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Review

Review on the effects of toxicants on freshwater ecosystem functions

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ABSTRACT

We reviewed 122 peer-reviewed studies on the effects of organic toxicants and heavy metals on three fundamental ecosystem functions in freshwater ecosystems, i.e. leaf litter breakdown, primary production and community respiration. From each study meeting the inclusion criteria, the concentration resulting in a reduction of at least 20% in an ecosystem function was standardized based on median effect concentrations of standard test organisms (i.e. algae and daphnids). For pesticides, more than one third of observations indicated reductions in ecosystem functions at concentrations that are assumed being protective in regulation. Moreover, the reduction in leaf litter breakdown was more pronounced in the presence of invertebrate decomposers compared to studies where only microorganisms were involved in this function. High variability within and between studies hampered the derivation of a concentration–effect relationship. Hence, if ecosystem functions are to be included as protection goal in chemical risk assessment standardized methods are required.

1. Introduction

The Millennium Ecosystem Assessment identified anthropogenic toxicants as a major threat for freshwater ecosystems (MEA, 2005), with pesticides and heavy metals being considered as most relevant. Both enter aquatic ecosystems via various paths such as mine waste water, industrial discharge, drainage, spray drift or runoff (Sierra and Gomez, 2010; Niyogi et al., 2002; Arts et al., 2006; Gjessing et al., 1984) and may in turn affect aquatic communities (e.g. Beasley and Kneale, 2003; Clements et al., 2000; Schäfer et al., 2011a; Liess et al., 2008; Widenfalk et al., 2008). To protect aquatic ecosystems, the Uniform Principles (UP) of the European Union (EU) require for the first tier in the authorization of pesticides that the pesticide exposure should be lower than 1/100 and 1/10 of the median effect concentration (EC50) for *Daphnia magna* and *Pseudokirchneriella subcapitata* (EEC, 1991), respectively. This corresponds to a toxic unit (TU; Sprague, 1970) of 0.01 and 0.1, and reflects a safety factor of 100 or 10, respectively. While the suitability of extrapolating effects on ecological communities from standard test organisms has been questioned (Cairns, 1986; Rubach et al., 2010), in retrospective risk assessment data are often limited to these test organisms (Strempel et al., 2012) and they are consequently used to standardize the risks from different toxicants.

By applying the abovementioned safety factors, concentrations below these thresholds are assumed to cause no or no unacceptable adverse effects on macroinvertebrates and algae, respectively.

In this context, a review of mesocosm studies on several pyrethroid, organophosphate and carbamate insecticides reported that a TU of 0.01 for the most sensitive species, which was *D. magna* in most cases, did not cause notable effects in freshwater communities (Van Wijngaarden et al., 2005). By contrast, a meta-analysis of field studies on pesticide effects showed that TUs 10–100-fold below the UP lead to a significant reduction in the abundance of sensitive macroinvertebrate taxa (Schäfer et al., 2012b). As structural alterations can compromise ecosystem functioning (Doledec et al., 2006; Gücker et al., 2006), the observed decrease in sensitive taxa was hypothesized to be the cause of the reported reduction in invertebrate-mediated leaf litter breakdown (Schäfer et al., 2012b). Thus, the UP thresholds for structural endpoints may not be protective for ecosystem functions (cf. Woodward et al., 2012), though no reduction in primary production and community respiration was found for a pesticide gradient ranging from a $TU_{D.\ magna}$ of 0.1 to 0.001 in 24 South-East Australian streams (Schäfer et al., 2012a).

Overall, reductions in leaf litter breakdown and primary production are of particular concern because these functions represent the main energy sources for local and downstream freshwater food webs (Wallace et al., 1997; Webster, 2007). While microbial decomposers and invertebrate detritivores degrade and shred leaf

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material, respectively (i.e. leaf litter breakdown; Graca, 2001; Hieber and Gessner, 2002), algae and macrophytes are the main groups responsible for the conversion of sunlight into biomass via photosynthesis.

