A comparison of chemical, toxicological and ecological monitoring data and modelling tools for the assessment of sediment pollution

J. Wang[1], L.S. Lautz[1], T.M. Nolte[1], J. Chai[1], W. De Cooman[2], J. Postma[3], K.R. Koopman[1,4], L. Posthuma[1,4], J.P.M. Vink[5], R.S.E.W. Leuven[1,6], A.J.M. Ragas[1], R. van Zelm[1], A.J. Hendriks[1]

[1] Department of Environmental Science, Institute for Water and Wetland Research, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen NL. [2] Flanders Environment Agency (VMM), Dr. De Moorstraat 24-26, B-9300 Aalst, B. [3] Ecofide, Singel 105, 1381 AT Weesp, NL. [4] Centre for Sustainability, Environment and Health, National Institute for Public Health and the Environment (RIVM), P.O. Box 1, 3720 BA Bilthoven, NL. [5] Deltares, Unit Soil and Subsurface Systems, PO-box 85467, 3508 AL Utrecht, NL. [6] Department of Animal Ecology and Physiology, Institute for Water and Wetland Research, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen NL

Interreg
North Sea Region
Sullied Sediments
European Regional Development Fund

EUROPEAN UNION

Contents

Sullied Sediments

Sediment Assessment and Clean Up Pilots in Inland Waterways in the North Sea Region

Many of the inland waterways in Europe are under threat due to the introduction of Watch List chemicals that are not currently regulated under the European Water Framework Directive. These chemicals enter our waterways as a result of our day-to-day activities and through industry and agriculture, and many have been shown to be harmful to wildlife and the wider aquatic environment. Regardless of their source, these pollutants accumulate in the sediments in our rivers and canals over time.

Water regulators and managing authorities do not always know the levels, locations or impacts of these pollutants. Nor do they have the tools to assess sediments confidently and make informed environmental management decisions. To address these issues, the Sullied Sediment project partnership of scientific experts, regulators and water managers is developing and testing new tools that will enable stakeholders to better assess, treat and prevent contamination from these chemicals. This work is being carried out at selected sites in the Elbe, Humber and Scheldt river catchments.

The intention of the Sullied Sediments project is therefore to help regulators and water managers make better decisions with regard to the management, removal and disposal of sediments, thereby reducing economic costs to private and public sector organisations, and the impact of these pollutants on the environment.

The partnership is also working to reduce the extent of chemicals entering the water system by raising awareness about what we, as consumers, are releasing into the environment through the use of common drugs and household products. This includes the involvement of volunteers in a sediment sampling initiative across the North Sea Region, which will inform and empower them as water champions in their local communities.

The Sullied Sediments project has been co-funded by the European Regional Development Fund through the Interreg VB North Sea Region Programme with match funding from the 13 partners involved. The project partnership includes public, private, community and voluntary sector organisations based in the United Kingdom, Germany, Belgium and the Netherlands.

The project has been supported under the Interreg VB North Sea Region Programme’s third priority, which is focused on a Sustainable North Sea Region, and is led by the University of Hull (UK).

Website: northsearegion.eu/sullied-sediments
Blog: sulliedsediments.wordpress.com
Twitter:@SulliedSediment

Executive Summary/Abstract

Setting. The North Sea region is one of the most densely populated areas worldwide, encompassing catchments of several large rivers. Sediment pollution has become problematic for navigation, nature development and other interventions in this region. Over the years, risks have been assessed in different ways. Well-standardised chemical detection techniques allow comparison across systems. By contrast, toxicological assays are not routinely applied, involve region-specific testing procedures and include a few species only. Ecological surveys differ even more across regions and over time. Data from chemical, toxicological and ecological monitoring often contradict each other, displaying large effects at low concentrations and vice versa. Usually, water management is recommended to combine all monitoring techniques and assess pollution using a weight of evidence approach. Suggestions to subject discrepancies by an in-depth experimental investigation are rarely followed because of financial, time and other constraints. Alternatively, to facilitate interpretation of monitoring and additional analyses, modelling may be employed, the more so as modelling also allows one to estimate improvements following prevention or remediation. In the present study we used the framework of the OMEGA model and some elements of the SIMPLEBOX model. **Objectives**. Consequently, we **aimed to compare and interpret chemical, toxicological and ecological monitoring** across countries, authorities and systems based on frequently used modelling tools linking chemical concentrations to biological effects.

Single-species. Monitoring data were obtained from programmes carried out in Flanders and the Netherlands. Based on different approaches, we converted total sediment concentrations to pore water levels. We subsequently translated water concentrations to effects using a database on effect concentrations of 12836 chemicals. The total effect of all substances for a tested species was calculated and compared to measured survival in lab assays. Depending on the region and species, **40-90% of the toxicity could be attributed to the chemical substances identified**. The variability in observed effects decreased substantially by fitting chromium, tin, ammonia and phosphate availability and toxicity to field data.

Multi-species. We also computed the potentially affected fraction of species expected from the measured concentrations. No correlation to macrofauna abundance in field surveys could be established. Yet, **low diversity was observed in the field if the fraction of potentially affected species was small**. While relationships between chemical and ecological monitoring have been firmly established for the water phase, sediments will require a more in-depth analysis in future.

Ecosystem services. As functioning of ecosystems is equally important as their structure, we also explored ways to extrapolate measured concentrations to ecological productivity and ecosystem services. While benefits that humans receive from nature have become crucial indicators for impact of anthropogenic pressures (e.g., in the global Millenium Assessment), impact of chemical pollution on ecosystem services has, so far, not been assessed. We showed, for the first time, how **financial benefits for humans from improving ecosystems by reducing chemical concentrations can be calculated**. While our relationships have not extensively been underpinned empirically, expressing benefits of emission prevention and sediment remediation in financial terms is likely to increase management priorities for chemical problems.

Recommendations. To **cost-effectively reduce emissions and remediate polluted sediments**, one needs to know the substances and sites that contribute most to the effects. Based on the present study, we therefore recommend to:

1. **Increase the number of chemical substances analysed in monitoring programs**.
In particular, **chromium**, **organotin**, **phosphates** and **ammonium** might be included. Additional physical-chemical characteristics of sediments not measured in current programmes but demonstrated to be important in transfer functions might decrease discrepancies between chemical and toxicological monitoring as well.

2. **Identify problematic substances and sites using the simple models of the present study**.

The model for widely applied indicators of toxicity (TU, PAF) as developed and used here provide a simple tool of the overall impact

3. Cautiously **extrapolate concentrations of chemicals** to **ecosystem services**, empirically underpinning the steps outlined.

4. **Assess** water and sediment quality by implementing our tools in monitoring databases in water management.

Management. To facilitate implementation of these recommendations by water management, the website

https://www.ru.nl/environmentalscience/research/themes-0/human-environmental-risk-assessment-hera/models/

provides all underlying data, (beta-versions of) models used, scientific papers, links to related activities (e.g., on water rather than sediment) and videos, so far used in various projects. Specific information on the application in Sullied Sediment is available at

https://www.ru.nl/environmentalscience/research/themes-0/human-environmental-risk-assessment-hera/models/societal-applications-us/sullied-sediments/

We have organised and participated in workshops involving different stakeholders and assist in application and implementation by end-users.

Research. The above-mentioned suggestions for research will be addressed in programmes for the SIMPLEBOX/TREAT and OMEGA models linking chemical emissions to ecological and health effects (See same websites).

1. Introduction

Pollution assessment. With human population density increasing exponentially with proximity to water, river areas are home to billions of people (Small and Cohen, 2004). One of the most densely populated areas worldwide is the **North Sea** region, encompassing catchments of several large rivers including the Rhine, Elbe, Scheldt and Humber. These river basins receive increasing amounts of agricultural, industrial and household **chemicals** that are ultimately deposited in sediments, posing threats to plants, animals and humans. Over the years, various tools have been developed to assess and manage pollution. So far, most efforts were directed to the **water** compartment. Modelling and monitoring of **sediments** have received less attention due to lower visibility and higher complexity. Despite decades of projects, sediment assessment still differs substantially across countries, regions, authorities and systems.

Chemical, toxicological and ecological monitoring. Traditionally, water and sediment quality has been monitored separately based on **chemical** analysis of approximately 100-200 substances (Hendriks and Van De Guchte, 1997). Improved detection techniques and well-standardised protocols allow comparisons across systems, but mixture assessments lack. By contrast, **toxicological** assays address the whole mixture risks but are not routinely applied, involving region-specific testing procedures and including only a few species. **Ecological** surveys differ even more across regions and over time but would cover impacts of both mixtures as well as other stressors. Simultaneous application of these three monitoring techniques to sediment pollution, known as the TRIAD approach, has been proposed to ‘harvest’ the advantages while in combination solving the limitations of each method (Chapman, 1990, Van de Guchte, 1992).

Chemical modelling. Similar differences apply to models. Decades of development have yielded **fate** models for **specific geographic areas** and **chemical substances** that are well-established in science and well-embedded in management (Laane et al., 2011). If time, resources or data do not allow for detailed calculations, **overall estimations** can be obtained by multimedia fate models. In the EU and UN, **SIMPLEBOX/TREAT** is the preferred fate model for risk assessment of substances and life cycle analysis of products (Schoorl et al., 2015). SIMPLEBOX/TREAT was conceived at the National Institute for Public Health and the Environment (RIVM) and further developed at Radboud University (RU). The model is especially useful in relating emissions to concentrations. Some relationships (e.g. partitioning) may also be applied stand-alone to calculate concentrations in (pore-)water from total sediment levels. Yet, sediment organisms take in pollutants mainly in the dissolved phase, potentially varying by more than an order of magnitude due to changes in physicochemical conditions (Vink and Hendriks, 1999).

Ecotoxicological modelling. While many ecotoxicological models have been developed for specific cases, few have been applied across (groups of) chemical substances, biological species and geographic regions (Hendriks and Van Straalen, 2019). So far, none of these ecotoxicological models has been embedded in international frameworks to the same extent as SIMPLEBOX/TREAT for chemical fate. As an alternative, the **OMEGA** model was developed, providing management with a tool to assess the accumulation of substances and subsequent impacts on populations and communities. Based on water or sediment concentrations entered by a user, OMEGA calculates concentrations in organisms along the food chain and abundances of populations and communities (Knoben et al., 1998, Hendriks et al., 2001, Hendriks et al., 2005). OMEGA has been developed in BSc-, MSc- and PhD-projects for governmental and industrial stakeholders, covering inhalatory, aqueous and dietary exposure of aquatic and terrestrial species to organic and inorganic substances in temperate and polar regions (Models - Environmental Science (ru.nl)). In **science**, reliability and plausibility of OMEGA were confirmed by benchmarks (Traas et al., 2004, Stadnicka et al., 2012, Ardestani et al., 2014) and widespread dissemination and application were demonstrated by 5000^{+} citations to papers describing the model and data. In **society**, OMEGA was implemented in Dutch legislation on sediment and soil pollution as part of the risk toolbox (VROM, 2007, Hin et al., 2010, Knoben and Snijders, 2010). Consecutive versions 1.0 to 7.0 were made available to managers and consultants (Durand-Huiting, 2001, Durand-Huiting, 2004). Over the years, (parts of) OMEGA have been applied for management and research purposes by third parties in the Netherlands and abroad of which 20^{+} projects could be traced in a quick scan (Models - Environmental Science (ru.nl)). Recently, specific tools with similar options have been developed for surface water (Posthuma and de Zwart, 2012, Posthuma L et al., 2016a, Posthuma L et al., 2016b, Posthuma et al., 2016, Verschoor et al., 2017, Posthuma et al., 2019b)).

Ecosystem service modelling. Ecosystem services (ESs) are ‘the benefits that people can obtain from ecosystems’ (Millennium Ecosystem Assessment, 2005)**.** As a connecting medium, sediments provide a variety of valuable ESs within aquatic systems (e.g. habitat provision, nutrient recycling and flood protection) (Apitz, 2012). Vice versa, contaminated sediments have the potential to pose ecological and human health risks. Therefore, strategies for evaluating chemical risks in waterways should consider effects on ESs regarding the sustainability of ecological, socio-cultural and economic objectives (Backhaus et al., 2012). Expression of ESs in **monetary units** has become an essential tool in the context of sustainable ecosystem management (Costanza et al., 2014). However, most valuations applied a book-keeping and pragmatic approach based on applicability to each specific ES and data availability (Brouwer et al., 2013). Yet, this is unfeasible for countless pressures and ecosystems. Consequently, quantification has been limited to a small number of ESs, calculated for a few regions only. The impacts of sediment pollution on a broad range of ESs have not been assessed.

Gaps. Monitoring and modelling of chemical, toxicological and ecological indicators is needed to identify both the cause and significance of sediment pollution. However, major knowledge gaps exist in terms of methods used and results obtained (Chapman, 1989). Chemical, toxicological and ecological **monitoring data** from the same location and period often **contradict** each other due to the **limited number of sites, substances, physical-chemical conditions, species, and endpoints covered** (Reinhold-Dudok and den Besten, 1999, Oguma and Klerks, 2020). To **understand** such contradictions and, more importantly, to **predict** changes, various chemical, toxicological and ecological **models** have been developed. However, existing models (e.g. SIMPLEBOX, OMEGA) assume standard partitioning, while exposure may vary substantially depending on the different forms that chemicals exist in (Vink, 2009). Overall, relations among sediment physicochemical properties, bioassays and macrofauna are scarce, and quantitative predictions based thereon remain elusive. Additionally, the **ecological and economic impacts** of sediment pollution on the entire aquatic system have not been quantified. In terms of **environmental management,** although the ultimate goal is to protect species (assemblages) from substance (mixture) exposure in the field, practice often focuses only on comparisons between chemical measurement and environmental quality standards (EQSs).

Objectives. Following these gaps, the present study aimed to **improve relationships** between chemical, toxicological and ecological indicators of pollution, interpreting monitoring by modelling across regions and authorities. Our comparison allows water managers to underpin and improve (tools for) assessing, preventing and remediating sediment pollution. Ultimately, the goal is to reduce the ecological impacts of chemicals as well as of the economic costs to private and public sector organisations. To this end, we improved, in particular:

1. **Data collection**. Inconsistency between chemical, toxicological and ecological monitoring data has been attributed to the small number of sites covered per study. Hence, we collected **all data available** on sediment pollution in the Netherlands and Flanders. Unfortunately, data on similar monitoring programs were unavailable (United Kingdom) or confidential (Germany) for the other countries.

2. **Data treatment**. **New state-of-the-art statistical techniques** were to derive correlations, potentially not found before.

3. **Chemical modelling**. To improve estimations of concentrations in (pore-)water, we compared **standard correction** of sediment with calculations by **transfer functions** reported in the literature as well as with **speciation equations** derived by ourselves.

4. **Ecotoxicological modelling**. Based on the concentrations of all substances in water, we estimated the reduction of **single-species** survival, reproduction or growth and we compared these to independent measurements of **population** effects in **lab experiments**. Based on the same concentrations in water, we also assessed **multi-species community** impact by calculating the **potentially affected fraction** (PAF) of species for both single and multi-substance exposures (yielding multi-substance PAF (msPAF) as metric). PAF, calculated from species sensitivity distributions (SSDs), is the standard endpoint for ecological impact in the registration of chemicals, derivation of

water-sediment quality standard and assessment of sites. Compared to previous assessments, we **substantially increased the number of substances** covered by using a recently developed SSD database for 12836 chemicals (Posthuma et al., 2019b), improving estimations of the **relative and cumulative impact** of all pollutants. As a common statistic in risk assessment, the ecological relevance of PAF has been demonstrated by comparisons with community impact indicators (De Vries et al., 2010, Posthuma and de Zwart, 2012, Hoeks et al., 2020). We linked our msPAF values to **field observations** of macrofauna. Additionally, msPAF variability was associated with **ecosystem services**, increasingly used in water management to evaluate interventions but so far have not been used for sediment remediation.

Contents. In this report, we will describe the overall project (Sullied Sediment Activity 8, 9 and 10) at a level relevant to a broader audience of managers, policymakers, citizens and other stakeholders involved in sediment pollution. Details of the underlying studies relevant to scientists are available as peer-reviewed articles published in journals to warrant quality assurance and academic embedding.

2. Methods

2.1 Sampling

Data on the Waal-Meuse estuary in the Netherlands were taken from the TRIAD monitoring program of Rijkswaterstaat (RWS, https://www.rijkswaterstaat.nl/), carried out from 1992 to 1999. Seven regions were included for field sampling (i.e. Haringvliet (1995), Hollandsch Diep (1993), Nieuwe Merwede (1992), Dordtsche Biesbosch (1993), Brabantsche Biesbosch (1994), Amer (1998), Sliedrechtse Biesbosch (1999)). In each region, sediment was sampled at several sites (Postma and den Besten, 2001).

Data on Flanders were taken from the TRIAD assessment of the Flemish Environment Agency (VVM, www.vmm.be) (De Deckere et al., 2000). In total, 438 sites were sampled (Figure 1). Each location was sampled approximately every four years in spring (March-June) using a Van Veen grab sampler.

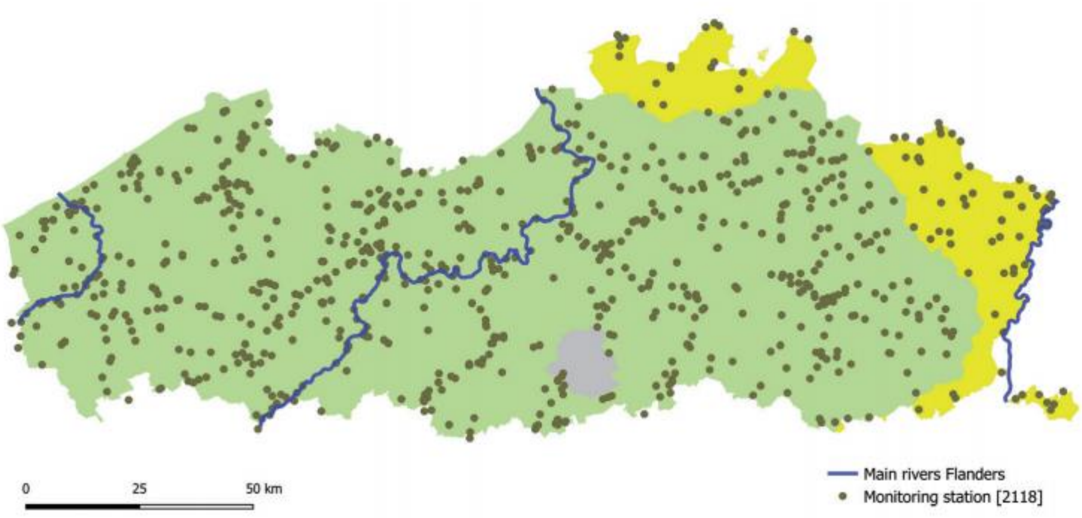


Figure 1. VMM monitoring locations in Flanders with the Yser, Scheldt and Meuse Rivers (taken from Vannevel et al. (2018)). Yellow is the catchment area district Meuse. Green is the catchment area district Scheldt. Blue is region of Brussels. Dots represent sampling locations ("Monitoring stations").

