 non-farming activities (Harding et al. 1998). 284

286 *Quantification of pesticide toxicity*

287	In 11 (\approx 17%), 12 (\approx 18%) and 35 (\approx 55%) of the storm water samples, pesticide concentrations
288	exceeded safety thresholds for daphnia (1/100 48h LC50), fish (1/100 96h LC50) and algae (1/10
289	96h EC50), respectively (Panel 2013) (Fig. 2, Table 2). Concentrations of legacy pesticides alone
290	exceeded the safety thresholds for daphnia and fish in six and three of the storm flow water
291	samples, respectively, while none of the samples contained legacy pesticide concentrations
292	exceeding the safety threshold for algae. Note however, that the average SumTU for daphnia, fish
293	and algae in agricultural streams all exceeded the respective safety thresholds (Table 2).
294	Importantly, and confirming the early findings of McKnight et al. (2015), the addition of
295	SumTU _{D.magna} based on legacy pesticides to the SumTU _{D.magna} based on contemporary pesticides
296	significantly increased the SumTU _{D.magna} in storm water samples from agricultural streams (Fig. 2B
297	P = 0.039). None of the base-flow water samples exceeded existing guideline values for
298	invertebrates, fish or algae (Fig. 2A, Table 2).

299

Sediment and suspended sediment samples contained pesticide concentrations exceeding safety thresholds in 10 of 20 samples from agricultural streams. In seven of these samples, legacy pesticide concentrations alone exceeded the safety threshold, and the addition of SumTU_{*C.riparius*} for legacy pesticides to the SumTU_{*C.riparius*} for contemporary pesticides significantly ($\alpha = 0.1$) increased the SumTU_{*C.riparius*} in suspended sediments (Fig. 3, P = 0.038) as well as in bed sediments (Fig. 3, P = 0.064). In fact, the average contribution of legacy pesticides to SumTU_{*C.riparius*} for bed sediments and suspended sediments was > 90%, and the average SumTU_{*C.riparius*} > 0.1 (Table 2).

308 Our results suggest that legacy pesticides can be highly significant contributors to the contemporary 309 toxic exposure of stream biota, especially macroinvertebrate communities, and that those 310 communities were primarily exposed to legacy pesticides via the sediment. However, Liess and von der Ohe (2005) and Schäfer et al. (2012) showed that stream dwelling macroinvertebrate 311 communities were significantly different in streams containing peak flow concentrations of 312 pesticides at 1/1000 48h LC50_{D.magna}, and this threshold was exceeded in approximately 50% of the 313 storm water samples in our study (30% for legacy pesticides alone) (data not shown). This clearly 314 315 suggests that the exposure of stream biota to dissolved phase legacy pesticides as well as legacy pesticides adsorbed to sediment particles are likely both important stressors in these streams. 316 Integrating past land use should therefore improve the prediction of pesticide impacts on 317 318 macroinvertebrate communities compared to the stringent focus on current use chemicals in the water and sediment phases (Harding et al. 1998). Highly important is the fact that our results, 319 supported by the findings of McKnight et al. (2015), strongly suggest that disregarding legacy 320 pesticides, in particular those adsorbed to sediment particles, in ecotoxicological field studies and 321 pesticide monitoring programs probably leads to significant underestimations of total risk and 322 323 significant underestimations of the relative importance of pesticides compared to other important anthropogenic stressors (Harding et al. 1998; Matson et al. 1997). However, we recognize that the 324 bioavailability of the highly lipophilic pesticides adsorbed to particles may decrease with increasing 325 326 age of the pesticide-particle complex (Xu et al. 2008). Hence the predicted sumTU for sedimentdwelling organisms may be overestimated when large proportions of the pesticide-particle 327 328 complexes have been long-established.

329

330 Predicting the toxicity of pesticide mixtures based on the assumption of toxic additivity

331 (Concentration Addition, CA), as done in the present study, may be problematic when the pesticides

in the sample have dissimilar Modes Of Action (MOA) (Belden et al. 2007; Cedergreen et al.
2013). However, CA appears to be a slightly conservative and broadly applicable model for
pesticide mixtures with similar, dissimilar and unknown MOAs and has a relatively small risk of
underestimating the effects (Backhaus and Faust 2012; Nowell et al. 2014). Moreover, the SumTU
approach has been shown to strongly correlate with an ecological indicator for pesticide pollution
(SPEAR) (Liess and von der Ohe 2005) and provides as strong a correlation to SPEAR as other
models that consider different MOAs of sample constituents, e.g. the msPAF (Schäfer et al. 2013).