Recent reviews mainly focused on heavy metal (Fleeger et al., 2003) or pesticide (Brock et al., 2000b, a; Van Wijngaarden et al., 2005) effects on community structure whereas ecotoxicological effects on ecosystem functions in lotic and lentic ecosystems have been largely ignored – with two exceptions: while Brock et al. (2000a) exclusively discussed herbicide effects on ecosystem functions, the review of DeLorenzo et al. (2001) was restricted to effects of pesticides on microorganisms, only considering the functions of community respiration and net primary production. In the present study effects of toxicants on three fundamental ecosystem functions (i.e. leaf litter breakdown, primary production and community respiration) are considered. Thereby, we aimed at identifying effect thresholds based on the relationship between ecosystem functions and standardized concentration–effect relationships. In this context, the second aim was to examine whether effects of organic toxicants on functional endpoints occur below thresholds of the UP. Finally, given that macroinvertebrates belong to the most sensitive group of organisms with regard to organic toxicants (Schäfer et al., 2011b), we hypothesized that ecosystem functions involving invertebrates (e.g. leaf litter breakdown) are more sensitive than those that do not (e.g. primary production or microbial respiration).

2. Material and methods

2.1. Literature selection

The databases "Web of Knowledge" and "Pubmed" were searched for publications on the effects of toxicants on three ecosystem functions, i.e. leaf litter breakdown, primary production and community respiration. The search was limited to articles published between January 1980 and March 2012. The databases were queried by combining different terms for freshwater ecosystems (freshwater* OR stream* OR river* OR pond* OR lake*) supplemented by terms specifying the toxicants (chemical* OR contaminant* OR pollutant* OR toxicant* OR pesticide* OR heavy metal* OR metal* OR fungicide* OR herbicide* OR insecticide*) and ecosystem functions (ecosystem function* OR primary product* OR respiration* OR leaf litter breakdown OR decomposition*) of interest. Moreover, the reference lists of identified articles were inspected for further literature. Given that our review focuses on lotic and lentic freshwater systems, publications regarding the influence of toxicants on ecosystem functions in the marine system, marsh land, coastal waters or groundwater were excluded. Also, investigations on eutrophication (10-fold higher nutrient load than the control) and acidification (pH < 5) were omitted irrespective whether originating from human activities or natural processes because both conditions may lead to dramatic changes in the ecosystems (Jüttner et al., 2010; Ormerod and Durance, 2009) and would be indistinguishable from toxicant effects. Finally, in situations where multiple studies relied on the same raw data, only the study providing the most complete required information (chapter *Minimum effect size*) was considered. An overview of all reviewed and excluded studies is given in the Supplementary data (Tables S1, S2).

2.2. Minimum effect size

The identified studies were grouped regarding the investigated toxicant: (1) heavy metals, (2) organic toxicants, and (3) miscellaneous (i.e. sodium hypochloride, and a mixture of cadmium and phenanthrene). The latter group comprised only two studies and was thus not considered in further analyses. The group of organic toxicants was further subdivided into fungicides, insecticides, herbicides, pharmaceuticals, pesticide mixtures and others (i.e. phenolic compounds and polycyclic aromatic hydrocarbons; Table S1). To derive a suitable effect concentration (EC) (in μg/L), we first determined the relative mean standard deviation (RMSD) for reference sites/control treatments for studies on the most frequently assessed ecosystem function (leaf litter breakdown). This was calculated as approximately 12%. To discriminate true effects from noise in terms of RMSD while retaining sensitivity to detect effects, the effect size considered for this review was set to ≥20%, which did not result in a bias against studies with brief or episodic exposures (cf. Table S3). Therefore, the EC causing a reduction of ≥20% in an endpoint related to an ecosystem function was selected as basis for all further analyses. From each study only one effect on functional endpoints per observation was extracted, i.e. once the minimum effect size was reached or exceeded. For studies on leaf litter breakdown, the effect size referred to breakdown rates or mass loss as endpoints, whereas for (gross) primary production it referred to the amount of fixed carbon, as well as oxygen production. For community respiration the amount of carbon consumed or oxygen produced was used as endpoint. Studies only reporting dissolved oxygen (DO) were excluded, since net DO can originate from multiple sources, such as aquatic plants and the ambient atmosphere, simultaneously. Additionally, five studies reporting hormesis-like effects (Calabrese and Baldwin, 1998) were omitted, since our review focused on adverse effects and an increase in one endpoint does not necessarily indicate improved ecological health (Kefford et al., 2008) or may be an indirect effect of a non-measured adverse effect (Preston, 2002).