2.2 Chemical analysis

Chemical analysis in the Netherlands was performed as described by Den Besten et al. (1995). 48 chemical compounds were analysed including 8 metals, 16 polycyclic aromatic hydrocarbons (PAHs), 13 persistent organochlorine pesticides (OCPs), 7 polychlorinated biphenyls (PCBs), 2 chlorobenzenes, mineral oil and extractable organic halogenated hydrocarbons (EOX) (Table 1).

Chemical analysis in Flanders was performed as described by De Deckere et al. (2000). Compared to the Dutch dataset, a few PAHs were not measured (Table 1). Yet, other physicochemical sediment characteristics were measured including pH, organic matter (OM), clay (including grain sizes) and chalk content, tin (Sn_{total}), nitrogen (KjN and N_{total}), phosphorous (P_{total}) and concentrations of 43 chemicals (Table 1).

Table 1. List of chemicals measured in the Netherlands and Belgium.

Chemical	Abbreviation	NL	B	Chemical	Abbreviation	NL	B
cadmium	Cd	x	x	pyrene	Pyr	x	x
mercury	Hg	x	x	DDD	DDD	x	x
copper	Cu	x	x	DDE	DDE	x	x
nickel	Ni	x	x	DDT	DDT	x	x
lead	Pb	x	x	dieldrin	Dieldrin	x	x
zinc	Zn	x	x	endrin	Endrin	x	x
chromium	Cr	x	x	aldrin	Aldrin	x	x
arsenic	As	x	x	telodrin	Telodrin	x	x
tin[a]	Sn		x	alpha-endosulfan	Endosulfan I	x	x
acenaphthene	Ace	x		α-hexachlorocyclohexane	α -HCH	x	x
acenaphthylene	Acy	x		β-hexachlorocyclohexane	β-HCH	x	x
anthracene	Ant	x		lindane	Lindane	x	x
benzo(a)pyrene	B(a)P	x	x	hexachlorobutadiene	HCBD	x	x
benzo(b)fluoranthene	B(b)F	x	x	heptachlor	Heptachlor	x	x
benzo(a)anthracene	B(a)A	x	x	Hexachlorobenzene	HCB	x	x
benzo(ghi)perylene	B(ghi)P	x	x	Pentachlorobenzene	PeCBz	x	x
benzo(k)fluoranthene	B(k)F	x	x	PCB28	PCB28	x	x
chrysene	Chr	x	x	PCB52	PCB52	x	x
dibenzo(a,h)anthracene	Db(a,h)A	x	x	PCB101	PCB101	x	x
phenanthrene	Phen	x	x	PCB118	PCB118	x	x
fluoranthene	Flah	x	x	PCB138	PCB138	x	x
fluorene	Flu	x	x	PCB153	PCB153	x	x
indeno(1,2,3-c,d)pyrene	InP	x		PCB180	PCB180	x	x
naphthalene	Naph	x	x	EOX	EOX	x	x
Oil	Oil	x	x				

[a] Tin was reported as total Sn and included different organotins (DBySn, DFySn, MBySn, MFySn, TbySn, TfySn and TtBySn).

2.3 Toxicological assays

In the Netherlands, sediment pore water was tested with *Daphnia magna* (water flea) (Table 2). Bioassays with *D. magna* (21d) were carried out according to standard methods by counting mortality and reproduction in pore water at concentrations of 1%, 3%, 10%, 32%, 56% and 100% (v/v) (Maas et al., 1993, Den Besten et al., 1995). The no observed effect concentration (NOEC) for mortality was set at the highest concentration of pore water with a mortality of ≤20%. The NOEC for reproduction was defined as the highest concentration of pore water in which the intrinsic rate of population increase did not significantly deviate from the control.

In Flanders, sediment pore-water was tested with *Raphidocelis subcapitata* (algae) following OECD-guideline No. 201 (OECD, 1984). The whole sediment was examined with *Hyalella azteca* (shrimp) and *Heterocypris incongruens* (ostracod) based on ASTM standard E1706-95b (ASTM, 1997) and ISO guideline 14371 (ISO 14371, 2012), respectively. The endpoint per species is shown in Table 2.

Table 2. List of bioassays and abbreviations.

Species	Endpoints	Abbreviation
Daphnia magna	$NOEC_{mortality}$	*D.magna* I
	$NOEC_{reproduction}$	*D.magna* II
Raphidocelis subcapitata	Mortality	*R. subcapitata*
Hyalella Azteca	Mortality	*H. azteca*
Heterocypris incongruens	Growth inhibition	*H. incongruens*

NOEC = No Observed Effect Concentration.

2.4 Ecological surveys

In both the Netherlands and Flanders, three samples were taken and reported as an average per measured location. Fauna samples were preserved with 40% formaldehyde. Macrofauna was identified to species of lowest attainable taxonomic level (Table 3). Density was expressed as the number of species per m^2.

Table 3. Determination of the different taxonomic groups included in macrofauna measurements.

Taxonomic group	Determination level
Plathelminthes	Genus
Oligochaetae	Presence
Hirudinea	Genus
Mollusca	Genus
Crustacea	Family
Plecoptera	Genus
Ephemeroptera	Genus
Trichoptera	Family
Odonata	Genus
Megaloptera	Genus
Hemiptera	Genus
Coleoptera	Family
Diptera	Family
Hydracarina	Presence

2.5 Statistical analysis

Chemical concentrations were log-transformed prior to the analysis. For the Dutch dataset, concentrations below the detection limit were marked as zero. A concentration of 0.00001 was used to replace 0 before log transformation, which is two orders of magnitude lower than the lowest observed chemical concentration.

Pearson **correlation coefficients** were calculated to determine linear relationships between the log-transformed concentrations of each pair of the total chemicals. A coefficient ($|r|$) exceeding 0.8 was defined as indicative for 'high' correlation between two variables. Only the correlation coefficients with significant levels of $P<0.05$ (slightly significant) are presented. All analyses were performed in R (version 3.4.2) and Microsoft Excel statistical packages.

Canonical redundancy analysis (RDA) was used to investigate the relationship between species abundances and chemical concentrations. Species with abundance lower than 4 individuals per m^2 were omitted from the subsequent analysis. Species abundance data were log(x+1) transformed to reduce the asymmetry of the species distribution, followed by the Hellinger-transformation to reduce the importance of extremely abundant taxa (Birks et al., 2012). Chemicals may covary due to co-emission from sources. Therefore, chemicals with the highest variance inflation factor (VIF) were removed from the analysis one at a time until all VIFs <20. The contribution to the explanation to the variation in species composition in RDA was evaluated by Monte Carlo permutation tests. Chemicals with low significance were removed.

2.6 Chemical modelling

We applied the OMEGA model to independently estimate responses in toxicological assays and ecological surveys from measured chemical levels. To that end, total sediment concentrations were converted to dissolved water concentrations according to standard correction, refined bioavailability and speciation equations and transfer functions, respectively.

2.6.1 Standard correction

Equilibrium partitioning was applied to convert chemical concentrations in sediments ($[C]_{\mathrm{sed}}$, mg/kg) into water concentrations ($[C]_{\mathrm{aq}}$, µg/L) (Van der Kooij et al., 1991):

$$[C]_{\mathrm{aq}} = \frac{r \times [C]_{\mathrm{sed}}}{K_{\mathrm{SW}}} \tag{1}$$

Where r is an empirical concentration ratio for suspended matter (taken as 2 and 1.5 for organics and metals, respectively) and K_{SW} is the solid-water partition coefficient in L/g.

While K_{sw} values show a variability depending on physicochemical factors (Van der Kooij et al., 1991), only the average binding capacity of metals to sediments was taken into account in standard correction. We obtained values of K_{SW} for metals from Van der Kooij et al. (1991) assuming to represent the standard 11% and 25% clay (Flanders and Netherlands, respectively) and 5% and 10% organic substances (Flanders and Netherlands, respectively) in sediments (Crommentuijn et al., 1997, De Deckere et al., 2000):

$$K_{\mathrm{SW,metal}} = \frac{\sum_1^n K_{\mathrm{SW,metal},n}}{n} \tag{2}$$

Where n is the sampling locations in the predefined ecosystems/rivers from Van der Kooij et al. (1991). Similar equations are used elsewhere (Batley et al. 2005).

Considering the high diversity in hydrophobicity for polycyclic aromatic hydrocarbons (PAHs) included in the measurement campaigns ($10^3 < K_{\mathrm{OW}} < 10^7$), $K_{\mathrm{SW,organic}}$ for organic chemicals was calculated via the octanol-water partition coefficients (K_{OW}, dimensionless) obtained from PubChem and literature (Mackay et al., 2006, Kim et al., 2016) and the fraction of organic substances (f_{OS}, dimensionless):

$$K_{\mathrm{SW,organic}} = 0.6 \cdot K_{\mathrm{OW}} \cdot f_{\mathrm{OS}} \tag{3}$$

Where 0.6 is the empirical conversion factor in L/g (Karickhoff et al., 1979).

2.6.2 Refined bioavailability and speciation

Despite increased sediment, all interactions of chemicals within the sediments cannot explicitly be described (Verschoor et al., 2017). Acknowledging this, we used a limited set of key sediment characteristics regularly monitored to determine chemical speciation and bioavailability. As a case study, we applied data from a standard monitoring program on Flemish sediments to test our predictions of mortality of *H. azteca* and growth inhibition of *H. incongruens*.

Refined bioavailability. Toxicity associates to the fraction of the chemical that is freely bioavailable. Metals bind stronger to sediment fractions (clays, organic substances) with high binding/retention capacity (Crommentuijn, 1997, Zhang et al., 2014), creating a natural 'bias' in local concentration. Therefore, we calculated local K_{SW} ($K_{\mathrm{SW,\,local}}$) values based on %clay and %OS content (de Bruijn and Denneman, 1992):

$$\log(K_{SW,local}) = \log(K_{SW}) - \left[a \cdot \log\left(\frac{5}{\%OS}\right) + b \cdot \log\left(\frac{11}{\%clay}\right)\right] \tag{4}$$

wherein we obtained K_{SW} from literature (Van der Kooij et al., 1991). a and b are the concentrations (mg/kg dry solids) of metals M per %clay and %OS, respectively, based on (log-log) multiple linear regression (MLR) for the complete Flanders dataset (N=1762):

$$\log([\mathrm{C}]_{sed}) = a \cdot \log(\%\mathrm{OS}) + b \cdot \log(\%\mathrm{clay}) \tag{5}$$

Speciation of chromium. Prominently, chromium (Cr) is a transition metal with redox behaviour higher than that of Zn, Ni or Cd (Panda, 2005, Haddad, 2012). Cr toxicity relates to the concentration of CrO_4^{2-} (Berry et al., 2004, Besser et al., 2004). Speciation and the redox conditions of Cr are affected by the microbial NO_3/NH_4^+ equilibrium (Wang and Choi, 2013): $[CrO_4^{2-}]$ positively correlates with $[NO_3^-]$ and negatively with pH (Rosales et al., 2017) and partially results from the following two reactions:

$$4[O_2] + 2[NH_4^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[NO_3^-] + 2[H_2O] + 4[H^+] \tag{6}$$

$$4[H^+] + 3[O_2] + [Cr^{3+}]_{sed}^{\downarrow} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2[H_2O] + \left[{CrO_4}^{2-}\right]_{\uparrow}^{aq} \tag{7}$$

Wherein relative concentrations of ammonia/ammonium in the whole-sediment were determined via the Kjeldahl nitrogen and Henderson-Hasselbalch relationships (subsequent section).

Prominently, $[CrO_4^{2-}]$ inhibits reaction k_{-1} (denitrification) (Viamajala et al., 2002, Chovanec et al., 2012, Hu et al., 2019) and affecting the phosphate/phosphorous (P) and the oxygen concentration $[O_2]$ (e.g. eutrophication (VLM, 2019)). These factors are indicators of the relative concentration of CrO_4^{2-}:

$$\left[{CrO_4}^{2-}\right]_{aq} \propto \frac{1}{[Cr^{3+}]_{aq}} = f([O_2],[NH_4^+],[P_T],pH) \tag{8}$$

As $K_{SW}(Cr^{3+})$ >>> $K_{SW}(CrO_4^{2-})$ (Van der Kooij et al., 1991), the total concentration in sediment $[Cr_T]_{sed}$ is dictated by $[Cr^{3+}]$ (i.e. $[Cr_T]_{sed} = \left[Cr^{3+}\right]_{sed} + \left[CrO_4^{2-}\right]_{sed} \approx (1+K_{SW}) \cdot \left[Cr^{3+}\right]_{aq}$). Therefore, based on the available data and Equation 6-7, we characterized the ratio between CrO_4^{2-} and Cr^{3+} via regression:

$$\frac{[{CrO_4}^{2-}]_{aq}}{[Cr^{3+}]_{aq}} \propto \frac{[{CrO_4}^{2-}]_{aq}}{[Cr_T]_{sed}} \propto \frac{1}{a[O_2] + b[NH_4^+] + c[P_T] + d\left[{HPO_4}^{2-}/H_2{PO_4}^{-}\right] + e[pH]} \tag{9}$$

Wherein we take $[CrO_4^{2-}]_{sed}$ on average to be 4.13% of total Cr (Rosales et al., 2017) and a-e are regression coefficients. Since K_{SW} of Cr^{VI} (<1-50 L kg^{-1}) <<< Cr^{III} (850-5,600 L kg^{-1}) (Hassan and Garrison, 1996), is about 90% of aqueous Cr present as CrO_4^{2-}.

Speciation of organotins, phosphate and ammonia (Henderson-Hasselbalch). Phosphate may act both as toxicant (Yu et al., 2009) and nutrient (Karanovic, 2012), whereas organotins and ammonium are toxicants. The fraction of non-ionized ammonium often relates to observed toxicity. The species (de)protonate according to:

$$[NH_4^+]_{aq} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [NH_3]_{aq} + H^+ \tag{10}$$

$$[H_2{PO_4}^{-}]_{aq} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \left[{HPO_4}^{2-}\right]_{aq} + H^+ \tag{11}$$

$$\left[Sn(OH)_{3-n}OH_2{R_n}^{+}\right]_{aq} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Sn(OH)_{4-n}R_n]_{aq} + H^+$$

(12)

We thus determine their speciation via Henderson-Hasselbalch (Ankley et al., 1995):

$$\log\left(\frac{[X^n]_{aq}}{[XH^{n+1}]_{aq}}\right) = pH - pK_{a,XH^{n+1}} \tag{13}$$

$$\log([XH^{n+1}]_{aq}) = \log([X^n]_{aq}) - (pH - pK_{a,CX}) \tag{14}$$

with $pK_a(XH^{n+1}=NH_4^+) = 9.25$ and $pK_a(XH^{n+1}=H_2PO_4^-) = 7.2$. We took p*K*a values for organotins from the literature (Table 4).

Table 4. Proton dissociation constants (pKa) values. By = butyl; Ph = phenyl.

Chemical	Formula	p*K*a	Reference
tetrabutyltinhydroxide	$Sn(By)_4$	n/a	n/a
tributyltinhydroxide cation	$(Sn(OH_2))^+(By)_3$	6.25	(Blunden, 1984, Fent, 1996, Meador, 2000)
dibutyltinhydroxide cation	$(Sn(OH_2)_1)^+(OH)_1(By)_2$	5.1(±0.2)	(Fang et al., 2012)
monobutyltinhydroxide cation	$(Sn(OH_2)_1)^{1+}(OH)_2(By)_1$	5.9(±0.1)	(Fang et al., 2012)
triphenyltinhydroxide cation	$Sn(OH_2)^+(Ph)_3$	5.2	(Blunden, 1984, Fent, 1996, Meador, 2000, Beyer, 2011)
diphenyltinhydroxide cation	$(Sn(OH_2)_1)^+(OH)_1(Ph)_2$	4.0	(Mohamed et al., 2001)*
monophenyltinhydroxide cation	$(Sn(OH_2)_1)^{1+}(OH)_2(Ph)_1$	4.8	**
dihydrogenphosphate	$H_2PO_4^-$	7.2	n/a
ammonia	NH_4^+	9.25	n/a

* In 75% dioxane–water solution. pK_a values of ligands in 75% dioxane–water solutions are higher than those reported in water (Mohamed et al., 2001).

** Estimation assuming the substitution of butyl by phenyl has a constant effect on pK_a: $pKa_{MPT} = pKa_{MBT}-((pKa_{TBT}-pKa_{TPT})+(pKa_{DBT}-pKa_{DPT})/2)$.

2.6.3 WHAM transfer functions

In an attempt for a further detailed speciation, transfer functions of the Windermere Humic Aqueous Model (WHAM) were applied. These functions characterise the free ion concentration in surface water based on *in situ* calcium and carbonate concentrations (Bootsma and Vink, 2016) (Table 5).

Table 5. Equations for free ion activities, anions included.