339

340 *Potential sources of the legacy pesticides*

The majority of the legacy pesticides included in this study (e.g. organochlorines and triazines) have 341 342 the potential to persist for several decades in agricultural soils to which the compounds have been applied in the past (Aliyeva et al. 2013; Manz et al. 2001). In consequence, agricultural soils may 343 still be important sources providing continuous fluxes of legacy pesticides to freshwater ecosystems 344 (Barth et al. 2007; Gilliom 2007). The detection frequency of legacy pesticides was highest in base-345 flow water samples and sediment samples; although their concentrations increased 2 to 15 fold in 346 347 water during storm flow (Table 2). This could indicate that a dominant source of legacy pesticides was upper soil layers in the catchments, originating from past agricultural applications, where 348 surface runoff occurs (Manz et al. 2001). Re-suspension of contaminated sediment may have altered 349 350 the partitioning between particle bound and dissolved phases of pesticides and hence could be an additional important source governing the observed increase in legacy pesticide concentrations 351 352 during storm flow (Quesada et al. 2014). Additional sources of potential importance may include 353 atmospheric deposition (Weber et al. 2010), point sources such as waste dumps (Aliyeva et al. 2013), industrial use and commercial products (Connor et al. 2007), and illegal private use (see 354

McKnight et al. (2015) for a detailed description of potential sources of legacy pesticides instreams).

357

Since the dominant source of legacy pesticides is likely agricultural soils, we expect the flux of 358 legacy pesticides to streams to be relatively comparable between summer and winter, i.e. peaks 359 associated with storm events in winter would be less strong than peaks associated with the 360 additional application of contemporary pesticides in the summer. Data from the extensive Swedish 361 362 pesticide monitoring program documents that legacy pesticides are still found in stream water outside the primary crop growing season of Nordic countries (Nanos et al., 2012). Hence, in 363 contrast to contemporary pesticides, the toxic pressure of legacy pesticides in streams is likely 364 365 relatively constant across seasons, additionally indicating that the relative toxic contribution of legacy pesticides to the sumTU increases outside the primary crop growing seasons. 366

367

368 Identifying compounds of concern

Among the legacy pesticides, the organophosphate chlorpyrifos and organochlorines such as DDT 369 370 (and degradation products) and lindane were the strongest drivers of high SumTU for daphnia, fish and sediment dwelling invertebrates, whereas diuron and the triazine herbicides (terbutylazine and 371 simazine) were the strongest drivers of high SumTU for algae (Table S5). Chlorpyrifos is still 372 373 permitted for agricultural purposes in some EU countries but has been banned in Denmark since 2008. The remaining pesticides mentioned are forbidden for agricultural purposes in the EU (DDT 374 since 1979, lindane since 2001 (but 1994 in Denmark), simazine since 2005, diuron since 2008 and 375 376 terbutylazine since 2009).

378 Since the legacy pesticides significantly increased the sumTU_{D,magna} in storm flow water and sumTU_{C,riparius} in sediments we further evaluated the relative contribution of specific groups of 379 pesticides to sumTU_{D.magna} and sumTU_{C.riparius} in storm flow water and sediment samples, 380 respectively. The sumTU_{D.magna} in storm flow water was most strongly influenced by contemporary 381 pyrethroid insecticides (62.6%) and the legacy pesticide chlorpyrifos (15.3%) in agricultural 382 streams, whereas the sumTU_{D,magna} was most strongly influenced by legacy and contemporary 383 pyrethroid insecticides (26.3% and 24.3%, respectively) and chlorpyrifos (42%) in control streams 384 385 (Table 3). The SumTU_{C.riparius} of suspended sediment and bed sediment samples were almost entirely governed by chlorpyirfos in agricultural streams whereas the sumTU_{C riparius}, especially for 386 bed sediments, was more influenced by organochlorine insecticides in control streams (Table 3). 387 388 Since the half-life of chlorpyrifos in aquatic sediments is proposed to be 20-180 days (Mackay et al. 2014), which is comparable to the half-lives of pyrethroids, our findings could indicate that this 389 active ingredient is illegally used in Denmark. Alternatively, as pointed out by McKnight et al. 390 (2015), chlorpyrifos is well-known for its ability to undergo long-range transport and/or may still be 391 392 permitted for use in material protection products (e.g. as a biocide).