2.3. Explanatory variables

Beside TU and a dummy variable coding the group of toxicants (i.e. heavy metals, organic toxicants, miscellaneous), five additional variables (I–V) were included to explain the variability in the functional endpoints. First, each observation derived from an included study was categorized with respect to the (I) group of organisms that provides the according ecosystem function: (a) microbial decomposer community (i.e. bacteria and fungi), (b) decomposer–detritivore community (i.e. macroinvertebrates and microorganisms), and (c) aquatic plants (i.e. phytoplankton, macrophytes, etc.). We followed the definitions of communities as described in the original studies. Note that for leaf litter breakdown the communities are defined based on litter bag mesh size, which can differ between studies (Pye et al., 2012). Second, the observations were classified according to (II) ecosystem type – (a) lotic and (b) lentic – and to (III) study system: (a) field, (b) semi-field studies (i.e. mesocosm, artificial streams, etc.), and (c) laboratory (i.e. microcosm experiments). We note that except for field studies, rather community than ecosystem functions are measured. However, to enhance readability the term ecosystem function is used for all studies. Moreover, the (IV) exposure scenario, either (a) episodic or (b) chronic, was included as explanatory factor. Episodic exposure refers to single applications of toxicants in laboratory studies or individual run-off events in field studies. The included studies did not feature multiple exposure scenarios. Chronic exposure refers to relatively constant concentration of toxicants under laboratory or field (e.g. mine waste water) conditions (Table S1). Finally, the exposure time (V) was determined as continuous variable (in days), i.e. the period until the minimum effect size of 20% was reached or exceeded (Table S1).

2.4. Calculation of toxic units

Comparing the effects from different toxicants requires a benchmark. Ideally, this would be related to the ecosystem function under scrutiny, for example EC(x) values of the different toxicants for the ecosystem function that were produced under standard laboratory conditions. Since such data are not available, we reverted to ecotoxicological standard test organisms to compare the toxic effects from different stressors. This procedure was successfully employed in recent studies on ecotoxicological effects on ecosystem functions (Rasmussen et al., 2012; Schäfer et al., 2012b). We note that this only serves the purpose to establish a basis for comparison of different toxicants but is by no means intended to suggest that these organisms would play a crucial role in the respective function. *D. magna* was selected as standard test organism for ecosystem functions provided by invertebrates. *P. subcapitata* was selected for ecosystem functions performed by aquatic plants or microorganisms, because only very few EC50 values for e.g. fungi were available (cf. Rasmussen et al., 2012; Schäfer et al., 2011a). However, if the required information was not available for *P. subcapitata* (see below) other algae species (e.g. *Raphidocelis subcapitata*) were selected. This was the case for ten toxicants (Table S4).

The logarithmic sum of toxic units (logTU) was calculated as follows:

$$\mathrm{logTU} = \log\left(\sum_{i=1}^{n} \frac{c_i}{\mathrm{EC50}_i}\right)$$

where c represents the concentration (μg/L) of each toxicant i, $\mathrm{EC50}_i$ is the median effect concentration of the respective toxicant i from standard laboratory toxicity tests and n gives the number of toxicants that caused a ≥20% reduction in the respective ecosystem function. EC50 values were taken from the ECOTOX (USEPA, 2012), Pesticide Properties (FOOTPRINT, 2011) and/or Veterinary Substances (VSDB, 2011) databases (Table S4). An exposure time of 48 h was selected or the nearest exposure time for toxicants where no data for 48-h was available (Table S4). Furthermore, when more than one EC50-value was available the arithmetic mean was calculated. Since the first tier of the UP for pesticide authorization employ *D. magna* and algae as benchmark organisms, our TUs for pesticides are directly comparable to this regulatory threshold of 0.01 and 0.1, respectively (EEC, 1991). Moreover, we adopted the TU of 0.1 for microbial biota. A corresponding threshold does not exist for heavy metals, though environmental quality standards (EQS) have been established. These EQS consider important determinants of metal toxicity in a site such as the chemical speciation of metals, their bioavailability and the background concentration of metals (cf. Bass et al., 2008; EC, 2000). In addition, EQS integrate different protection goals and rely on toxicity data from different trophic levels, which further decreases their suitability as benchmark for the risks from different compounds regarding one endpoint. Hence, the results for metals are only described and not related to regulatory thresholds.