Metal	Model description	R^2
log(Cd_ion)	= -0.00085563 + 1.0822 * log(Cd_total) - 0.21108 * log(DOC) + 0.056259 * log(Ca) - 0.081587 * pH - 0.019479 * DOC	0.985
log(Cu_ion)	= -1.3158 + 1.8086 * log(Cu_total) - 2.0549 * log(DOC) + 0.38043 * log(Ca) - 0.34905 * pH - 3.7836e-06 * CO3	0.991
log(Hg_ion)	= -1.2681 + 8.4744 * log(Hg_total) - 2.9851 * log(DOC) - 1.952 * pH	0.998
log(Ni_ion)	= 0.29167 + 1.075 * log(Ni_total) + 0.14183 * log(Ca) - 0.19815 * pH - 0.010255 * DOC - 1.7256e-06 * CO3	0.966
log(Pb_ion)	= -0.55052 + 1.1825 * log(Pb_total) - 0.98928 * log(DOC) + 0.53735 * log(Ca) - 0.46855 * pH - 1.4685e-06 * CO3	0.967
log(Zn_ion)	= -0.22876 + 1.0963 * log(Zn_total) - 0.050781 * log(DOC) + 0.12606 * log(Ca) - 0.11606 * pH - 0.012963 * DOC - 9.2237e-07 * CO3	0.983
log(Cr_ion)	= -0.928 + 2.18 * log(Cr_total) – 2.32 * log(DOC) + log(Ca) – 1.29 * pH	1.000

All variables are in ug/L except DOC (mg/L). Cd=cadmium; Cu=copper; Hg=mercury; Ni=nickel; Pb=lead; Zn=zinc; Cr=chromium. %chalk content was used to estimate the total calcium content.

2.7 Toxicological modelling

In the present study, the toxic unit (TU) and multi-substance potentially affected fraction of species at the HC50 level (msPAF(HC50)) were used to estimate the mixture toxic pressure to single species and the whole aquatic community (ranging from algae to fish), respectively. Both methods are based on the chemical concentration in sediment pore water (i.e. $[C]_{aq}$).

2.7.1 Toxic unit

Toxic unit of a chemical (TU, dimensionless) is defined as the ratio of the water concentration $[C]_{aq}$ to its toxicity (effect concentration (EC50), lethal concentration (LC50)) (Sprague, 1970). TUs were calculated based on available EC50 data on *D. magna* and *H. incongruens* and LC50 data on *H. azteca*. The EC50 and LC50 values were derived from the RIVM e-toxbase (Posthuma et al., 2019b) and the U.S. Environmental Protection Agency ECOTOX database (U.S. EPA, 2019). The LC50s of some PAHs, OCPs and PCBs were not available and were estimated from quantitative structure activity relationships (QSAR) (Lee et al., 2001). The total risk of the polluted sediment was assessed by summing the toxic units for all contaminants based on chemical groups:

$$TU = \sum_{i=1}^{n} \frac{[C]_{aq,i}}{\gamma_i \times E(L)C50_{aq,i}} \tag{15}$$

wherein *n* reflects the number of pollutants *i*, taken as PCBs, PAHs, OCPs, heavy metals and NH_3/NH_4^+. γ is the calibration factor (γ=1 for standard correction).

Assuming a logistic distribution of species sensitivity towards the polluted sediment, the fraction effect *P* was estimated via the cumulative logistic distribution function (de Zwart and Posthuma, 2005):

$$P = \frac{100}{1 + e^{-\left[\frac{\log TU}{\beta}\right]}} \tag{16}$$

Wherein β is slope of the exposure-response curve as a fitting constant.

2.7.2 Multi-substance potentially affected fraction

The toxic pressure exerted by chemical mixtures to aquatic communities is expressed as multi-substance PAF at the HC50 level (msPAF(HC50), %), representing the fraction of field species likely affected (de Zwart and Posthuma, 2005). The msPAF(HC50) was calculated based on estimated concentrations of pollutants in water and SSDs constructed from the laboratory-based toxicity data. Species sensitivity parameters for each chemical included the hazardous concentration at which 50% of the aquatic community is affected (HC50, µg/L) for population-level relevant effect criterion (e.g. reproduction, growth, development) and the respective SSD slope (β, dimensionless). Species sensitivity parameters were collected from the RIVM e-toxbase (Posthuma et al., 2019b) (Table A1 in Appendices). The toxic pressure was first calculated within each chemical group *j* (i.e. eight individual metal, PAHs, polychlorinated biphenyls (PCBs) and persistent organochlorine pesticides (OCPs)), assuming concentration additivity as an approximation of mixture impacts (de Zwart and Posthuma, 2005):

$$msPAF_j = \frac{1}{1 + \ e^{-\log\left(\sum \frac{[C]_{aq,i}}{HC50_{aq,i}}\right)/\overline{\beta_J}}} \tag{17}$$

Where $[C]_{aq,i}$ is the water concentration and $HC50_{aq,i}$ is the hazardous concentration for the chemical *i* in the same chemical group. $\overline{\beta_j}$ is the average SSD slope of the chemical group *j*.

The response addition method was then applied to predict the mixture toxicity across the groups of chemicals (de Zwart and Posthuma, 2005):

$$msPAF(HC50) = 1 - \prod_{j=1}^{11}(1 - msPAF_j) \tag{18}$$

2.8 Ecosystem service modelling

To assess the impacts of sediment pollution of waterways on ESs, we developed a approach consisting of five steps from (1) to (5) (Figure 2). We first converted sediment concentrations into water concentrations according to standard correction (Section 2.6.1). We subsequently calculated the multi-substance PAF for the whole aquatic community (msPAF(HC50), Section 2.7.2). We then linked msPAF(HC50) to diversity based on previous studies (Section 2.8.1). The association between diversity and total ES values (i.e. in monetary units) was based on literature review and data analysis, using productivity as a proxy for ESs (Section 2.8.2 and 2.8.3). We applied the quantitative relationships between msPAF(HC50) and total ES values to the Waal-Meuse estuary and Flemish waterways to gain insights into impact magnitudes (Section 2.8.4).

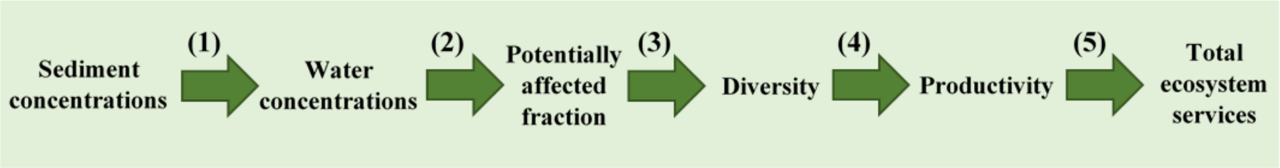


Figure 2. Steps to assess the environmental impact of chemical mixtures in sediments on ecosystem services (ESs) of waterways. Step (1): Convert sediment concentrations into water concentrations. Step (2): Calculate the multi-substance potentially affected fraction msPAF(HC50) of aquatic species based on water concentrations. Step (3): Link msPAF(HC50) to diversity. Step (4): Identify the quantitative diversity-productivity relationship. Step (5): Update the correlation between productivity and the total value of ESs.

2.8.1 Relationship between msPAF(HC50) and diversity

Empirical research has shown the ecological relevance of PAF as the value of diversity indicators (e.g. Shannon-Wiener index) reduces when the PAF(HC50) increases (De Vries et al., 2010). Based on the evidence, we assumed that an increase in the msPAF(HC50) would result in a reduction in diversity (*D'*, %) expressed in various metrics, including species richness, species evenness and functional diversity:

$$D' = 100 - msPAF(HC50) \tag{19}$$

2.8.2 Relationship between diversity and productivity

Productivity is related to many ESs, such as food or wood provisioning (Millennium Ecosystem Assessment, 2005). Experimental studies at multiple scales employed aboveground plant biomass (i.e. productivity) in diversity-ecosystem functioning research (Costanza et al., 2007). Productivity has also been correlated with the total value of ESs (Costanza et al., 1998). To explore the full cause-effect chain shown in Figure 2, we used productivity as a proxy for ESs.

Dataset description. We applied filtered and updated versions of datasets published in several meta-analyses (i.e. Cardinale et al. (2006), Balvanera et al. (2006), Daam et al. (2019), Duffy et al. (2017)) reporting experimental and observational evidence in both terrestrial and aquatic realms. Given our focus on quantifying the effect of diversity on productivity, we selected studies from each published dataset that met three criteria: (i) the study used diversity measurements (e.g. species richness) as an independent variable; (ii) the study statistically controlled for the influence of variation in climate or resources; (iii) the study measured the direct effect of diversity within a trophic group (mostly producers and herbivores) on community biomass or productivity of all species. We removed the overlapping records reported in different datasets. To update the dataset, we conducted a literature search on Google Scholar using the keyword sequence: (diversity OR biodiversity) AND ecosystem AND (productivity OR biomass). To be included in the updated dataset, studies had to meet the same criteria described. Our database included a total of 75 studies, 51 of which were conducted in experimental settings (32 in terrestrial and 19 in aquatic ecosystems) and 24 in observational settings (17 in terrestrial and 7 in aquatic ecosystems) (Table A2, A3 and A4 in Appendices).

Data analysis. We characterised the relationship between diversity and productivity by the effect direction (i.e. positive or 0) and function form (e.g. Michaelis-Menten, log-linear, linear functions) (Figure A1 in Appendices). In order to allow for comparison and facilitate interpretation of the quantitative diversity-productivity relationships, we performed data scaling and curve fitting for experimental studies in terrestrial ecosystems. We chose experimental terrestrial studies since most diversity-productivity research focused on terrestrial systems in the past decades (Loreau et al., 2001, Wardle, 2016, Daam et al., 2019), and quantitative patterns in aquatic (freshwater, transitional and marine) and terrestrial ecosystems were similar (Figure A1 in Appendices). Only studies that explicitly reported the mathematical function between diversity and productivity were included in the analysis.

Data scaling. We scaled the reported diversity-productivity relationships into a 0-100% range without affecting the shape of curves through a linear transformation. We calculated the minimum (P_{min}) and the maximum values (P_{max}) of productivity (e.g. aboveground biomass in g/m^2) from the minimum (D_{min}) and the maximum values (D_{max}) of diversity measurements (e.g. species richness) according to the reported mathematical functions. The values of productivity and diversity P and D were scaled to P' and D' in the range of 0-100% according to:

$$P' = (P - P_{min}) / (P_{max} - P_{min}) \times 100 \tag{20.1}$$

and

$$D' = (D - D_{min}) / (D_{max} - D_{min}) \times 100 \tag{20.2}$$

Curve fitting. The average, minimum and maximum impacts (the upper and lower boundary encompassing all the reported diversity-productivity curves) of diversity loss on productivity were identified through optical fitting. The decreasing power function ($P' = D'^{\theta}$, $\theta < 1$), Michaelis-Menten and linear functions represented the average, minimum and maximum impacts, respectively.

2.8.3 Relationship between productivity and ecosystem services

While productivity has been related to the total value of ESs in monetary units (Costanza et al., 1998), estimates of productivity and total ES values for each biome have changed over the years due to environmental changes (e.g. climate change, El Niño events) and improved estimation methods. Therefore, we provided an updated linear correlation between logarithmically transformed values of mean productivity (P, kg/m^2/yr) and mean total ES values (V, 2007\$/ha/yr) (Costanza et al., 2007):

$$\log_{10}(V) = a + b \times \log_{10}(P) \tag{21}$$

Wherein a and b are empirical fitting constants (Costanza et al., 2007).

Dataset description. The fitting constants *a* and *b* were determined based on literature data. Papers that reported the total ES value for each biome (i.e. the sum of the mean value of each ES within the biome) were included (Costanza et al. (1997), De Groot et al. (2012), Costanza et al. (2014)). A total of 12 biomes and 17 ESs were included (Table A5 in Appendices). To update the quantitative correlation between *P* and *V*, we chose to use the most recent available data from Costanza et al. (2014) and calculated the geometric mean of productivities for each biome (Table A6 in Appendices).

2.8.4 Application of derived relationships

Based on the stepwise approach described above (Figure 2), the relative ES value loss as a function of msPAF(HC50) was estimated. In order to obtain an absolute value of ES loss, we considered the sediments in the Waal-Meuse estuary and Flanders as estuarine/freshwater sediments (Den Besten et al., 2003, De Deckere et al., 2011). Therefore, we calculated the geometric mean of ESs provided by lakes/rivers, estuaries and swamps/floodplains reported in Costanza et al. (2014) to represent the sediment ecosystems in the present study.

3. Results

3.1 Correlations

The Netherlands. Figure 3 shows the correlation coefficients between each pair of the 48 measured chemicals. Concentrations were strongly correlated for the substances that belong to the same chemical groups (i.e. metals, PAHs, and PCBs). The only negative correlation is found between lindane and EOX with a correlation coefficient value around -0.2.

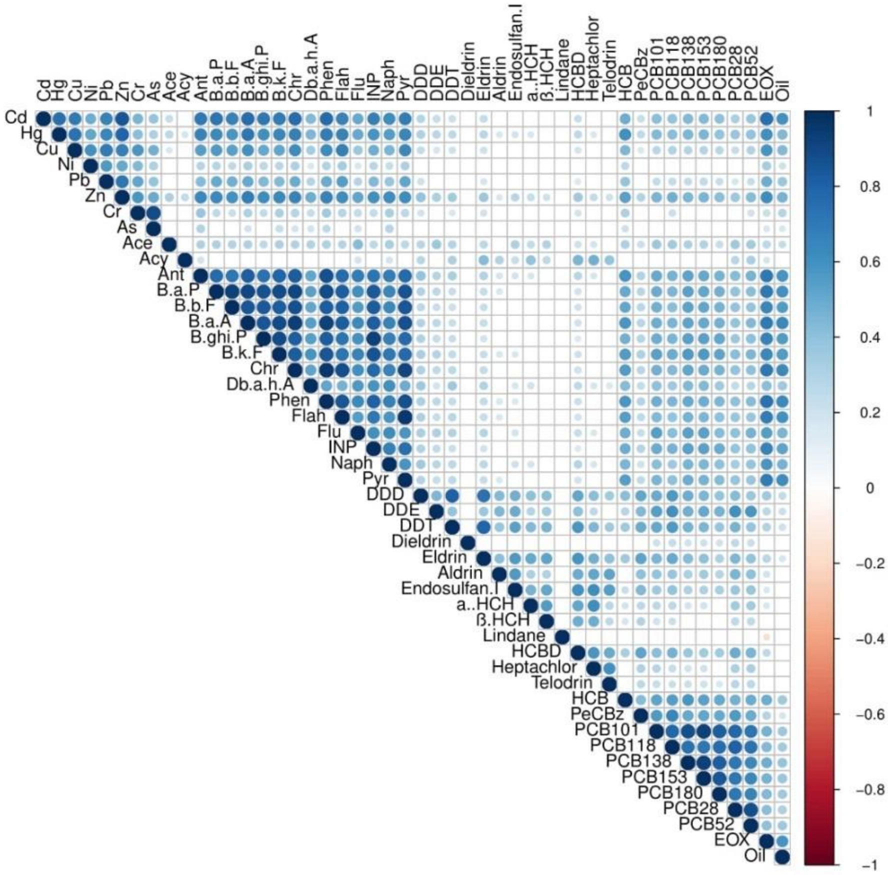


Figure 3. Correlation coefficients for 48 chemicals measured in Dutch sediments. Positive and negative correlation are by blue and red, respectively. A dark colour (|r|> 0.8) indicates high correlations between two variables. Only the correlation coefficients with significant levels below 0.05 are presented. Abbreviations of chemicals are given in Table 1.

Flanders. Figure 4 shows the correlation coefficients between each two of the 24 chemicals, three bioassays and sediment characteristics (percentage clay, organic matter). Chemicals which belong to the same groups, i.e. metals, PAHs, showed a high positive correlation. PAHs and PCBs were also highly correlated to chrome, copper and lead.

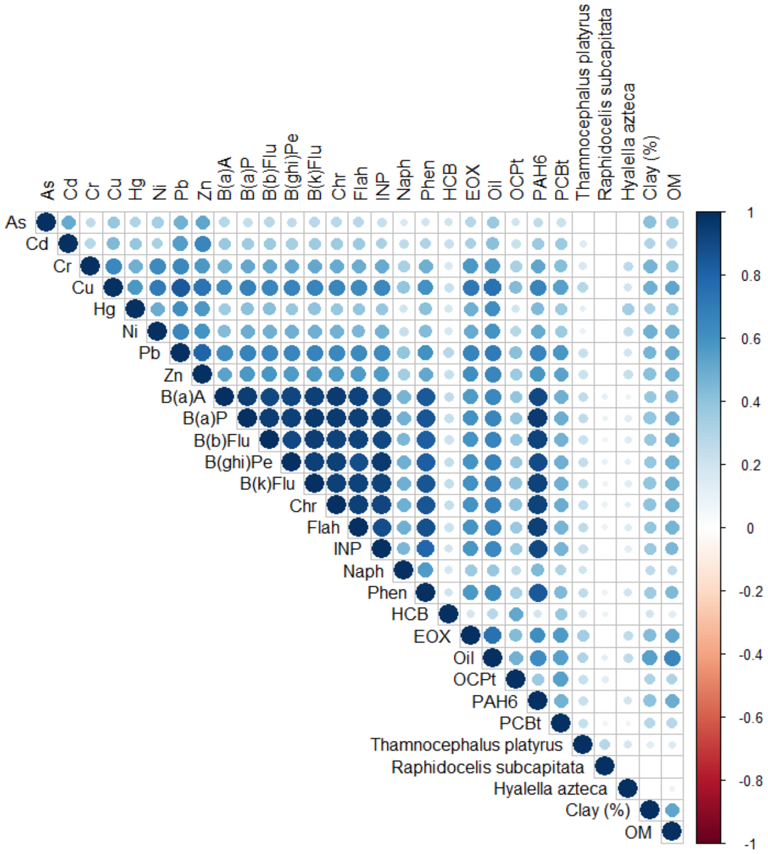


Figure 4. Correlation coefficients for 24 chemicals, bioassays, percentage clay, and organic matter (OM) measured in Flanders. Strong correlations are indicated by larger circles. The colour of the scale bar denotes the nature of the correlation with 1 indicating perfect positive correlation (dark blue) and -1 indicating perfect negative correlation (dark red). Blanks indicate no significant correlation ($p < 0.01$). Abbreviations of chemicals are given in Table 1.