393

394 Conclusions

Risk assessment, the identification of pesticides of particular concern and the prioritization of
mitigation activities strongly rely on monitoring data from streams, and keeping up with the
increasing number of (emerging) active ingredients entering the market remains a serious challenge.
However, our results suggest that increasing attention should additionally be directed towards
legacy pesticides due to their predicted high impacts on the biota of especially agricultural streams.
Neglecting central legacy pesticides in stream monitoring programs may underestimate the
predicted toxicity of stream sediments by up to 90%. Future assessment schemes and management

402 strategies should seek to quantify the actual toxicity of sediments containing high concentrations of legacy pesticides, and moreover seek to benchmark ecological entities of streams against more 403 404 extensive pesticide screening programs, including legacy pesticides, in order to evaluate if the combined measurements of past and current use pesticides increase the explanatory power of 405 correlations between all types of pesticides and their ecological effects. Monitoring programs 406 407 should continuously re-address the status of legacy pesticides in freshwater systems to register developments in long term exposure profiles. To reduce costs, the frequency and concentration 408 409 might be related to land-use history which can then be used as a proxy for potential exposure risk. Our understanding of pesticide exposure in streams needs expansion and should progress towards 410 interpreting ecosystem responses in a temporal context where land use history is a key determinant 411 412 to when and where to sample.

413

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419

420 SUPPORTING INFORMATION

421 Figures providing a schematic overview of the study sites, correlations between pesticide

422 concentrations between sample types and relationships between compound-specific effect

423 concentrations for *D. magna* and *C. riparius*. Tables presenting legal status and analytical detection

424 limits for pesticides included in the field screening, stream and catchment characteristics,

425 supporting statistical information and an overview of compounds responsible for highest sumTU.

426 References

427	Aliyeva G, Halsall C, Alasgarova K, Avazova M, Ibrahimov Y, Aghayeva R (2013) The legacy of
428	persistent organic pollutants in Azerbaijan: an assessment of past use and current
429	contamination. Environmental Science and Pollution Research 20(4):1993-2008
430	doi:10.1007/s11356-012-1076-9
431	Backhaus T, Faust M (2012) Predictive Environmental Risk Assessment of Chemical Mixtures: A
432	Conceptual Framework. Environmental Science & Technology 46(5):2564-2573
433	doi:10.1021/es2034125
434	Barth JAC, Steidle D, Kuntz D, et al. (2007) Deposition, persistence and turnover of pollutants:
435	First results from the EU project AquaTerra for selected river basins and aquifers. Science
436	of the Total Environment 376(1-3):40-50 doi:10.1016/j.scitotenv.2007.01.065
437	Beketov M, Kefford BJ, Schafer RB, Liess M (2013) Pesticides reduce regional biodiversity of
438	stream invertebrates. Proceedings of the National Academy of Sciences of the United States
439	of America 110:11039–11043
440	Belden JB, Gilliom RJ, Martin JD, Ludy MJ (2007) Relative toxicity and occurrence patterns of
441	pesticide mixtures in streams draining agricultural watersheds dominated by corn and
442	soybean production. Integrated Environmental Assessment and Management 3:90-100
443	Bundschuh M, Goedkoop W, Kreuger J (2014) Evaluation of pesticide monitoring strategies in
444	agricultural streams based on the toxic-unit concept - Experiences from long-term
445	measurements. Science of the Total Environment 484:84-91
446	doi:10.1016/j.scitotenv.2014.03.015
447	Cedergreen N, Svendsen C, Backhaus T (2013) Chemical mixtures: Concepts for predicting
448	toxicity. In: Jørgensen SE (ed) Encyclopedia of Environmental Management. Taylor &
449	Francis, New York, p 2601-2610