2.5. Data analysis

Data analysis was performed separately for each ecosystem function, with its percentage reduction as relative response variable and including the explanatory variables outlined in chapter *Explanatory variables*. These variables were log- or double square-root transformed in case of strong deviation from the normal distribution, which was evaluated based on visual inspection. Linear models were established for each ecosystem function. We conducted automatic stepwise model building, starting with the null model or a reduced model containing one variable expected to be relevant and defining the null model (no explanatory variable included) as lower and the full model (all explanatory variables included) as upper limit. The statistical procedure was backward and forward entering of variables with Bayesian Information Criterion (BIC) as stepwise model selection criterion (Schwarz, 1978). Model checking included homogeneity of variance as well as normal distribution of model residuals and identification of influential observations using residual-leverage plots and Cook's distances. Observations more than ± 2 standard deviations from the mean and/or a Cook's distance ≥ 0.5 were omitted and the model was refitted. All calculations and graphics were done in R 2.15.2 (R Development Core Team, 2012) and the R script is available in Supplementary data (Script.R).

3. Results and discussion

3.1. Overview on studies and observed effects

A total of 122 studies on the effects of toxicants on ecosystem functions in lotic and lentic systems were found. Out of these, 76 studies were not considered, as they did not meet our selection criteria, e.g. no effect size was extractable, effects were found under acidic or elevated nutrient conditions or no control treatment was available (Table S2). Therefore, this review focuses on 46 studies with a total of 75 observations. With 48 observations, the majority of studies were related to toxicant effects on leaf litter breakdown. Reductions in this ecosystem function may be attributed to a decline in feeding activity and/or mobility of macroinvertebrates, as suggested by Forrow and Maltby (2000) and Rasmussen et al. (2008). Although primary production is also an important energy source for freshwater ecosystems, studies on potential adverse effects of toxicants on this ecosystem function are rare (14 observations). The same holds for community respiration with 13 observations. The highest reduction in leaf litter breakdown (84%) and microbial community respiration (44%) was caused by heavy metal exposure originating from copper (Sridhar et al., 2001) and gold mining (Medeiros et al., 2008), respectively. An insecticide (bifenthrin) caused the highest reduction in primary production (75%; Hoagland et al., 1993). This effect may be explained by the high direct toxicity of this particular substance towards algae (Lal, 1984).

As mentioned above, *D. magna* was selected as standard test organism for invertebrate-related ecosystem functions and *P. subcapitata* was selected for ecosystem functions related to aquatic plants and microorganisms. The studies reporting effects for heavy metals spanned a logTU range of −3.6 to 4.6 (Fig. 1a), whereas organic toxicants showed effects at a logTU range of −5.2 to 2.3 (Fig. 1b). Since for both organic toxicants and heavy metals acute toxic effects on the most sensitive species can be approximated to occur up to 100-fold below effects on *D. magna* (Von der Ohe and Liess, 2004), which corresponds to a logTU of −2, we expected a similar effect ranges in invertebrate mediated ecosystem functions for both toxicant groups. For pesticides two observations described reductions in leaf litter breakdown (20% and 57%) below a logTU of −2 (i.e. −2.7 and −2.11, respectively). Similarly, one observation for heavy metals (64% at a logTU of −3.6) described effects below a logTU of −2. For community respiration, four observations showed effects of heavy metals (23%–29%) at logTUs of −3.3 to −2.7. Thus, despite metal toxicity in the field being strongly influenced by various factors such as bioavailability and speciation, metals can generally impact ecosystem functions at similarly low trace levels as organic toxicants.