3.2 Toxic unit

3.2.1 Standard correction

The Netherlands. The results of the TU analysis at EC50 and LC50 levels are presented in Table 6. The values for $\sum TU_{total}$ range from 0.64 to 1.91. Dordtsche Biesbosch is the site with the highest value, followed by Sliedrechtse Biesbosch, Amer and Nieuwe Merwede, for which the $\sum TU_{total}$ values were always found to be higher than 1. At all sites, metals appeared to be the main contributors to the $\sum TU_{total}$. PAHs also contributed to the total toxicity values albeit with minor contributions. OCPs and PCBs contributed minimally, as the values of $\sum TU_{OCPS}$ and $\sum TU_{PCBs}$ were almost 0.

Table 6. Toxic unit (TU) values per river distributary at EC50- and LC50-level.

Distributary code[a]	$\sum TU_{metals}$	$\sum TU_{PAHs}$ [b]	$\sum TU_{OCPs+}$ [c]	$\sum TU_{PCBs}$	$\sum TU_{total}$
DB	1.78	0.12	0.01	0.00	1.91
SB	1.19	0.06	0.00	0.00	1.25
AM	1.02	0.11	0.00	0.00	1.13
NM	0.89	0.10	0.01	0.00	1.01
BB	0.79	0.12	0.00	0.00	0.91
HD	0.73	0.10	0.00	0.00	0.83
HV	0.54	0.10	0.00	0.00	0.64

[a] Distributary code: Haringvliet (HV), Hollandsch Diep (HD), Nieuwe Merwede (NM), Dordtsche Biesbosch (DB), Brabantsche Biesbosch (BB), Amer (AM), Sliedrechtse Biesbosch (SB).

[b] QSAR data were applied for NOEC for *D.magna*.

[c] OCPs+ includes OCPs and two chlorobenzenes (i.e. pentachlorobenzene and hexachlorobenzene).

The toxic unit of each metal in the metal group is shown in Figure 5. Copper is the metal with highest TU at all sites, accounting for more than 70% of $\sum TU_{metals}$. It is followed by zinc, mercury and nickel, which also to chronic toxicity.

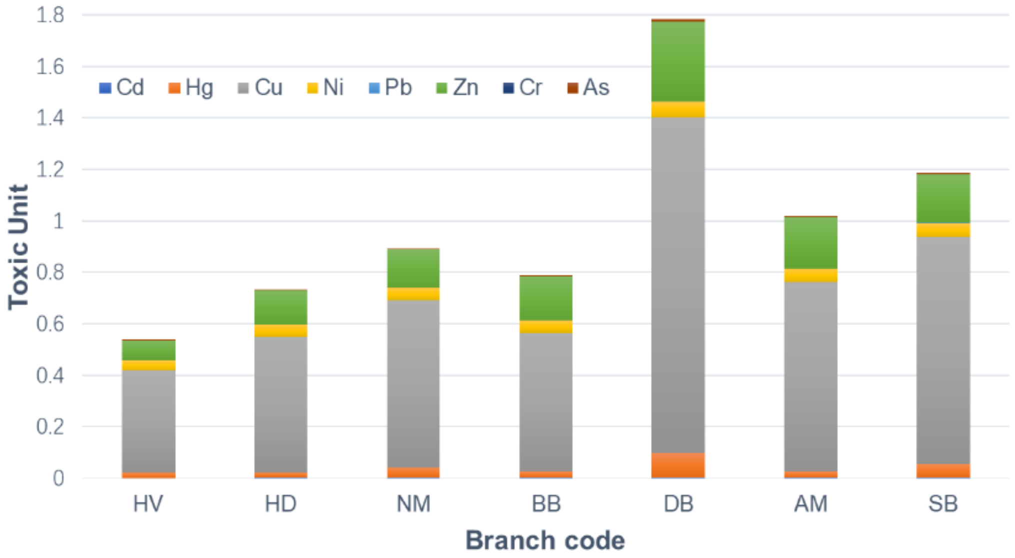


Figure 5. Toxic unit distribution within metal group. Branch code: Haringvliet (HV), Hollandsch Diep (HD), Nieuwe Merwede (NM), Dordtsche Biesbosch (DB), Brabantsche Biesbosch (BB), Amer (AM), Sliedrechtse Biesbosch (SB).

The relationship between exposure to chemical groups and effects observed in the bioassays of *D.magna* is shown in Figure 6. However, there is no clear trend between TU and survival fraction of the species. This suggests that standard correction for metal bioavailability is not refined enough to predict *D. magna* toxicity from sediment bioassays.

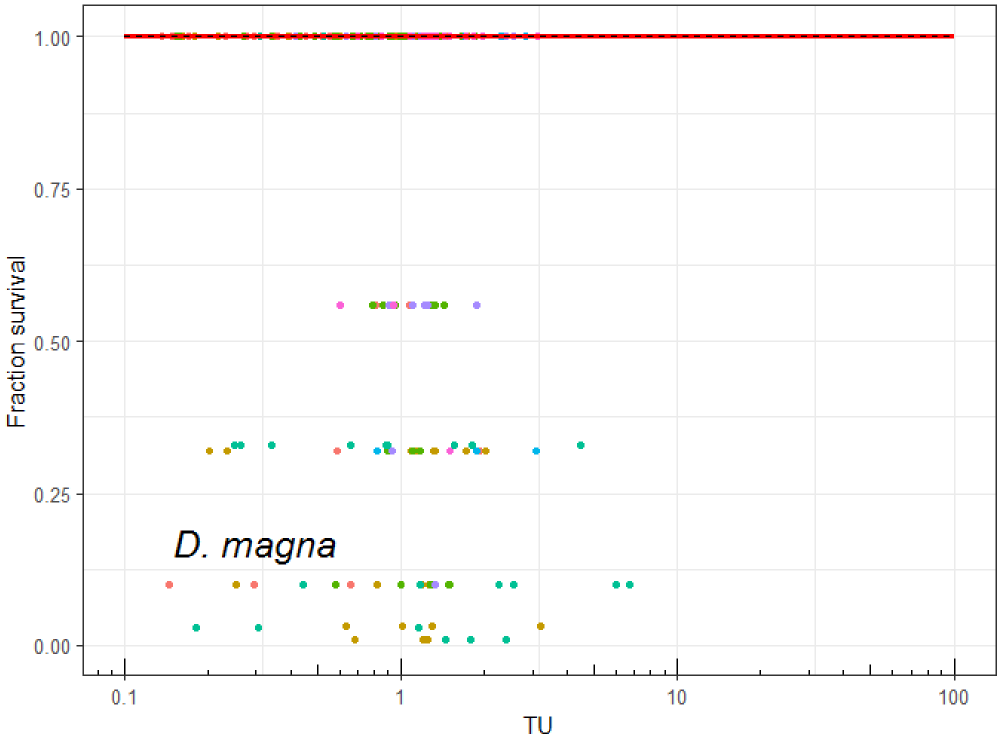


Figure 6. Fraction survival of *Daphnia magna* in lab experiments versus toxic units based on measured total sediment concentrations converted to dissolved concentrations using standard correction for different regions (represented by different colours). Red solid line represents quantile regression.

Flanders. The TU method resulted in a higher toxic pressure in the Meuse and Scheldt compare to the Yser (Figure 7). Overall, the mixture toxic pressure was higher for *H. azteca* than *R. subcapitata*. Metals contributed most to the TU of *H. azteca*, followed by organochlorine pesticides. PAHs were contributing least to the total TU. The contribution of PCBs to the $\sum TU_{total}$ was minor for *R. subcapitata*. Metals were the main contributors to toxicity of *R. subcapitata*. TUs of metals ranged from 0.17 to 0.32. Zinc was the main contributor, followed by nickel and copper. The TU of other metals (arsenic, cadmium, chrome, lead and mercury) was below 0.01. Total organic TUs ranged from 0.03 to 0.08, with phenanthrene and naphthalene as the main contributors. However, the real toxicological risk might be underestimated due to the absence of toxicological data for some OCPs.

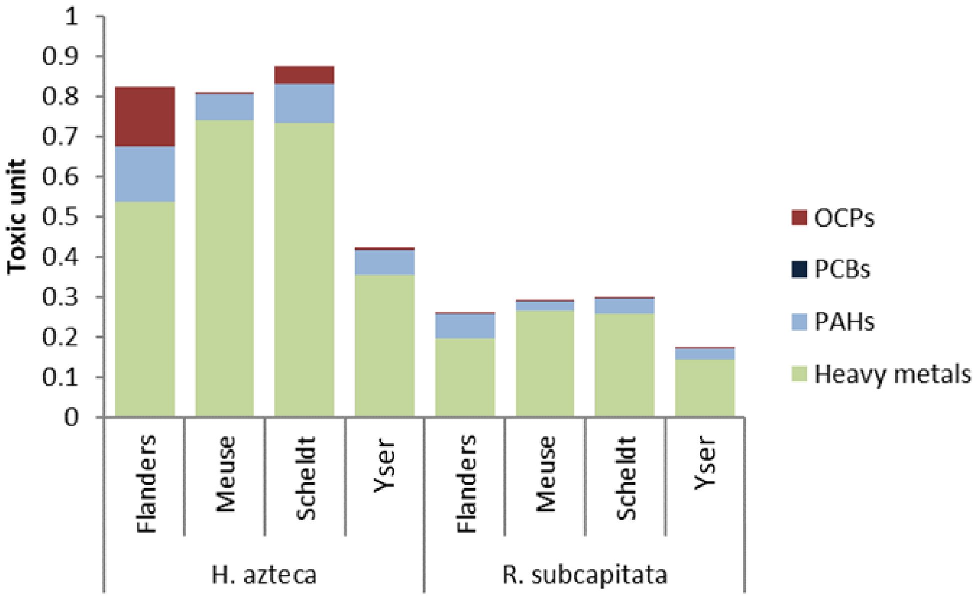


Figure 7. Results of TU analysis for *H. azteca* and *R. subcapitata* in Flanders (all waterways included) and the three main rivers Meuse, Scheldt and Yser.

Effects on *H. azteca* based on standard correction were reasonably anticipated (Figure 8). Yet, relationships were further improved when local conditions determining bioavailability and speciation were considered (Section 3.2.2).

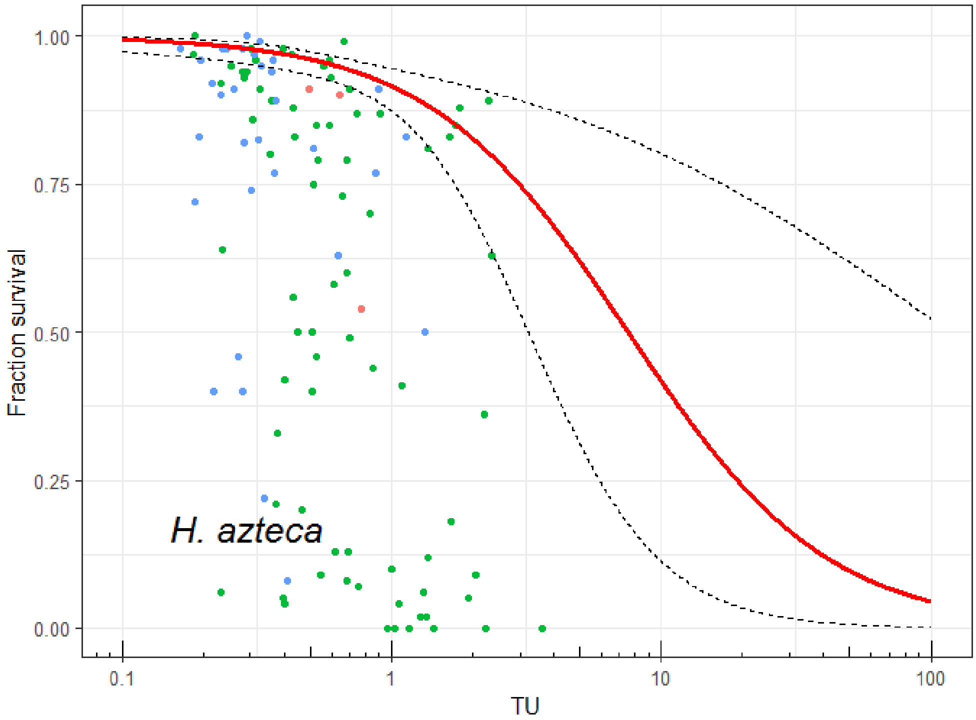


Figure 8. Fraction survival of *Hyalella azteca* in lab experiments versus toxic units based on measured sediment concentrations converted to dissolved concentrations using standard correction for different rivers (represented by different colours). Red solid line represents quantile regression.

3.2.2 Refined bioavailability and speciation

Hyalella azteca. The final calibrated TU analysis for *H. azteca* is shown in Figure 9 and 10*.* Among the toxicants considered, metals and NH_3/NH_4^+ dominate the TU (Figure 9). The LC50 values for Cr, NH_4^+/NH_3 and Cd applied to the final, calibrated analysis (Table 6, the last column) differed from those for initial analysis. For several ‘uniform’ water bodies, the calibrated analysis explains on average ~70% of the observed variance in mortality percentage of *H. azteca* (Figure 10).

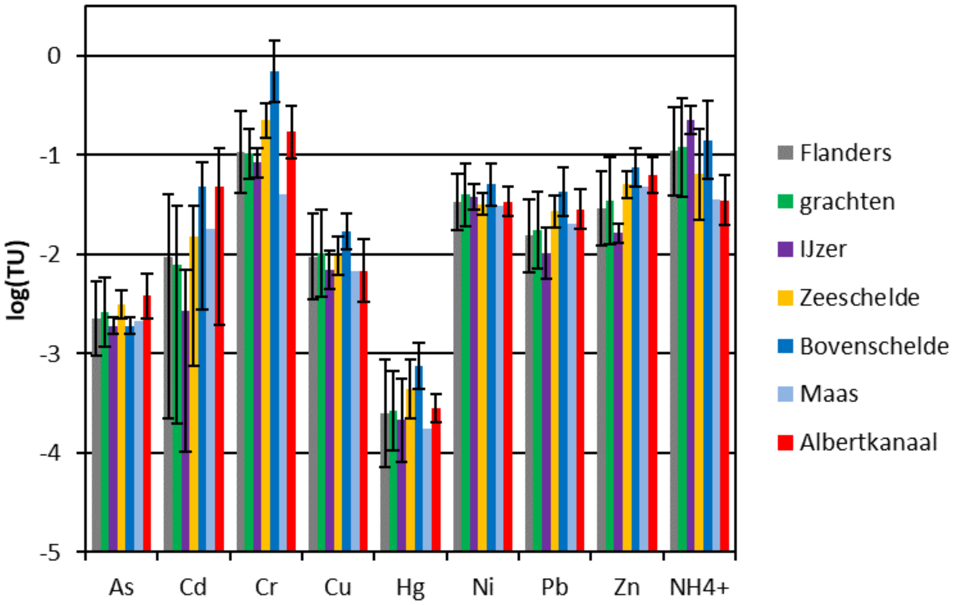


Figure 9. Toxic units for *H. azteca* for in Flemish water bodies. Limited information on pH and potential mixture effects, deemed taking LC50(NH_4^+) empirically as 400,000 mg/L as plausible, as a higher-end of ranges (Table 7). Thus, TUs for NH_4+ may be underestimations. Considering 47% of Cd concentrations were below limit of detection (LoD), we took negative errors as 10-fold the SD including the values set as the LoD.

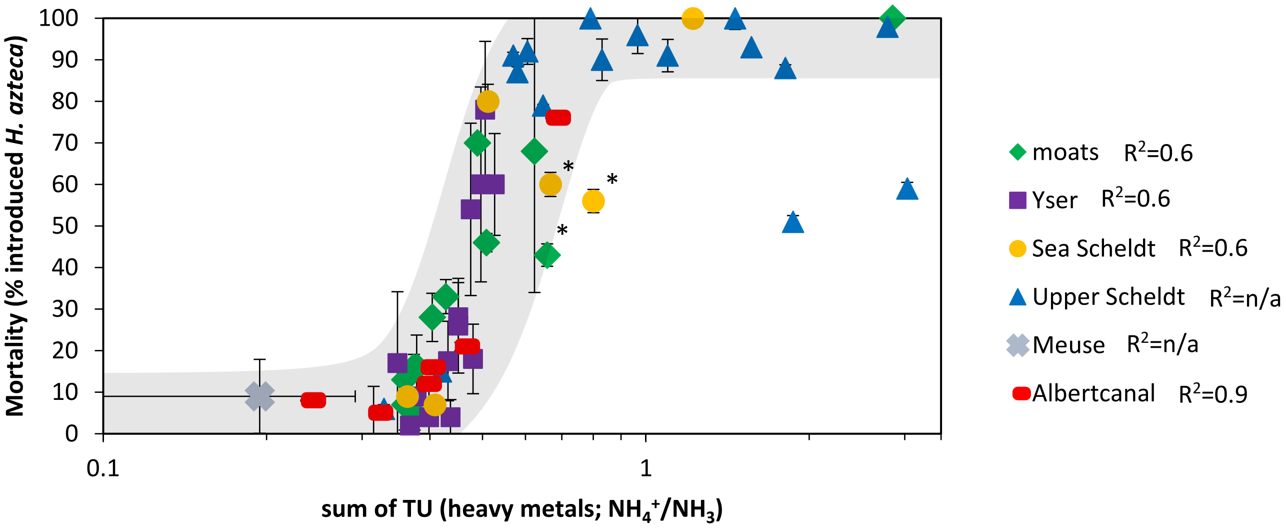


Figure 10. *H. azteca* mortality (%) versus Toxic Units (dimensionless) for 8 heavy metals and NH_4^+/NH_3. By calibration of γ_i, we took LC50 for Cr as 1 mg/L, representing CrO_4^{2-}, and LC50(Cd) as >1000 µg/L for a better fit. We distinguished between high/low quality data by excluding sediments with unknown KjN and P_T (except Upper Scheldt), with unknown [Ca^{2+}] or [Ca^{2+}] < 3.5 mg/L. Simulation gave an average TU of 0.55 and *β* of 0.015 (dimensionless). Asterisks denote values with lower KjN than the respective water body average, but not statistically significant (p>0.05).

Table 7. 7-day and 28-day LC50 values for *H. azteca* from the open literature as well as LC50 values used in the final TU simulation (Figure 11D). With corresponding uncertainties and ranges.