450	Connor MS, Davis JA, Leatherbarrow J, et al. (2007) The slow recovery of San Francisco Bay from
451	the legacy of organochlorine pesticides. Environmental Research 105(1):87-100
452	doi:10.1016/j.envres.2006.07.001
453	Dai G-H, Liu X-H, Liang G, Gong W-W (2014) Evaluating the exchange of DDTs between
454	sediment and water in a major lake in North China. Environmental Science and Pollution
455	Research 21(6):4516-4526 doi:10.1007/s11356-013-2400-8
456	Ditoro DM, Zarba CS, Hansen DJ, et al. (1991) Technical basis for establishing sediment quality
457	criteria for nonionic organic-chemicals usig equilibrium partitioning. Environmental
458	Toxicology and Chemistry 10(12):1541-1583 doi:10.1897/1552-
459	8618(1991)10[1541:tbfesq]2.0.co;2
460	Gilliom RJ (2007) Pesticides in U.S. streams and groundwater. Environmental Science &
461	Technology 41(10):3408-14 doi:10.1021/es072531u
462	Harding JS, Benfield EF, Bolstad PV, Helfman GS, Jones EBD (1998) Stream biodiversity: The
463	ghost of land use past. Proceedings of the National Academy of Sciences of the United
464	States of America 95(25):14843-14847 doi:10.1073/pnas.95.25.14843
465	Jansson C, Kreuger J (2010) Multiresidue Analysis of 95 Pesticides at Low Nanogram/Liter Levels
466	in Surface Waters Using Online Preconcentration and High Performance Liquid
467	Chromatography/Tandem Mass Spectrometry. Journal of AOAC International 93(6):1732-
468	1747
469	Konstantinou IK, Hela DG, Albanis TA (2006) The status of pesticide pollution in surface waters
470	(rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environmental
471	Pollution 141(3):555-570 doi:10.1016/j.envpol.2005.07.024
472	Kreuger J, Tornqvist L (1998) Multiple regression analysis of pesticide occurrence in streamflow
473	related to pesticide properties and quantities applied. Chemosphere 37:189-207

474	Kronvang B, Laubel A, Larsen SE, Friberg N (2003) Pesticides and heavy metals in Danish
475	streambed sediment. Hydrobiologia 494:93-101
476	Kuivila KM, Hladik ML, Ingersoll CG, et al. (2012) Occurrence and Potential Sources of
477	Pyrethroid Insecticides in Stream Sediments from Seven U.S. Metropolitan Areas.
478	Environmental Science & Technology 46(8):4297-4303 doi:10.1021/es2044882
479	Laubel A, Kronvang B, Fjordback C (2001) Time-integrated suspended sediment sampling from a
480	small lowland stream. International Association for Theoretical and Applied Limnology
481	28:1420-1424
482	Leonard RA (1990) Movement of pesticides into surface waters. In: Cheng HH (ed) Pesticides in
483	the soil environment: Processes, impacts and modelling. Soil Science Society of America,
484	Maddison, WI, p 303-349
485	Li HZ, Sun BQ, Lydy MJ, You J (2013) Sediment-associated pesticides in an urban stream in
486	Guangzhou, China: Implications of a shift in pesticide use patterns. Environmental
487	Toxicology and Chemistry 32(5):1040-1047 doi:10.1002/etc.2147
488	Liess M, Schulz R, Liess MHD, Rother B, Kreuzig R (1999) Determination of insecticide
489	contamination in agricultural headwater streams. Water Research 33(1):239-247
490	Liess M, Schulz R, Neumann M (1996) A method for monitoring pesticides bound to suspended
491	particles in small streams. Chemosphere 32(10):1963-1969
492	Liess M, von der Ohe PC (2005) Analyzing effects of pesticides on invertebrate communities in
493	streams. Environmental Toxicology and Chemistry 24:954-965
494	Mackay D, Giesy JP, Solomon KR (2014) Fate in the Environment and Long-Range Atmospheric
495	Transport of the Organophosphorus Insecticide, Chlorpyrifos and Its Oxon. In: Giesy JP,
496	Solomon KR (eds) Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic