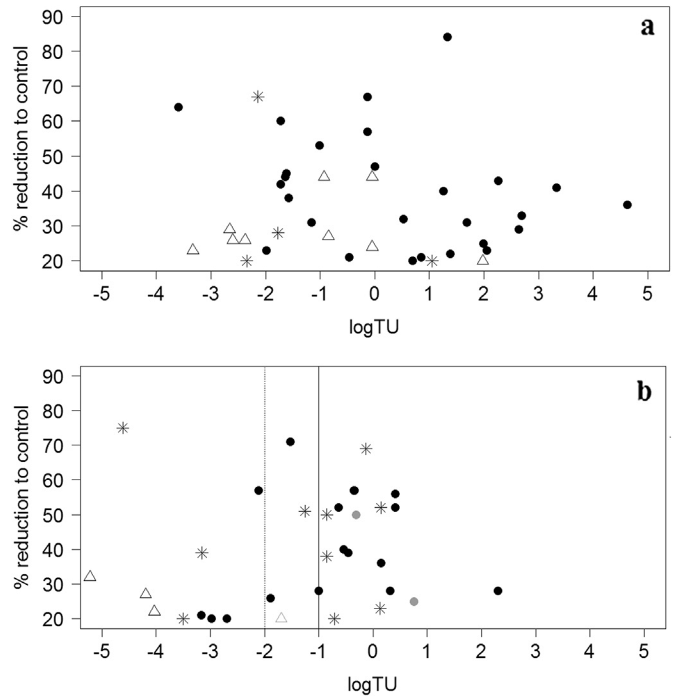

Fig. 1. a Reductions in leaf litter breakdown (filled dots), primary production (asterisk) and community respiration (triangle) in % relative to the control depending on the logTU (based on *D. magna* as standard test organism for invertebrate-related ecosystem functions and *P. subcapitata* for ecosystem functions related to aquatic plants and microorganisms) for heavy metals (40 observations). b Reductions in leaf litter breakdown (filled dots), primary production (asterisk) and community respiration (triangle) in % relative to the control depending on the logTU for organic toxicants (33 observations). The applied UP thresholds of 0.01 (dotted line) and 0.1 (solid line) refer to ecosystem functions provided by invertebrates and microorganisms or aquatic plants, respectively. Grey sampling points indicate organic substances that are no pesticides.

For pesticides, more than one third (12 observations) of 30 observations indicated reductions in one of the ecosystem functions at TUs below the UP thresholds. Of these, two observations indicated effects up to 5 times below the threshold of 0.01, and 10 indicated effects up to 17,000 times below the threshold of 0.1 (Fig. 1b). Our findings suggest that the three ecosystem functions considered can be adversely affected by pesticides at concentrations up to 1000-fold below TUs of 0.01 and 0.1 for *D. magna* and *P. subcapitata*, respectively. This is in agreement with a previous meta-analysis that reported effects on the macroinvertebrate community structure at a similar TU range (Schäfer et al., 2012b). However, since community data were not available for the majority of studies covered in the present review, we could not assess whether functional effects below the UP thresholds were associated with effects on structural endpoints. Hence, for pesticides it remains open, whether a protective threshold for structural endpoints would also be protective for functional endpoints. Otherwise, ecosystem functions should be considered in risk assessment.

3.2. Relationship between standardized concentrations and effects on ecosystem functions

No concentration–effect relationship could be derived for the three ecosystem functions because the TUs exhibited no explanatory power for the investigated endpoints (linear model for TU and respective ecosystem function: leaf litter breakdown: $r^2 = 0.04$, $p = 0.2$; community respiration: $r^2 < 0.01$, $p = 0.8$; primary production: $r^2 = 0.05$, $p = 0.44$). Consequently, it was not possible to establish a statistical model, which could serve the purpose to derive an effect threshold and subsequently to compare the sensitivity of ecosystem functions. Though effects below 20% were not considered, we expected an increasing effect with an increase in TU. With respect to organic toxicants, this general trend was indicated: Only 2 of 10 observations showed effects ≥50% for a TU < 0.01, whereas 11 of 23 observations showed effects ≥50% for a TU > 0.01 (Fig. 1b). No such tendencies were found for heavy metals (Fig. 1a). Two main reasons may explain these results: First, the TU approach used here may have been an unsuitable indicator of ecotoxicity hampering the establishment of a relationship with ecosystem functions. For example, the selected standard test organisms might not be an appropriate benchmark for ecosystem functions (chapter *Calculation of toxic units*). Second, two substances with the same EC50 may exhibit substantially different slopes with regard to their concentration–effect relationship. Hence, the same nominal TU for two substances may result in distinctly variable effects on organisms, which in turn increases the variation in the relationship between TU and the functional endpoints reviewed in the present study. However, the applied TU approach lead only to minor variation in previous studies e.g. (Liess et al., 2008; Rasmussen et al., 2012; Schäfer et al., 2012b) and two further studies found a strong relationship between TU and ecosystem functions for organic toxicants (Rasmussen et al., 2012; Schäfer et al., 2012b). Moreover, differences in the slopes of concentration–effect relationships should only lead to higher variability but not to biasing complex mixtures, since under- and overestimation would cancel out. We therefore argue that primarily the high variability in biotic and abiotic factors among studies hampered the derivation of a concentration–effect relationship.