		U.S. EPA (2019) inter-laboratory variance (µg/L)	Borgmann et al. (2005) inter- and intra-laboratory variance (µg/L)	This study (Figure 9; 11D) (µg/L)
CrO_4^{2-} *	Average (SD)	33.6 (±24.8)	38.6 (±33.2)	1.0 (±0.7)****
	Min – max	1.4 – 61.4	1.0 – 94.8	-
NH_4^+	Average (SD)	40,017.0 (±49,637.2)	36,878.5 (±49,818.8)	400,000.0 (±200,000.0)****
	Min – max	1,371.0 – 199,513.2	2,345.1 – 233,607.2	-
NH_3**	Average (SD)	43,464.6 (±40,400.3)	33,313.8 (±37,603.1) ***	400,000.0 (±200,000.0)****
	Min – max	1,084.9 – 95,834.6	507.1 – 120,284.9***	-

* Expressed in the MW of Cr.

** LC50 values for NH_3 are expressed in terms of its concentration at pH=7.6, i.e. 10^($pK_{a,NH4+}$ - 7.6) wherein $pK_{a,NH4+}$ is 9.3.

*** 4-day LC50 values.

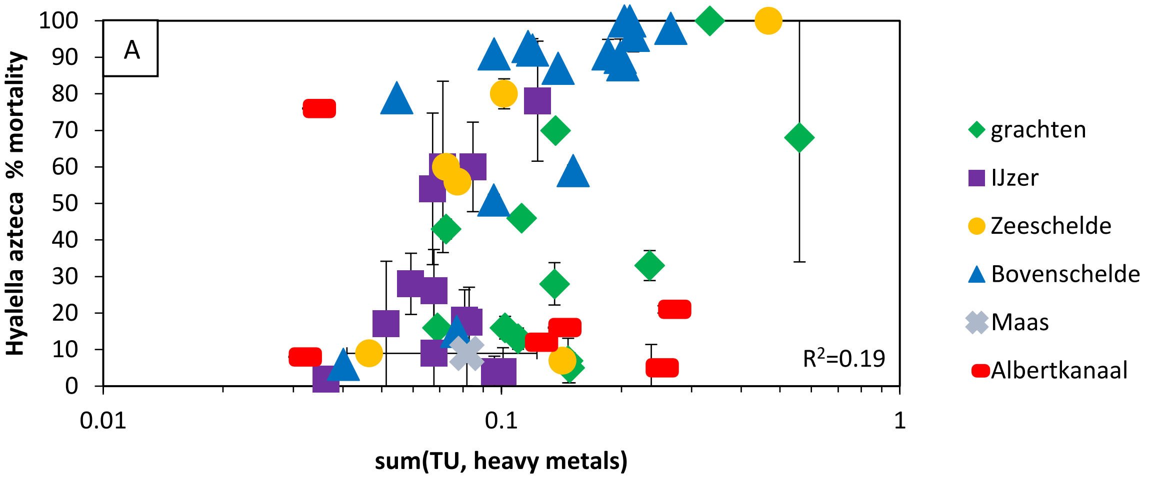
**** The errors for CrO_4^{2-} and NH_4^+/NH_3 in this study are those carried over from bioavailability errors.

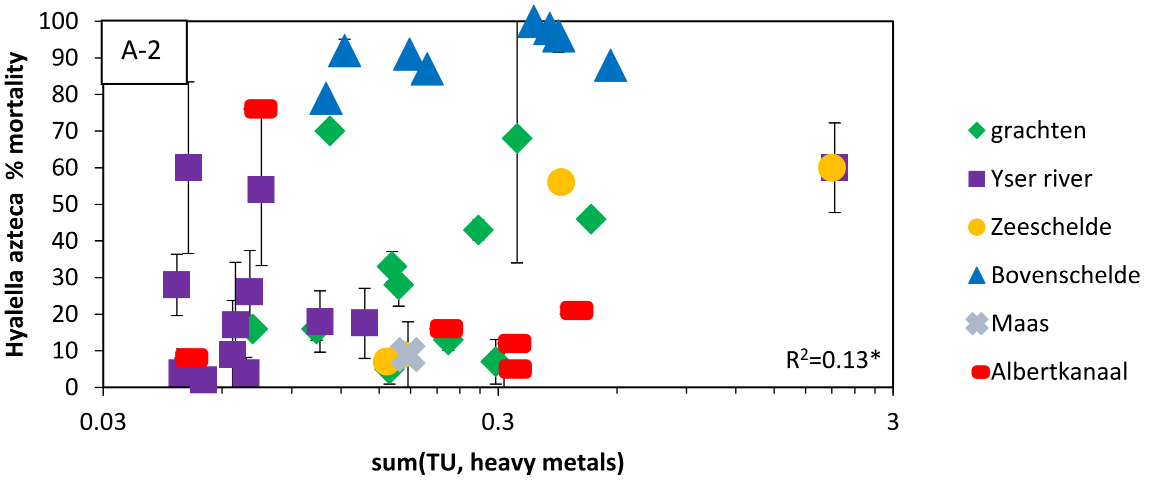
Regression of chromium speciation according to Equation 8 gave us the equation:

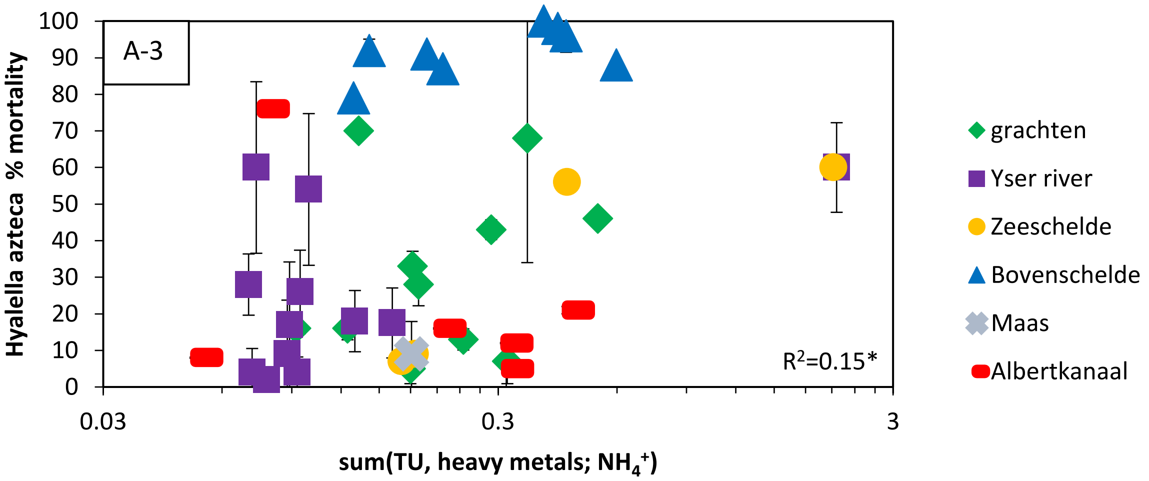
$$\log([CrO_4{}^{2-}]_{aq}) \propto \log([Cr_T]_{sed})/(0.15(\pm 0.05)\cdot\log([KjN]_{sed}) + 0.28(\pm 0.03)\cdot\log([P_T]_{sed}) + 0.11(\pm 0.02)\cdot [pH]_{sed} - 0.23(\pm 0.04)\cdot\log([O_2]_{sed}) - 0.54(\pm 0.20)) \tag{22}$$

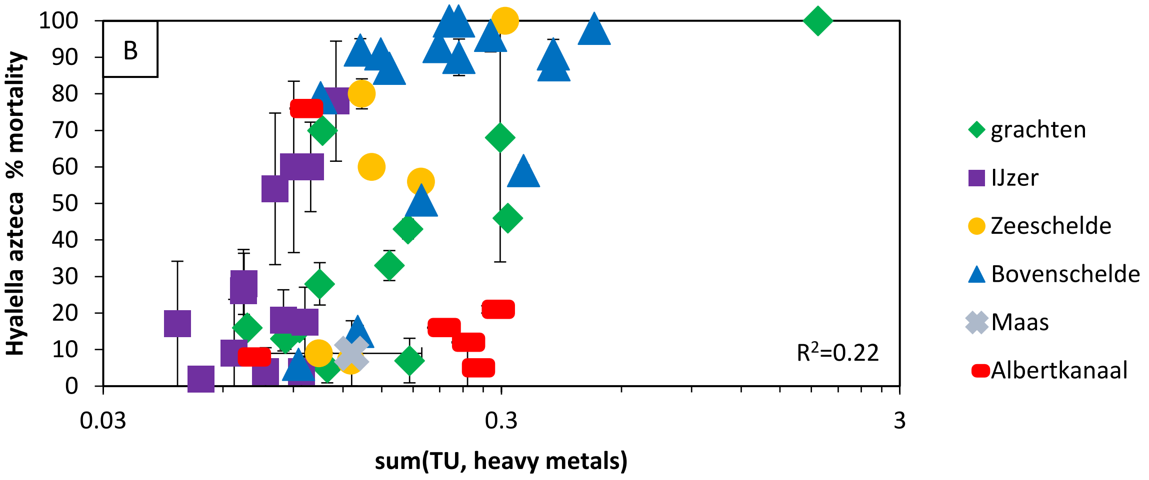
with R^2=0.52. However, implementing Equation 22 to describe speciation of Cr did not appear to improve the predictions for *H. azteca* mortality. Nor did the application of WHAM transfer functions based on total calcium content (Figure 11A-2 and 11A-3), though lack of (coherent) data limited our capability to use the transfer functions (Bootsma and Vink, 2016). Specifying the ratio of NH_3/NH_4^+ based on pH did not appear to enhance results. We noted high spatial variance in Kjeldahl nitrogen (KjN) and uncertainty in *in situ* NH_4, P_T pH, O_2 and Ca. Determining bioavailability by including local OC and clay content (Equation 4 and 5), only marginally improved the result (Figure 11A and 11B).

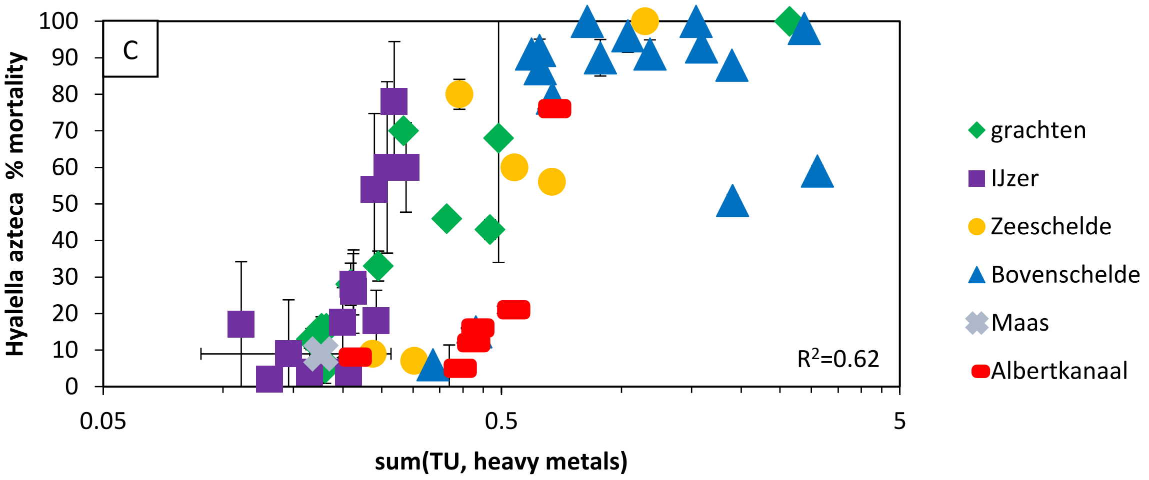
Predicting the mortality using the 'pre-set' M^{n+} LC50 values (Borgmann et al., 2005) gave poor predictions: the explained variance did not exceed 5% (N=1762, for Flanders), with slightly better results for 'larger' water bodies (e.g. Yser; Scheldt) (Figure 11A and 11B). According to these initial TU analyses (Figure 11A), among all toxicants considered, metals (esp. Zn) appeared to contribute most to *H. azteca* $\sum TU_{total}$. Metals' TU ranged from 0.2-0.3. Besides Zn, other contributors were Ni and Cu, and TUs of As, Cd, Cr Pb, and Hg were <0.01. With exception of endosulfan, phenanthrene and naphthalene (TU=0.03-0.08), OCPs, PCBs and PAHs did not appear to contribute to *H. azteca* lethality (TU<0.01). In contrast to Figure 11A and 11B, Cr most highly correlated with *H. azteca* mortality (Figure 4). By including NH_4^+/NH_3, the offsets (Figure 11C) in *H. azteca* mortality between water bodies disappeared. NH_4^+/NH_3 had an average TU of 0.2 (taking γ_{NH4}LC50=400,000 µg/L) across Flanders, with high values for Yser and upper Scheldt rivers. By reducing the LC50 value for Cr, the logistic curve describes more of the variance in *H. azteca* mortality Figure 11B and 11C). Two 'outliers' remained, of which we had no SDs for mortalities, and we could not further characterize speciation of Cr (via Equation 18) due to the lack of $[O_2]$, [KjN], $[P_t]$ or pH data. Letting Cd not contribute to the TU (by modifying γ_{Cd}LC50$_{Cd}$ to >1000 µg/L) slightly increased R^2 (Figure 11D and 11E).

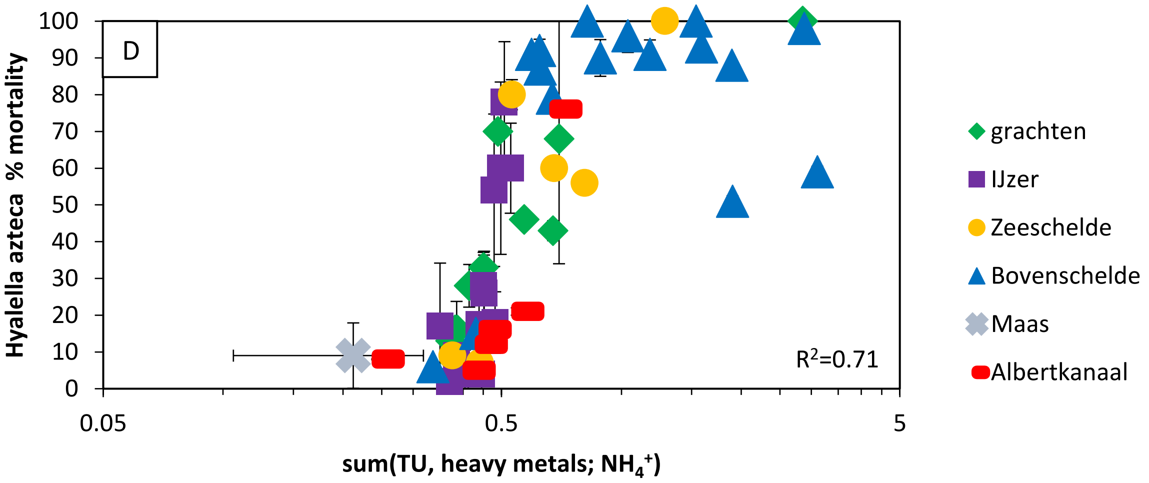

A
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.01
0.1
1
sum(TU, heavy metals)
R^2=0.19
grachten
IJzer
Zeeschelde
Bovenschelde
Maas
Albertkanaal


A-2
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.03
0.3
3
sum(TU, heavy metals)
R^2=0.13*
grachten
Yser river
Zeeschelde
Bovenschelde
Maas
Albertkanaal


A-3
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.03
0.3
3
sum(TU, heavy metals; NH_4^+)
R^2=0.15*
grachten
Yser river
Zeeschelde
Bovenschelde
Maas
Albertkanaal


B
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.03
0.3
3
sum(TU, heavy metals)
R^2=0.22
grachten
IJzer
Zeeschelde
Bovenschelde
Maas
Albertkanaal


C
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.05
0.5
5
sum(TU, heavy metals)
R^2=0.62
grachten
IJzer
Zeeschelde
Bovenschelde
Maas
Albertkanaal


D
Hyalella azteca % mortality
100
90
80
70
60
50
40
30
20
10
0
0.05
0.5
5
sum(TU, heavy metals; NH$_4^+$)
R^2=0.71
grachten
IJzer
Zeeschelde
Bovenschelde
Maas
Albertkanaal

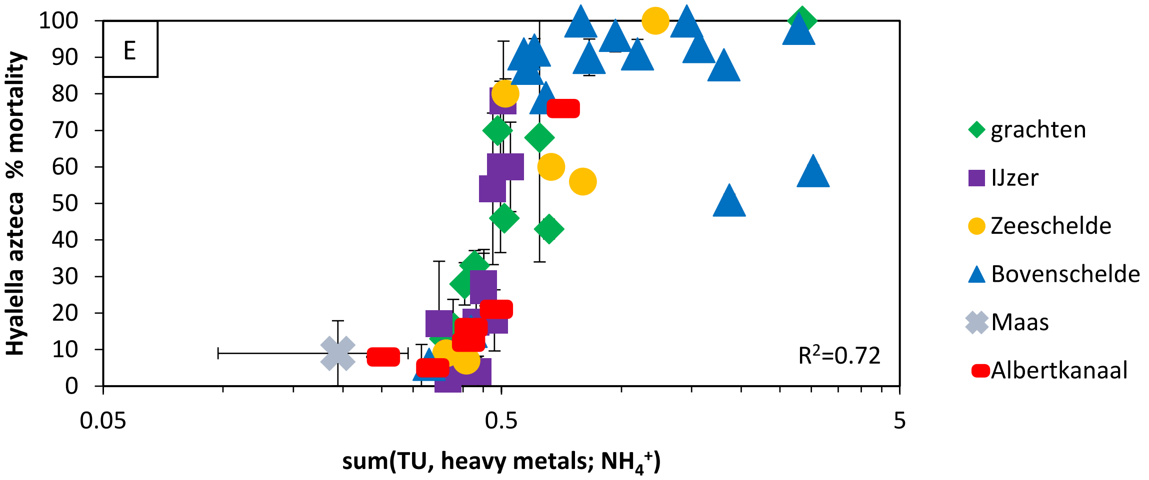


Figure 11. % *H. azteca* mortality versus the calculated TU (heavy metals+NH_4^+/NH_3). R^2 represent log-log best fits excluding outliers. The 5 separate calculations reflect the 4 LC50 input ranges as given in Table 7:

A: LC50(Cr) = LC50(Cr^{3+}); LC50(NH_4^+) = ∞ mg/L; taking *a* = *b* = 0 in equation 4

A-2: same as A; transfer functions*

A-3: same as E; transfer functions*

B: LC50(Cr) = LC50(Cr^{3+}); LC50(NH_4^+) = ∞ mg/L

C: LC50 (Cr) = LC50(CrO_4^{2-}); LC50 (NH_4^+) = ∞ mg/L

D: LC50 (Cr) = LC50(CrO_4^{2-}); LC50 (NH_4^+) = 400 mg/L

E: same as D but with LC50(Cd) = ∞ µg/L instead of 0.57 µg/L

Heterocypris incongruens. We performed analyses to elucidate the toxicity of sediments in Flanders to *H. incongruens*. According to initial TU results, NH_3 (TU = 0.1) contributed most to *H. incongruens* growth inhibition. Other contributors were Ni and Cu (TU ≤ 0.1), whereas the individual TUs of Zn, Cd, CrO_4, Hg and Pb were ≤0.01. Predicting the growth inhibition via initial TU using standard EC50 values yielded maximal explained variance lower than 30%. Initially, speciation calculations (Equation 9 and 14) did not appear to improve these results.