- 497 Systems in the United States. Reviews of Environmental Contamination and Toxicology,
- 498 vol 231. Springer Int Publishing Ag, Cham, p 35-76
- Malaj E, Von der Ohe PC, Grote M, et al. (2014) Organic chemicals jeopardize the health of
 freshwater ecosystems at the continental scale. Proceedings of the National Academy of
 Sciences of the United States of America 11:9549-9554
- Manz M, Wenzel KD, Dietze U, Schuurmann G (2001) Persistent organic pollutants in agricultural
 soils of central Germany. Science of the Total Environment 277(1-3):187-198
 doi:10.1016/s0048-9697(00)00877-9
- Matson PA, Parton WJ, Power AG, Swift MJ (1997) Agricultural intensification and ecosystem
 properties. Science 277(5325):504-509 doi:10.1126/science.277.5325.504
- McKnight US, Rasmussen JJ, Kronvang B, Binning PJ, Bjerg PL (2015) Sources, occurrence and
 predicted aquatic impact of legacy and contemporary pesticides in streams. Environmental
 Pollution 200:64-76
- Moschet C, Wittmer I, Simovic J, et al. (2014) How a Complete Pesticide Screening Changes the
 Assessment of Surface Water Quality. Environmental Science & Technology 48(10):5423 5432 doi:10.1021/es500371t
- Nanos T, Boye K, Kreuger J (2012) Results from the environmental monitoring of pesticides (In
 Swedish). Ekohydrologi 132. Swedish University of Agricultural Sciences, Uppsala. 80 pp.
- 515 Nowell LH, Moran PW, Gilliom RJ, et al. (2013) Contaminants in stream sediments from seven
- 516 United States metropolitan areas: Part I: Distribution in relation to urbanization. Archives of 517 Environmental Contamination and Toxicology 64(1):32-51 doi:10.1007/s00244-012-9813-0
- 518 Nowell LH, Norman JE, Moran PW, Martin JD, Stone WW (2014) Pesticide Toxicity Index-A tool
- 519 for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms.
- 520 Science of the Total Environment 476:144-157 doi:10.1016/j.scitotenv.2013.12.088

521	Panel EP (2013) Guidance on tiered risk assessment for plant protection products for aquatic
522	organisms in edge-of-field surface waters. EFSA Journal 2013, vol 11, p 268
523	Quesada S, Tena A, Guillen D, et al. (2014) Dynamics of suspended sediment borne persistent
524	organic pollutants in a large regulated Mediterranean river (Ebro, NE Spain). Science of the
525	Total Environment 473:381-390 doi:10.1016/j.scitotenv.2013.11.040
526	Rasmussen JJ, Wiberg-Larsen P, Baattrup-Pedersen A, Monberg RJ, Kronvang B (2012) Impacts of
527	pesticides and natural stressors on leaf litter decomposition in agricultural streams. Science
528	of the Total Environment 416:148-155 doi:10.1016/j.scitotenv.2011.11.057
529	Schulz R (2004) Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source
530	insecticide pollution: A review. Journal of Environmental Quality 33(2):419-448
531	Schwarzenbach RP, Westall J (1981) Transport of non-polar organic-compounds from surface-
532	water to groundwater - Laborartory sorption studies. Environmental Science & Technology
533	15(11):1360-1367 doi:10.1021/es00093a009
534	Schäfer RB, Gerner N, Kefford BJ, et al. (2013) How to characterize chemical exposure to predict
535	ecologic effects on aquatic communities? Environmental Science & Technology 47:7996-
536	8004 doi:dx.doi.org/10.1021/es4014954
537	Schäfer RB, Von der Ohe PC, Rasmussen JJ, et al. (2012) Thresholds for the effects of pesticides
538	on invertebrate communities and leaf breakdown in stream ecosystems. Environmental
539	Science & Technology 46:5134-5142
540	Wauchope RD (1978) Pesticide content of surface-water draining from agricultural fields - review.
541	Journal of Environmental Quality 7(4):459-472
542	Weber J, Halsall CJ, Muir D, et al. (2010) Endosulfan, a global pesticide: A review of its fate in the
543	environment and occurrence in the Arctic. Science of the Total Environment 408(15):2966-
544	2984 doi:10.1016/j.scitotenv.2009.10.077