With respect to biotic factors, differently composed communities provided the ecosystem functions in each of the studies considered in the present review. Beketov et al. (2008) have shown that such structural differences may influence the sensitivity to toxicants. Moreover, effects from the same exposure concentration on ecosystem functions may vary due to differences in the ability of communities to compensate for toxicant-induced species loss (Cadotte et al., 2011). Finally, the exposure times of the included studies ranged from 1.5 h to 385 days and given that the sampling was conducted episodically and not continuous, it is very likely that most studies did not measure the largest effect. In other studies partial recovery at the time of sampling may have lead to lower reported effect sizes.

Abiotic factors can also cause high variability in toxicant effects on ecosystem functions. Several studies demonstrated that differences in physicochemical parameters such as pH and temperature can strongly affect bioavailability of toxicants and subsequent effects (e.g. Kashian et al., 2004; Franklin et al., 2000; Fisher, 1991; Lydy et al., 1990). For example, Franklin et al. (2000) found a decline in copper toxicity to green algae with decreasing pH, while Fisher (1991) observed the opposite tendency for pentachlorophenol effects on midge larvae. Furthermore, Lydy et al. (1990) have shown increasing parathion toxicity for midge larvae with raising temperature. Finally, a recent study argued that the abiotic conditions may lead to 1–2 orders of magnitude differences in the sensitivity to toxicants (Liess and Beketov, 2011). Overall, we suggest that differences in the abiotic conditions, biological systems and experimental design among the reviewed studies impede the derivation of a joint concentration–effect relationship and do not allow for a systematic risk assessment.

3.3. Explained variability in ecosystem functions

The decomposer-detritivore community explained 21% of the variability in leaf litter breakdown among studies ($r^2 = 0.21$, $F = 12.23$, $p < 0.01$, BIC = 245.4). The effect was greater when invertebrate detritivores were involved (mean reduction of 58%) than when microorganisms decomposed the organic material alone (mean reduction of 44%). The more pronounced effect in invertebrate mediated leaf decomposition may be attributed to a decline in the functional ability of detritivores (Cadotte et al., 2011; Schäfer et al., 2012b), which play a dominant role in leaf litter breakdown (Peterson and Cummins, 1974; Iversen et al., 1982; Wallace et al., 1982). Detritivores have longer reproduction cycles than microorganisms, which increases the time until recovery. In addition, due to their faster reproduction microorganisms may have acquired a greater tolerance to toxicants (Blanck and Wangberg, 1988). Finally, microorganisms can be assumed to possess greater functional redundancy compared to detritivore communities (Cadotte et al., 2011).

The automatic model building for community respiration and primary production suggested only the inclusion of the type of ecosystem (lotic or lentic) in the final model (community respiration: $r^2 = 0.18$, $F = 2.47$, $p = 0.14$, BIC = 55.1; primary production: $r^2 = 0.18$, $F = 2.58$, $p = 0.13$, BIC = 85.4). For community respiration the effect was greater in lotic (mean = 38%) than in lentic (mean = 31%) study systems, whereas primary production showed the opposite tendency (lotic mean = 13%, lentic mean = 30%). Neither exposure time (community respiration: $n = 13$, $p = 0.23$; primary production: $n = 14$, $p = 0.73$) nor the logTU (community respiration: $n = 13$, $p = 0.38$; primary production: $n = 14$, $p = 0.62$) were significantly different between the ecosystem types for the respective functional endpoints and can therefore not explaining the differences. The results for community respiration are in agreement with a comparison of the sensitivity of organisms in lentic and lotic freshwater ecosystems in the United Kingdom, which indicated a higher sensitivity of lotic organisms (Biggs et al., 2007).

Nevertheless, the variable ecosystem type exhibited no statistical significance (community respiration: $p = 0.14$, primary production: $p = 0.13$) and the null model exhibited only negligibly higher BIC values (community respiration: null model BIC: 55.2 vs. final model BIC: 55.1, primary production: null model BIC: 85.5 vs. final model BIC: 85.4). Hence, these results should be interpreted with caution and may only represent a statistical artifact or be driven by experimental differences between the conditions in the lotic and lentic studies.

4. Conclusions

A safety factor of 100 or 10 of the EC50 for *D. magna* or *P. subcapitata*, respectively, may not be sufficient for pesticides to protect functional endpoints. Since neither estimated toxicity nor other experimental conditions explained variability in the ecosystem functions in our study, working towards method standardization is required if ecosystem functions are to be considered as protection goal in chemical risk assessment. However, it remains open whether protection of structure would also protect function and consequently whether consideration in risk assessment is required.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.05.025.

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