We then performed ‘semi-empirical’ analyses to further elucidate the toxicity of sediments by letting EC50 values fit to the growth inhibition data. This ‘calibrating’ procedure allowed a robust TU analysis for *H. incongruens*. According to the semi-empirical analysis, NH_3 dominates the TU (TU = 0.3) (Figure 12). Additional toxic pressure arises from organotins (as represented by tributyltin, TU = 0.3). The contributions from Ni and Cu appear minor (≤0.1). Inclusion of chemicals other than NH_3, HPO_4^{2-} and By_3SnOH_2 only marginally improved the fit. Instead, we found a positive influence by PO_4, i.e., growth promoting (TU = -0.3).

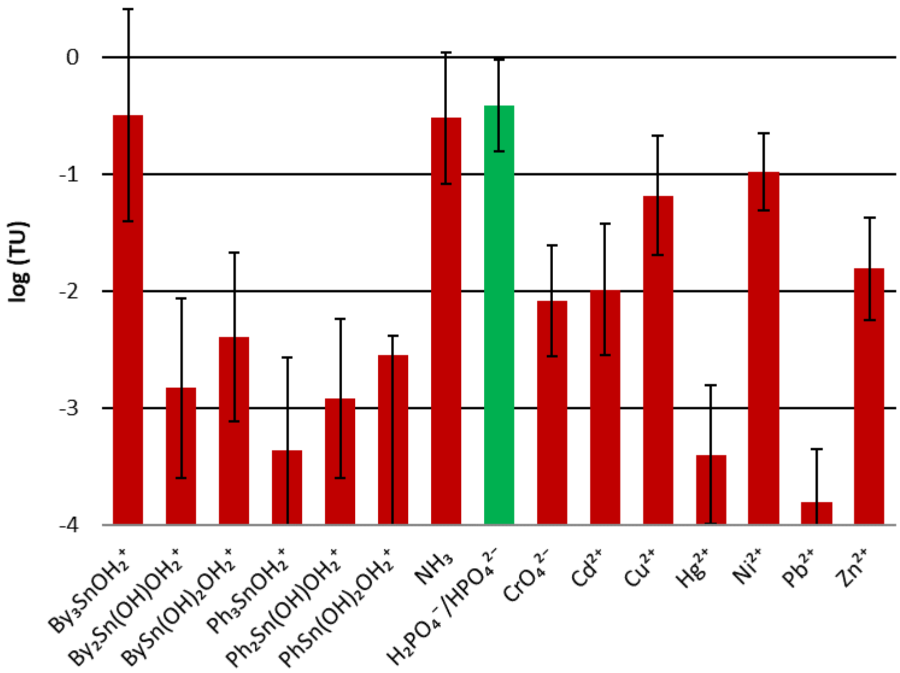
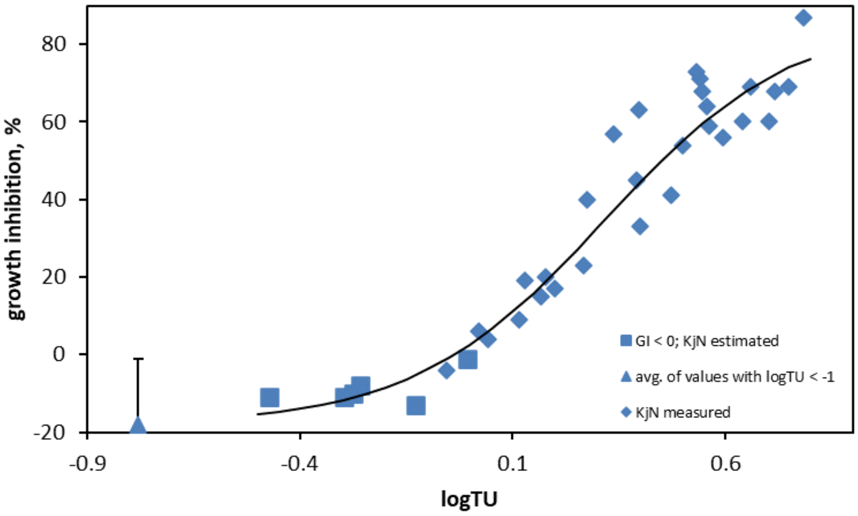


Figure 12. Toxic units for *H. incongruens* ($[C]_{aq}/EC50_{aq}$) for individual pollutants in sediments from water bodies in Flanders. Error bars denote variability throughout Flanders. For MFT (assumed porewater pH=7.5) 99% of samples were below the detection limit (DL); negative errors are 10-fold the SD including the values set at the DL.

After calibration, we found that speciation calculations (Equation 14) significantly improved the result (Figure 14B and 14C). NH_3, organotins and HPO_4^{2-} could explain up to 90% of the observed variance in the growth inhibition for water bodies throughout Flanders. The relative importance of the toxicants differs between water bodies. In general, predictions for *H. incongruens* growth inhibition are more precise for 'uniform' (e.g. large rivers and canals) water bodies as compared to small 'non-uniform' water bodies.



chemical	coefficient (fit)	log(average concentration)	average concentration (ng/L)	contribution (%)	γ_iEC50 (ng/L)
NH_3 NH_4^+	17.8	5.7	512,226	30.1	153,932(±76,966)
HPO_4^{2-}	-22.6	5.0	103,904	38.2	-39,699(27,145-85,840)
$By_3SnOH_2^+$	18.8	-2.0	0.00998	31.7	0.0032(±0.0016)
By_3SnOH					0.06(±0.03)

Figure 13. *H. incongruens* growth inhibition (%) versus the Toxic Unit. EC50 for organotin cations was taken as 0.003 ng/L, representing $By_3SnOH_2^+$. Simulation performed using θ=4.5 (dimensionless). Far-left triangle denotes the weighted average of values with logTU < -1. Squares denote data wherefore KjN was unknown, and taken as a regional average. The table provides corresponding uncertainties/ranges. For EC50 values, the errors are those carried over from errors in bioavailability.

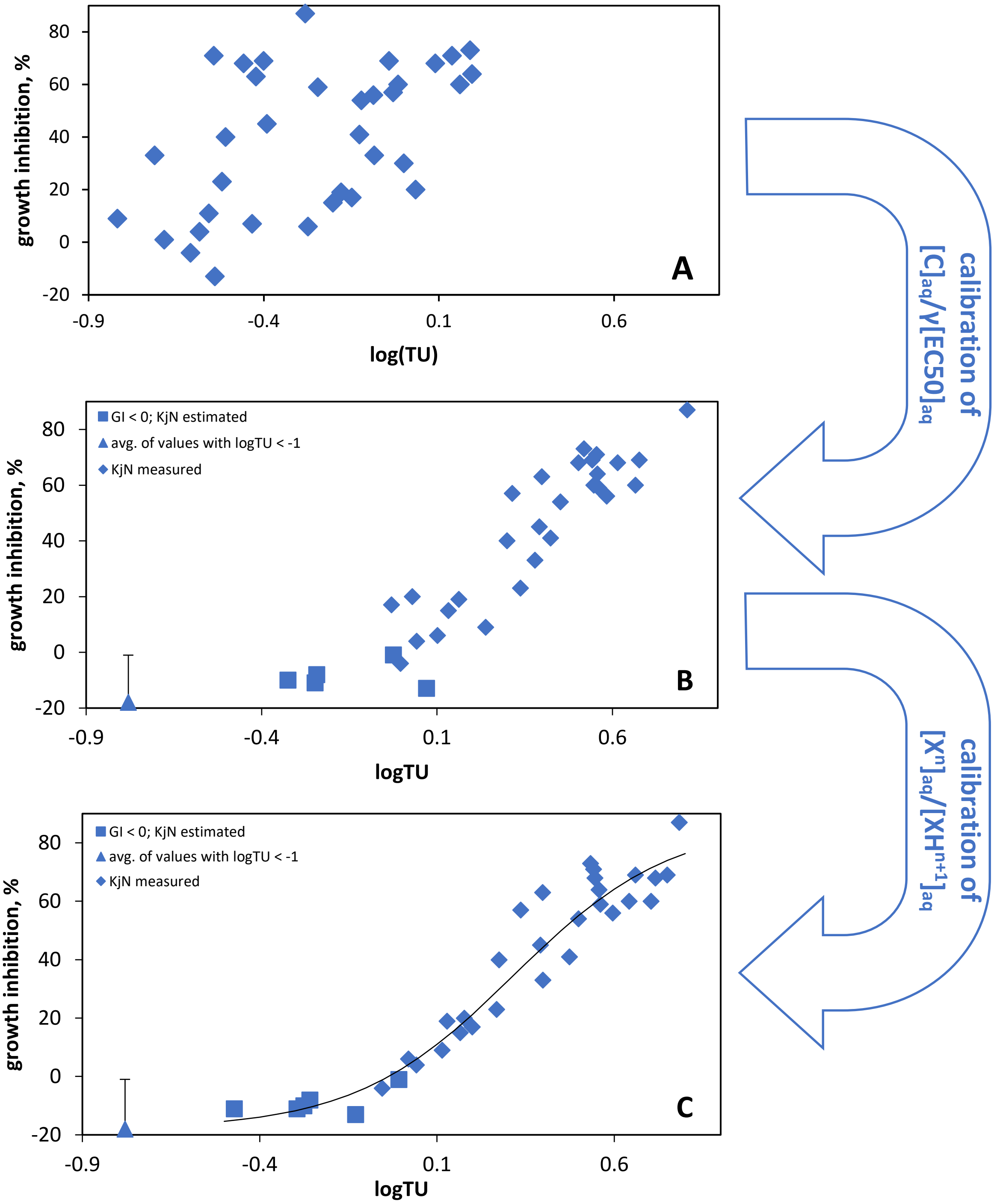


Figure 14. *H. incongruens* growth inhibition (%) versus the Toxic Unit. GI=growth inhibition.
A: EC50 for organotins (cations) represented 3 ng/L; pH assumed to be 7.5. R^2=0.26.
B: EC50 for organotins (cations) represented 0.003 ng/L; pH assumed to be 7.5. R^2=0.82
C: EC50 for organotins (cations) represented 0.003 ng/L; pH taken for the porewater. R^2=0.90

3.4 (Multi-substance) potentially affected fraction

The Netherlands. Based on standard correction of bioavailability, the msPAF(HC50) for sediment samples in the Waal-Meuse estuary was estimated to be 18.5% (±6.3%) (Table 8). Metals (10.1%) and PAHs (8.7%) were the main contributors to the total pressure, while OCPs (0.5%) and PCBs (0.2%) had limited contribution.

Table 8. The msPAF(HC50) (%) for sediments in the Waal-Meuse estuary

Chemical groups	msPAF per distributary (%)[b]							$\overline{msPAF}$ (%)[c]
	HV	HD	DB	NM	AM	BB	SB	
Metals[a]	7.0	9.4	13.2	10.3	10.7	9.8	11.3	10.1 (±1.8)
PAHs	8.0	8.0	10.4	7.6	9.9	10.0	7.6	8.7 (±1.2)
OCPs	0.1	1.1	7.1	2.0	0.2	0.1	0.4	0.5 (±2.4)
PCBs	0.1	0.1	0.5	0.7	0.2	0.1	0.3	0.2 (±0.2)
msPAF(HC50)(%)	14.6	17.6	28.0	19.4	19.9	19.0	18.6	18.5 (±6.3)

[a] Metals include arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc.

[b] Distributary code: Haringvliet (HV), Hollandsch Diep (HD), Dordtsche Biesbosch (DB), Nieuwe Merwede (NM), Amer (AM), Brabantsche Biesbosch (BB), Sliedrechtse Biesbosch (SB).

[c] The geometric mean and ±1 standard deviation (variation) based on msPAF per distributary.

Flanders. The msPAF(HC50) for Flemish sediments was estimated to be 35.6% (±21.1%) (Table 9). The mixture toxic pressure in the Waal-Meuse estuary (18.5%) was slightly lower than that of the Meuse River in Flanders (25.5%). One explanation may be that the 'cleaner' Waal River diluted the Meuse River. It was estimated that the mixture toxic pressure of all three rivers in Flanders was lower than that of all waterways, indicating that other waterways (e.g. canals) were more heavily polluted. The chemicals exerting the highest pressure to the ecosystems were those of PAHs, nickel and copper.

Table 9. The msPAF(HC50) (%) and ±1 standard deviation for three rivers and all waterways in Flanders

Chemical groups	msPAF (%)			
	Meuse River	Scheldt River	Yser River	All waterways in Flanders
Metals[a]	9.2 (±1.7)	10.1 (±3.7)	9.3 (±2.3)	9.4 (±4.3)
PAHs	17.3 (±2.5)	20.2 (±5.2)	13.6 (±4.0)	23.1 (±10.9)
PCBs	0.6 (±0.2)	0.6 (±0.4)	0.2 (±0.2)	0.7 (±1.0)
OCPs	0.2 (±0.1)	5.0 (±9.4)	2.6 (±4.2)	7.0 (±19.2)
msPAF(HC50) (%)	25.5 (±11.1)	32.2 (±18.6)	23.9 (±12.1)	35.6 (±21.1)

[a] Metals include arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc.

Quantile regressions of the macrofauna species richness observed in field survey as a function of multi-substance potentially affected fraction of species (msPAF(HC50)) estimated based on standard correction indicated no relationship (Figure 15). At the same time, the upper right corners of the plot do not contain data points, indicating that, as expected, species richness is not large for high msPAF(HC50) levels.

.

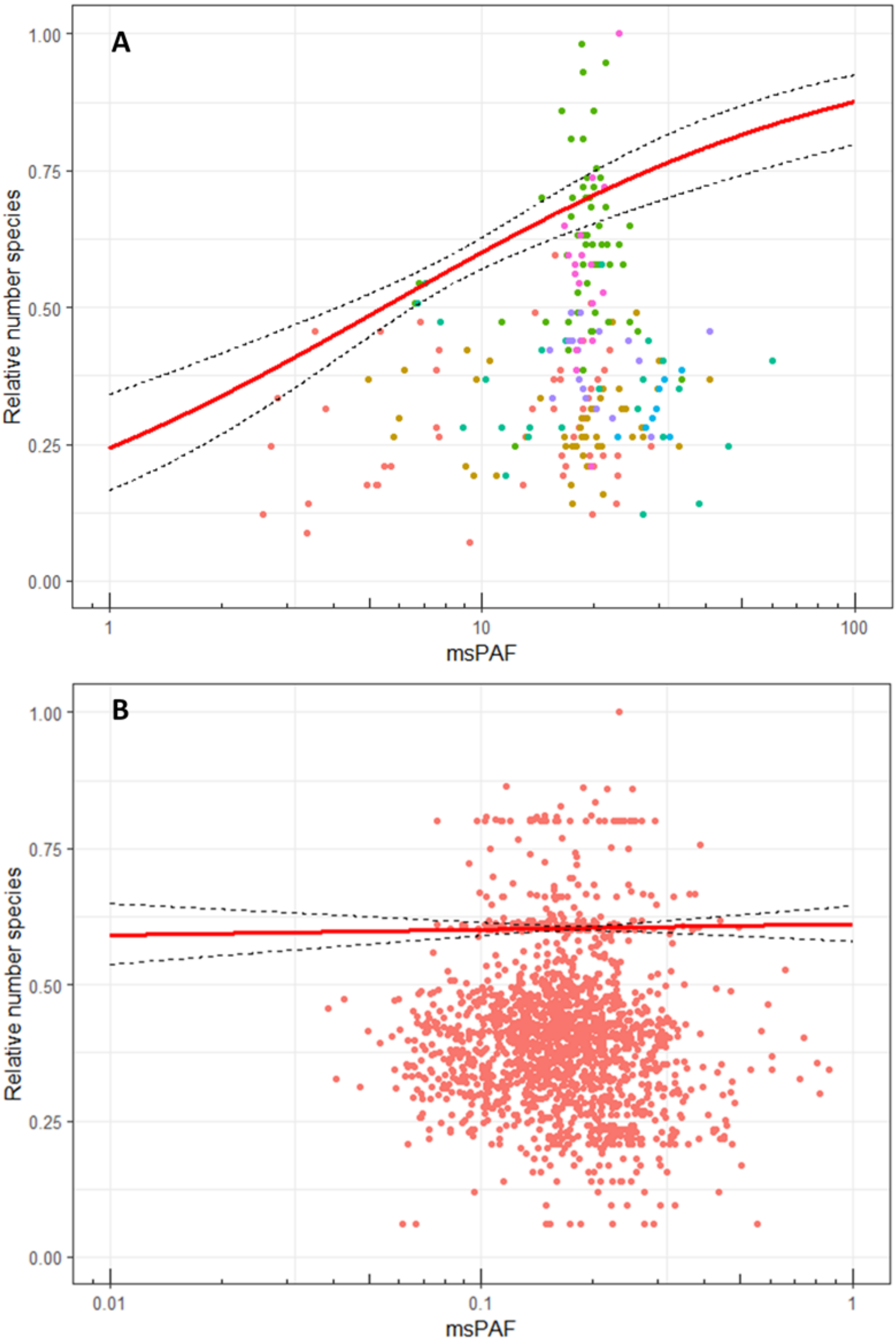


Figure 15. Relative number of macrofauna versus msPAF calculated per location for the Netherlands (A) and Flanders (B). Different colours in A represent different sampling regions. Red solid line represents quantile regression.