545	Xu Y, Gan J, Wang Z, Spurlock F (2008) Effect of aging on desorption kinetics of sediment-
546	associated pyrethroids. Environmental Toxicology and Chemistry 27(6):1293-1301
547	doi:10.1897/07-382.1
548	Xu YP, Spurlock F, Wang ZJ, Gan J (2007) Comparison of five methods for measuring sediment
549	toxicity of hydrophobic contaminants. Environmental Science & Technology 41(24):8394-
550	8399 doi:10.1021/es071911c

Fig. 1. SumTU for legacy pesticides as a function of the SumTU for contemporary pesticides for
base flow water samples (A), storm flow water samples (B) and sediment samples (C). Sediment
was sampled with two methods representing the bed sediment and suspended sediment. The
diagonal lines indicate 1:1 relationships. For all water samples, the SumTU was calculated for algae
(*R. subcapitata*), fish (*O. mykiss*) and invertebrates (*D. magna*), whereas SumTU calculations for
sediment samples were based on *C. riparius*.

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Fig. 2. Average SumTU for base-flow water samples (A) and storm flow water samples (B).
SumTU is grouped according to stream category (control, n=9; agricultural, n=10) and according to
benchmark organisms (*D. magna*, *O. mykiss* and *R. subcapitata*). Asterisks indicate significant
differences in the pairwise tests at the 5% level (**). The boxplots display the median (bold line),
first and third quartiles (upper and lower end of box) and the 1.5-fold interquartile range (error
bars). Outliers are indicated with open circles.

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Fig. 3. Average SumTU_{*C.riparius*} for bed sediment and suspended sediment samples. SumTU is grouped according to stream category (control, n=9; agricultural, n=10). Asterisks significant differences at the 10% level (*) and 5% level (**). The boxplots display the median (bold line), first and third quartiles (upper and lower end of box) and the 1.5-fold interquartile range (error bars). Outliers are indicated with open circles.

- Table 1. Results from the Spearman Rank analyses comparing the summed pesticide concentrations
- 575 (ppm) between all sample types. The correlation coefficients (r, first line) and significance levels (P,
- 576 second line) are given.

	Base-flow water	Storm flow water	Suspended sediment	Bed sediment
Base flow water		0.658	0.523	0.694
Dase-now water		0.002	0.026	< 0.001
Storm flow water			0.794	0.782
Storm now water			< 0.001	< 0.001
Suspended sediment				0.984
Suspended sediment				< 0.001
Bed sediment				

- Table 2. Overview of central parameters for the pesticides monitored during base-flow and storm
- flow as well as in bed sediments (BS) and suspended sediments (SS). Parameter values are given \pm
- 580 SE for control streams (n=9) and agricultural streams (n=10).

