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Review

# Review on the effects of toxicants on freshwater ecosystem functions

K. Peters [a,*], M. Bundschuh [a,b,1], R.B. Schäfer [a,2]

[a] Quantitative Landscape Ecology, Institute for Environmental Science, University of Koblenz-Landau, Fortstraße 7, D-76829 Landau, Germany
[b] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Lennart Hjelms väg 9, 750 07 Uppsala, Sweden

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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

* Corresponding author.
*E-mail addresses:* peters@uni-landau.de (K. Peters), mirco.bundschuh@slu.se, bundschuh@uni-landau.de (M. Bundschuh), schaefer-ralf@uni-landau.de (R.B. Schäfer).
[1] Tel.: +46 72 516 97 68.
[2] Tel.: +49 6341 280 31536.

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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