3.5 Redundancy analysis of ecological data

After removing chemicals with low significance using Monte Carlo permutation tests, sixteen chemicals were retained: Hg, Cu, Ni, Pb, Zn, Cr, As, B(a)P, INP, DDT, β-HCH, Lindane, Telodrin, PeCBz, PCBt and Oil. Also, the number of species shrank to 129 after removing the species with a low abundance (<4 individuals per m^2). The final transformation-based canonical redundancy analysis (tb-RDA) was computed using the 16 retained chemicals to illustrate the relationship between the explanatory variables and the species assemblages.

Table 10. Linear correlation coefficients obtained between the 16 chemicals having a significant influence on the species and axes 1, 2, and 3 of the canonical redundancy analysis (RDA) (significance tested at $P<0.05$)

Chemicals	Correlation coefficients		
	RDA1	RDA2	RDA3
Hg	0.19	0.25	0.14
Cu	0.56	0.27	0.11
Ni	0.67	0.27	0.14
Pb	0.65	0.06	0.03
Zn	0.7	0.18	0.08
Cr	0.35	0.24	0.21
As	0.39	0.08	-0.01
B(a)P	0.7	0.04	-0.16
INP	0.79	-0.23	0.09
DDT	0.15	0.33	0.43
β-HCH	0.18	0.05	0.3
Lindane	-0.11	0.3	0.42
Telodrin	-0.02	0.21	0.25
PeCBz	0.16	0.34	0
PCBt	0.17	0.3	0.12
Oil	0.35	0.53	-0.45

Chemicals abbreviation see Table 1. PCBt = total concentration of PCB group.

The three RDA axes in total appeared to account for 62.7% of the explainable variance. Table 10 shows the correlation coefficients of the first three RDA axes, using data on 129 taxa. Figure 16 shows the relation between distributaries according to species and chemicals using the RDA analysis. The variables most significantly correlated with the first axis were the metals (Ni, Pb, Cr, Cu, Zn, As) and PAHs (B(a)P, INP), with higher axis values implying higher impacts. Therefore, distributaries on the right side of the panel (Dordtsche Biesbosch, Amer, Brabantsche Biesbosch and Sliedrechtse Biesbosch) had higher contamination ranks in metals and PAHs than tributaries on the left. The chemical most correlated with the second axis was oil, indicating that the difference of species assemblage between the lower (Haringvliet and Brabantsche Biesbosch) and upper panels was likely due to exposure to oil.

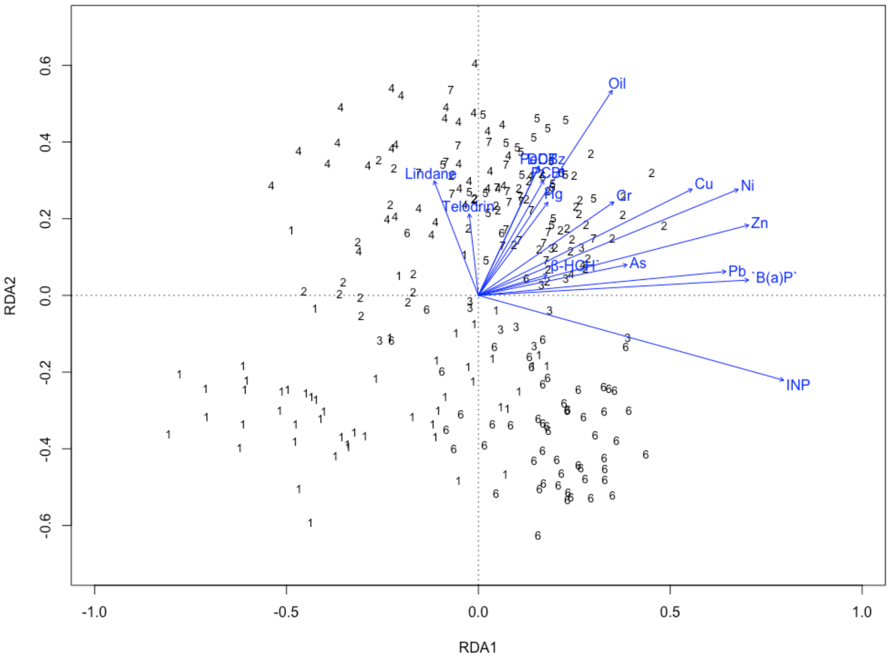


Figure 16. Transformation-based canonical redundancy analysis (tb-RDA) representing the positions of the 7 distributaries in relation to the 16 retained chemicals based on species assemblage data. The chemicals (abbreviation see Table 1) are represented by blue arrows and branches by black numbers. Distributary code: 1: Haringvliet (HV), 2: Hollandsch Diep (HD), 3: Dordtsche Biesbosch (DB), 4: Nieuwe Merwede (NM), 5: Amer (AM), 6: Brabantsche Biesbosch (BB), 7: Sliedrechtse Biesbosch (SB). The direction and distance of the arrows indicate the importance of the contaminant.

3.6 Ecosystem service modelling

3.6.1 Relationship between diversity and productivity

The ‘average’, ‘minimum’ and ‘maximum’ loss of productivity were obtained by fitting a power ($P'=D'^{0.35}$), Michaelis-Menten ($P'=1.04\times\frac{D'}{D'+0.04}$) and linear functions ($P'=D'$), respectively (Figure 17). So, on average, approximately 50% and 80% of productivity was still maintained at 15% and 50% of pristine species richness. In other words, x% of msPAF(HC50) (i.e. (100-x)% of remaining diversity) would relate to an average of $\left(1\text{-}\left(1-\frac{x}{100}\right)^{0.35}\right)\times 100\%$ (from minimum $\frac{4x}{104\text{-}x}$% to maximum x%) of productivity loss.

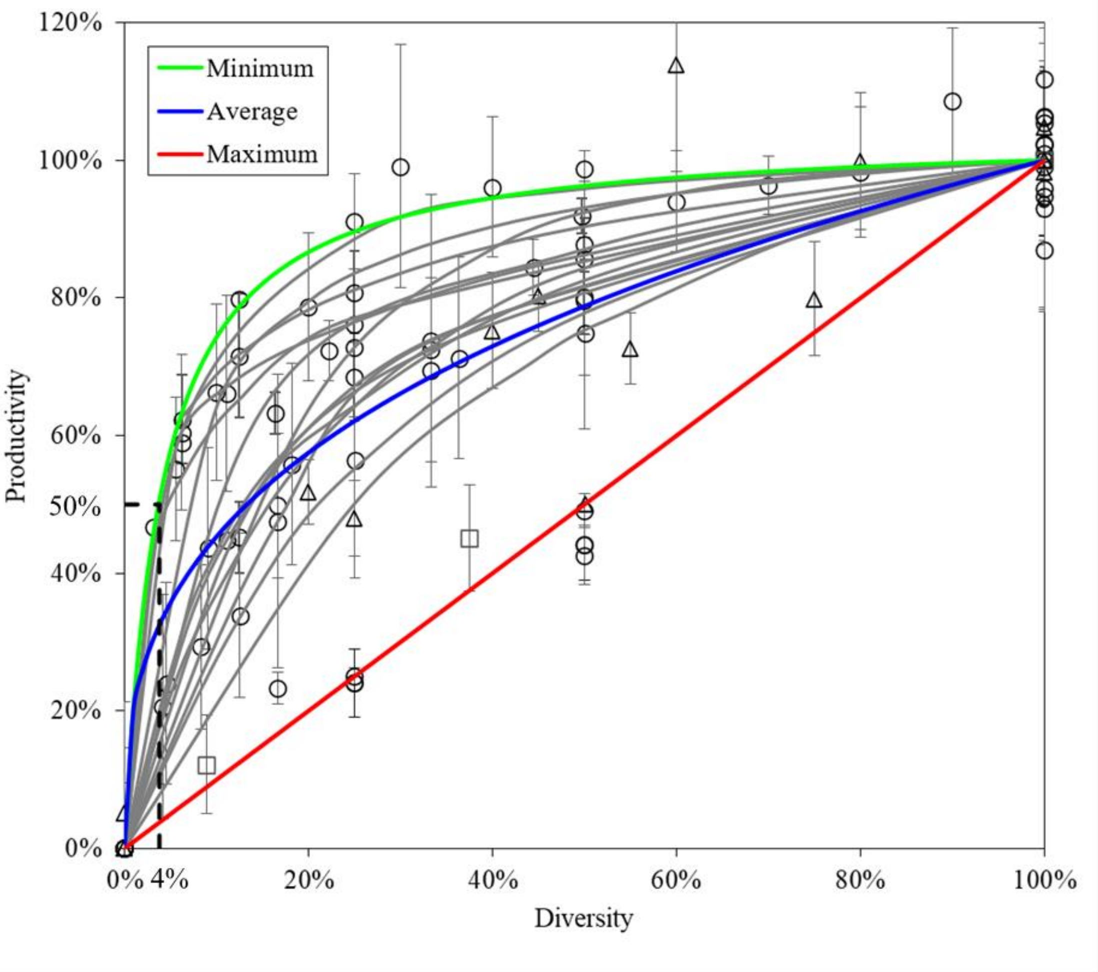


Figure 17. Relationships between diversity (D’, %) and productivity (P’, %) in experimental terrestrial ecosystems based on reported scaled relationships (solid grey curves). The average, minimum and maximum loss of productivity are shown in solid blue, green and red curves, respectively. Minimum impact shows that 96% of diversity loss results in 50% of productivity loss (dashed black line). Type of diversity is classified as species richness (open circles), functional richness (open triangles) and species evenness (open squares). Means and standard errors are shown.

3.6.2 Relationship between productivity and ecosystem services

Based on the data from Costanza et al. (2014), we found a positive correlation between the geometric mean of productivity per biome and total ES values (Figure 18). An increase of productivity generally led to an increase of economic values of ESs (note the logarithmic axes for both variables). Regardless of the differences between terrestrial and aquatic systems, the fitted relationship between the geometric mean of productivity (P, kg/m^2/yr) and total ES value (V, 2007$/ha/yr) was: $\log_{10}(V)=4.14+1.40\log_{10}(P)$ with $R^2=0.53$. In other words, x% of productivity loss resulted in $(1-(1-\frac{x}{100})^{1.4})$ ×100% of total ES value loss.

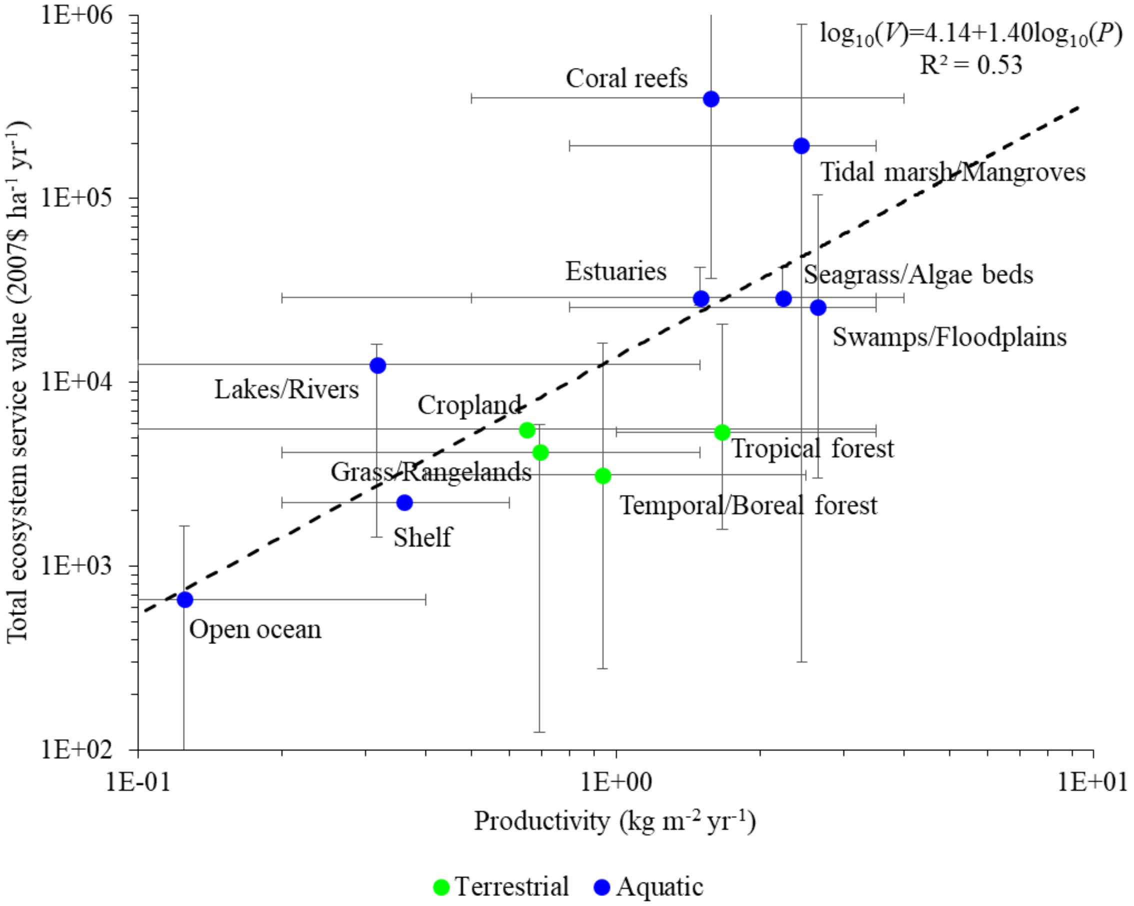


Figure 18. Relationship between productivity (P, kg/m^2/yr) and total ecosystem service value (V, 2007$/ha/yr) per biome. Bars show the range of productivity and the total value of ecosystem services per biome based on Whittaker (1975) and De Groot et al. (2012), respectively. The black dashed line is a regression of ecosystem services from Costanza et al. (2014) an the geometric mean of productivity based on literature listed in Table A6.

3.6.3. Application of derived relationships

The relationships between msPAF(HC50) and diversity, between diversity and productivity in terrestrial ecosystems, and between productivity and total ES value were combined. Consequently, an x% of msPAF(HC50) implies an average reduction in total ES value (V_{loss}, %) of (Figure 19):

$$V_{\text{loss,avg}}= \left(1-\left(1-\frac{\text{msPAF(HC50)}}{100}\right)^{0.49}\right) \times 100 \tag{23.1}$$

with minimum ES loss of

$$V_{\text{loss,min}}= \left(1-\left(1-\frac{0.04\times\text{msPAF(HC50)}}{104-\text{msPAF(HC50)}}\right)^{1.4}\right) \times 100 \tag{23.2}$$

and maximum ES loss of

$$V_{\text{loss,max}}=\left(1-\left(1-\frac{\text{msPAF(HC50)}}{100}\right)^{1.4}\right) \times 100 \tag{23.3}$$

As an outcome of the complete set of assessment steps, 1% of msPAF(HC50) was estimated to correspond to on average 0.5 (minimum-maximum: 0.05-1.4) % of total ES value loss. Chemical mixtures in sediments of Waal-Meuse estuary and all waterways in Flanders would reduce 9.5 (1.2-24.9) % and 19.4 (2.9-46.0) % of total ES value, resulting in an ES loss of 0.3-5 and 0.6-10 thousand 2007$/ha/yr, respectively (Table 11).

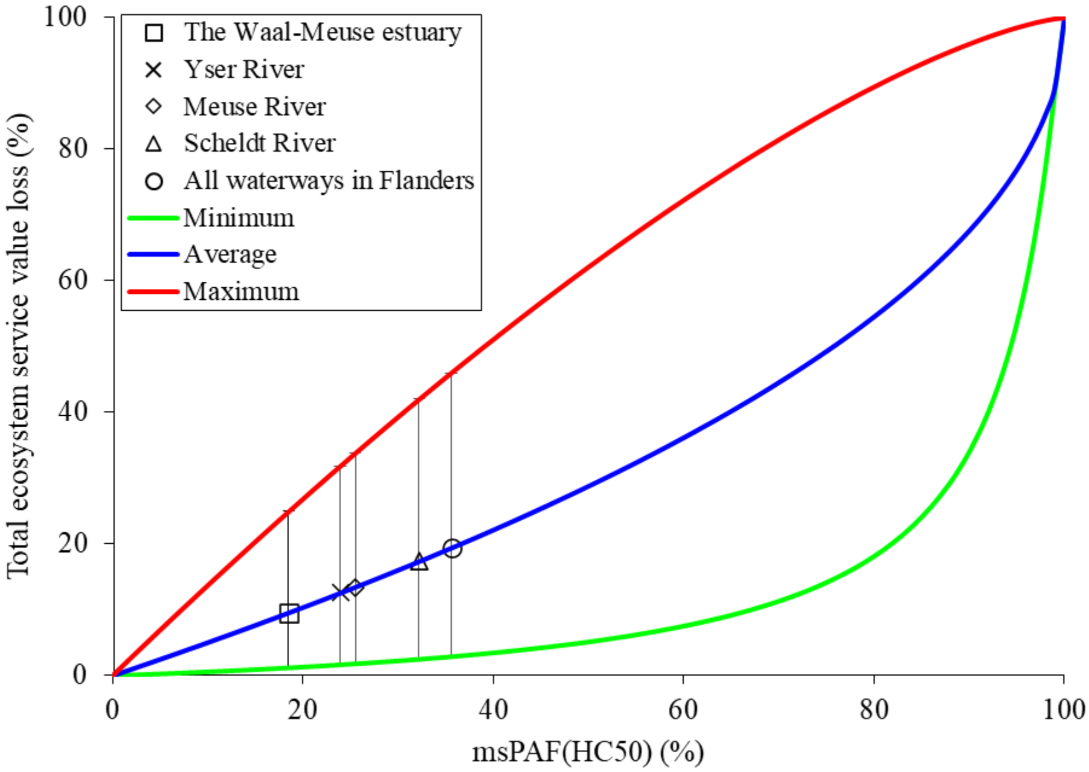


Figure 19. Relationship between multi-substance potentially affected fraction of species (msPAF(HC50), in %) and total ecosystem service (ES) value loss (in %). The average, minimum and maximum toxic pressure impacts on total ES value loss are shown in solid blue, green and red curves, respectively. Sediment sampling sites are shown in different shapes.