Parameter	Control streams	Agricultural streams
Base-flow water samples		
Average # compounds (all)	3.1 ± 0.9	8.8 ± 1.6
Average # compounds (legacy)	2.1 ± 0.4	4.1 ± 0.9
Average sum conc. ($\mu g L^{-1}$) (all)	0.033 ± 0.014	0.192 ± 0.099
Average sum conc. ($\mu g L^{-1}$) (legacy)	0.003 ± 0.001	0.055 ± 0.045
Average SumTU _{D.magna} (all)	$6.8*10^{-6} \pm 3.9*10^{-6}$	0.0007 ± 0.0004
Average SumTU _{D.magna} (legacy)	$1.3*10^{-7} \pm 1.7*10^{-8}$	0.0006 ± 0.0003
Average SumTU _{O.mykiss} (all)	$1.7*10^{-5} \pm 8.7*10^{-6}$	0.0004 ± 0.0002
Average SumTU _{O.mykiss} (legacy)	$6.3*10^{-7} \pm 6.8*10^{-9}$	$0.0002 \pm 6.3^{*}10^{-5}$
Average SumTU _{P.subcapitata} (all)	0.006 ± 0.003	0.036 ± 0.008
Average SumTU _{P.subcapitata} (legacy)	0.0002 ± 0.00008	0.002 ± 0.002
Storm flow water samples		
Average # compounds (all)	77 + 09	213+14
Average # compounds (legacy)	3.5 ± 0.3	69 ± 0.5
Average sum conc. ($\mu g L^{-1}$) (all)	0.277 ± 0.088	1.845 ± 0.339
Average sum conc. ($\mu g L^{-1}$) (legacy)	0.277 ± 0.000 0.045 ± 0.015	0.129 ± 0.018
Average SumTU _b (all)	0.013 ± 0.013 0.002 ± 0.001	0.016 ± 0.007
Average SumTU _D (legacy)	0.002 ± 0.001 0.001 ± 0.001	0.003 ± 0.001
Average SumTU _{O multice} (all)	0.001 ± 0.001 0.004 ± 0.003	0.000 ± 0.001 0.011 ± 0.003
Average SumTU _{O mykiss} (legacy)	0.001 ± 0.001	0.001 ± 0.000
Average SumTU _{P subsanitate} (all)	0.101 ± 0.045	0.892 ± 0.292
Average SumTU _{P subcapitata} (legacy)	0.004 ± 0.002	0.012 ± 0.005
riverage Samri Or.subcaphala (logaey)	0.001 - 0.002	0.012 - 0.005
Sediment samples		
Average # compounds (BS, all)	1.3 ± 0.5	5.9 ± 1.2
Average # compounds (SS, all)	2.1 ± 0.5	6.9 ± 1.1
Average # compounds (BS, legacy)	0.9 ± 0.4	3.8 ± 0.9
Average # compounds (SS, legacy)	1.3 ± 0.4	4.2 ± 0.8
Average sum conc. ($\mu g k g^{-1} DW$) (BS, all)	6.0 ± 2.5	65.1 ± 14.2
Average sum conc. ($\mu g k g^{-1} DW$) (SS, all)	13.1 ± 3.6	167.6 ± 57.0
Average sum conc. (μ g kg ⁻¹ DW) (BS, legacy)	2.5 ± 1.1	22.7 ± 7.6
Average sum conc. (μ g kg ⁻¹ DW) (SS, legacy)	6.6 ± 2.8	48.4 ± 21.3
Average SumTU _{C.riparius} (BS, all)	0.0003 ± 0.0001	0.141 ± 0.083
Average SumTU _{C.riparius} (SS, all)	0.001 ± 0.001	0.117 ± 0.090
Average SumTU _{C.riparius} (BS, legacy)	$7.8^*10^{\text{-5}} \pm 2.6^*10^{\text{-5}}$	0.137 ± 0.082
Average SumTU _{C.riparius} (SS, legacy)	0.001 ± 0.001	0.108 ± 0.090

Table 3. Relative contribution of selected groups of pesticides to the sumTU based on *D. magna* for
storm flow water samples and *C. riparius* for sediment samples. The values are grouped according
to the stream category (control and agriculture). The median sumTU values for the respective
samples are given.

		Storm flow water		Suspended sediment		Bed sediment	
		Control	Control Agriculture (Control Agriculture		Agriculture
	median sumTU	< 0.001	0.004	< 0.001	0.011	< 0.001	0.014
	Herbicide	5.9	6.9	70.4	0.9	22.8	2.3
Contemporary	Fungicide	1.5	9.5	< 0.1	< 0.1	< 0.1	< 0.1
pesticides	Pyrethroid	24.3	62.6	< 0.1	1.5	8.7	5.2
	Other insecticide	< 0.1	0.9	< 0.1	< 0.1	< 0.1	< 0.1
	Herbicide	< 0.1	< 0.1	4.0	< 0.1	< 0.1	0.1
	Fungicide	< 0.1	< 0.1	25.6	< 0.1	1.1	< 0.1
Legacy	Organochlorine	NA	NA	< 0.1	0.2	67.4	0.8
pesticides	Organophosphate	42.0	15.4	< 0.1	97.4	< 0.1	91.6
	Pyrethroid	26.3	2.7	< 0.1	< 0.1	< 0.1	< 0.1
	Other insecticide	< 0.1	2.0	< 0.1	< 0.1	< 0.1	< 0.1