Table 11. Total loss of ecosystem service value (in 2007$/ha/yr) due to chemical pollution in the Waal-Meuse estuary and Flemish waterways

Site	msPAF(HC50) (%)[a]	Productivity loss (%)[b]	Total ES loss (%)[b]	Total ES value (2007$/ha/yr)[c]	Total ES loss (2007$/ha/yr)[b]
The Waal-Meuse estuary	18.5 (± 6.3)	6.9 (0.9-18.5)	9.5 (1.2-24.9)	21023 (±7095)	2005 (255-5242)
Flemish waterways	35.6 (± 21.1)	14.3(2.1-35.6)	19.4 (2.9-46.0)		4078 (611-9679)

[a] The average mixture toxic pressure (± 1 standard deviation) in each site.

[b] The average value (minimum-maximum). The range only reflects the conversion from diversity to productivity based on the average mixture toxic pressure.

[c] The geometric mean (± 1 standard deviation) of ecosystem services provided by lakes/rivers, estuaries and swamps/floodplains based on Costanza et al. (2014).

4. Discussion

In the present study, we linked sediment monitoring in Flanders and the Netherlands with modelling to explain the differences between chemical, toxicological and ecological indicators. Based on different methods, we converted total sediment concentrations to total water levels. The sum of the toxic unit of all substances for a given species at the E(L)C50 level was calculated and was compared to measured survival in lab assays. We also estimated the multi-substance potentially affected fraction (msPAF) of the aquatic community and compared these msPAF values to measured macrofauna abundance in field inventories. Additionally, a novel methodology was proposed and applied to extend toxicological endpoints (i.e. msPAF) to ecosystems services that appeal to water managers and policy-makers. The traditional sediment quality TRIAD approach has been accepted on an international scale as the most comprehensive approach (Den Besten et al., 1995, Chapman and McDonald, 2005). However, the TRIAD approach requires intensive laboratory and field measurements without providing a cause-and-effect relationship linking chemical concentrations to adverse biological effects. In order to understand and better predict the changes, we compared and interpreted chemical, toxicological and ecological monitoring across countries, authorities and systems using the extended version of the OMEGA model. In the following sections, we discuss the implications of our results on the application of risk assessment tools in water and sediment management.

4.1 Chemical, toxicological and ecological relationships

This study presents the results of a comprehensive data analysis of mixture pollution information on sediments, exploring multiple aspects of exposure and impacts for both lab organisms and field species. The obtained results, suggesting the presence of mixture impacts and the relative contributions of individual chemicals to those effects, are discussed in a stepwise manner.

Correlations among chemicals. The correlation coefficients showed that chemicals within the same chemical group (i.e., metals, PAHs and PCBs) were significantly positively correlated. This pattern was also observed in De Lange et al. (2004). These correlations probably reflect that the contaminants in the same group originate from common emission sources and are likely co-emitted as mixtures (Von der Heyden and New, 2004). Such information is relevant for understanding impacts at the (subgroup) mixture level as well as for management where a dominant chemical group can be identified and regulated at the common source.

Chemical analysis toxicological assays. The OMEGA model was used to predict ecotoxicological impacts of contaminants based on the indicators TU, msPAF and ES. The methods were based on the definitions by Malaj et al. (2014) for the water phase, focusing on impacts for specific test species (TU) and the species assemblage (PAF and msPAF). Based on **standard correction** of bioavailability, we estimated the potential toxicity (i.e. TU) at the E(L)C50 level of sediment contamination to *D.magna* and *H. azteca.* The results indicated that *D.magna* and *H. azteca*, exposed to samples from the various rivers (branches) were likely most affected by metals (Figure 5 and 7). The sum of TUs of all substances was repeatedly **less than 1** (Figure 6 and 8). In Spain, ΣTUs at the EC50 level varied between nearly 0 and 5 with large contributions of organophosphate pesticides not analysed in our study (de Castro-Català et al., 2016).

Chemical analysis and ecological surveys. We calculated an average msPAF of 18.5% at the HC50 level in the Netherlands (Table 8), close to a median of about 20% estimated using a much smaller toxicity database (Posthuma and de Zwart, 2012). Apparently, the increase of the number of substances covered by toxicity data did not lead to substantially higher msPAFs. The relationship between msPAF and macrofauna species richness in the field was generally poor (Figure 15). Yet, the fraction of species affected by a >50% abundance change in the field was proportional to the potentially affected fraction msPAF calculated from measured concentrations and toxicity databases (Posthuma and de Zwart, 2012). In addition, the ecological status of European rivers was demonstrated to increase with a decrease of msPAF (Posthuma et al., 2020). Such correlations are increasingly underpinned by mechanistic approaches, relating msPAF to mean species abundance (MSA) and field occurrences (Hoeks et al., 2020, Thunnissen et al., in preparation)

Bioassay calibration of toxic units. As the standard solid-water partitioning K_{sw} does not evidently consider bioavailability and chemical speciation in various physicochemical properties, we focused on refining methods to quantitatively explain and estimate toxicity from sediment bioassays of a given species.

Hyalella azteca. The relationships between TU and measured effects in lab assays **improved substantially** (up to r^2=90%) by a **detailed analysis of chromium, and ammonia availability and toxicity**. For ***H. azteca*****,** the final analyses best elucidated the toxicity of sediments in Flanders and entailed satisfactory predictions with **heavy metals** and **NH_4/NH_3** dominating the TU (Figure 9 and 10). Although Cr and NH_4/NH_3 are toxic on their own, the higher explained variance obtained from the calibrated analysis can be understood from physicochemical **interactions** between Cr and NH_4/NH_3 (Figure 20). Depending on pH, NH_3 volatilises ($NH_4^+ \rightarrow NH_3(\uparrow) + H^+$), producing acid. NH_4^+ concentrations are linked to pH (nitrification) and O_2 (eutrophication). A drop in pH solubilises $Cr^{III}(s)$ (Rifkin, 2004). Moreover, acid can increase the toxicity of Cr^{VI} (Reynolds and Zhitkovich, 2007, Abbasi et al., 2009). By adding a proton to CrO_4^{2-} ($HCrO_4^-$) increases it oxidation potential (Palmer, 1994, Takeno, 2005) ((6) in Figure 20). Apart from pH, NO_3^- and other non-endemic ions (e.g. ~80 mg/L SO_4^{2-} in EPA medium) can solubilize (*(7)* in Figure 20) Cr^{3+} and hence, indirectly CrO_4^{2-} (Equation 7). The high solubility of $Cr^{III}(NO_3^-)_3$, $8.1 \cdot 10^8$ µg/L (compared to 29-76 µg/L or <0.01 µg/L for $Cr^{III}Cl_3$ and $Cr^{III}{}_2O_3$, respectively) might contribute to the apparent higher toxicity of Cr (Wilbur, 2012). NO_3^- (and PO_4^{2-}, SO_4^{2-}) can desorb CrO_4^{2-} via ion exchange ((8) in Figure 20). There was little room to characterise the residual variance in *H. azteca* mortality (Figure 11E) in terms of additional exposure or detailed speciation calculations (i.e. WHAM transfer functions).

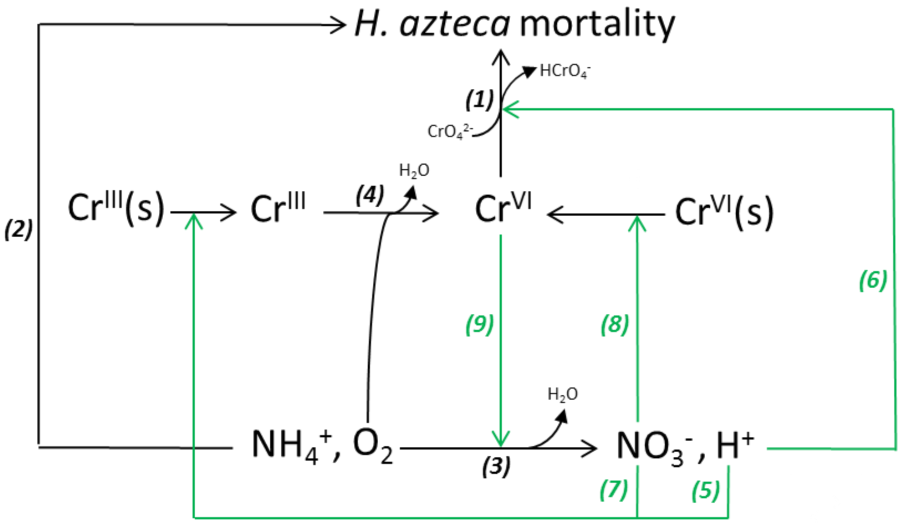


Figure 20. Simplified schematic of chromium chemistry as affected by sediment constituents. Cat denotes clay- or microorganism-based catalysis. Green arrows imply positive feedback.

Heterocypris incongruens. For ***H. incongruens***, the standard error of model prediction (Figure 13) is lower than similar modelling for *H. azteca*. This is likely related to a better-defined testing system and lower physical or metabolic complexity of the organism (De Deckere et al., 2000). The average toxic pressure for *H. incongruens* is comparable to that for *H. azteca*. Both initial and calibrated TU analysis support our hypotheses that NH_3, along with heavy metals, dominate the effects on *H. incongruens*. Yet, in contrast to *H. azteca*, CrO_4^{2-} did not appear to contribute to the apparent toxicity. Instead, organotins (TBT) appeared significantly more toxic to *H. incongruens* probably due to endocrine activity of TBT in crustaceans, in particular interactions with the ecdysteroid receptor – retinoid-X receptor dimer (CrcEcR-CrcRXR) complex (Verhaegen, 2012, Parmentier et al., 2019). The analysis also shows that the **mixture of organotins, NH_3 and HPO_4^{2-}** acts distinctly towards *H. incongruens*, which is partially interpreted as a bioconcentration effect.

In terms of **phosphorous-tin interaction**, extraction of organotins from sediment co-extracts phosphorus compounds (Staniszewska et al., 2008). Plants absorb phosphate; ostracods feed on dead/living plants. Thus, the influence of sediment's organic phosphate on the distribution of TBT in ostracods may relate to dietary assimilation via periphyton (Li et al., 2012, Yavuzatmaca et al., 2017). Prominently, *H. incongruens* accumulates HPO_4^{2-}, hence TBT, via molting. Additionally, the TPT^+ cation sorbs of the onto liposomes via complex formation with phospholipids

(Hunziker et al., 2001). Guanosine-5-monophosphate (G-5-MP) most efficiently forms a competitive organotin complex (Shoukry et al., 2014); as an essential enzyme for cell growth, G-5-MP kinase converts GMP to GDP. Therefore, the interactions with phosphate compounds indicates an effective bioconcentration larger than based on thermodynamic (hydrophobic) maximum ((1) in Figure 21).

In terms of **nitrogen-tin interaction**, NH_3/NH_4 may be converted to NO_2^-/NO_3^- in the aerobic condition (Figure 21), which would be enhanced by bioturbation (Henriksen et al., 1983). Conversion to NO_3^- could contribute to the high apparent γEC50-value of NH_3 (Figure 21). NO_3^- is likely not directly toxic, but metal-nitrates are well-soluble and thus bioavailable (Wilbur, 2012). Heavy metals may influence nitrification (Chovanec et al., 2012, Sangwan et al., 2015). In turn, nitrification and volatilization ($NH_4^+ \rightarrow NH_{3(\uparrow)} + H^+$) affect pH. Changes in pH in sediment/ecotoxicity tests are therefore reported. Surplus H^+ increases the cation concentration and interactions of the TBT metal-type behaviour by complex formation with ligands in phospholipids and proteins (Strand and Jacobsen, 2005, Parmentier et al., 2019) ((2) in Figure 21). NO_3^- and SO_4^{2-} (also in EPA medium) may solubilise organotins. In addition, the relative concentrations of NH_4 and metals may influence the uncoupling of mitochondrial oxidative phosphorylation.

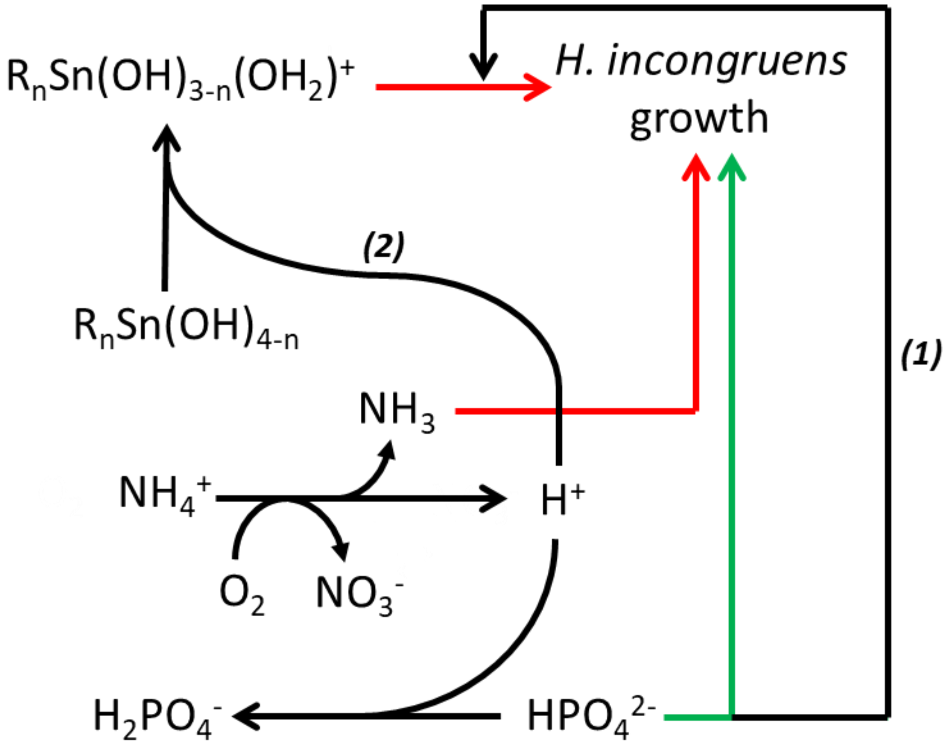


Figure 21. Simplified schematic of interactions between sediment constituents affecting bioassay toxicity. Green and red arrows denote positive and negative effects on *H. incongruens* growth, respectively. According to De Deckere et al. (2000), O_2 ought to remain ≥60% during bioassays.

Redundancy analysis. The ultimate goal of environmental assessment is to provide meaningful information on the impacts of chemical pollution in the field and to support management by identifying the most problematic sites and chemicals. Hence, the RDA-study was undertaken to explore associations between predicted and observed impacts. According to the RDA, only about 18% variance of species assemblage can be explained by the measured chemicals. The results indicate that the variance in species assemblage explained the variability in chemical exposure concentrations to a limited extent, but the effects are not negligible. A previous study showed a similar pattern. De Lange et al. (2004) found that the sediment pollution was the second important factor to explain the variance in the benthic community for a study area, while the most important factor was the habitat characteristics (33%). Predation pressure also appeared to have a specific influence (5%) on community structure. Hence, next to the analysis of chemical mixture effects, the inclusion of multiple stress factors is warranted for understanding impacts of humans on ecosystems.

4.2 Sediment pollution impacts on ecosystem services

So far, the impacts of sediment pollution on a broad range of ESs have not been assessed. Therefore, we proposed a novel methodology for assessing the impacts of chemical mixtures in sediments on ESs using a stepwise approach, based on msPAF(HC50)-diversity-productivity-total ES values relationships. The feasibility and potential utility of the methodology was illustrated by an application to chemical pollution in Dutch and Flemish sediments. Such an economic output could be a necessary component in the cost-benefit analysis regarding waterquality improvement measures. The present study is, to our best knowledge, the first to derive and apply a holistic method to estimate changes in total ES values as a function of changes in chemical pollution indicator (i.e. mixture toxic pressure, msPAF). It should be noted that the derived relationships and the total ES loss estimate in the case study are tentative due to data limitations and uncertainties in each step. Below, we discuss the three main uncertainties of our study, i.e. the msPAF-diversity relationship, diversity-productivity relationship, and productivity-ES value relationship, respectively.

The msPAF-diversity relationship. Toxicity is associated with the fraction of the chemical that is freely bioavailable (i.e. bioavailability), which was roughly approximated via the average binding capacity of metals. Besides, observed toxicity often relates to the different (speciation) forms chemicals can exist in (Vink, 2009). One possible solution for predicting the bioavailability and toxicity of metals in freshwaters is the Biotic Ligand Model (BLM), explaining the effect of water chemistry in metal toxicity (Merrington et al., 2016). However, we envision that a proportion of the variance in the msPAF per biome (Table 8 and 9) characterises uncertainty due to unknown speciation and bioavailability for the whole aquatic community. Additionally, while the ecological relevance of the SSD is being explored by comparisons with community indicators such as diversity (De Vries et al., 2010), relationships in sediments are generally weaker than those in surface water. We assumed a proportional diversity loss of taxa associated with an increase in toxic pressure (i.e. msPAF(HC50)). Yet, it is recommended to test this assumption by a comparison lab experiments and field studies for various mixtures of chemicals.

Diversity-productivity relationship. Regardless of the inherent differences between terrestrial and aquatic ecosystems (e.g. phylogenetic diversity, ecological processes), diversity generally increases with ecosystem productivity, as reported in the present study (Figure 17). In the last few decades, the consequences of diversity loss have become a central issue in the field of ecological and environmental sciences, while experimental work has mainly been carried out in grasslands (Loreau et al., 2001). Early studies have explored two main classes of underlying mechanisms (while contradictory) indicating how diversity promotes productivity. ‘Complementarity effects’ refers to better performance in diverse communities due to niche partitioning and facilitation in shared resource use. ‘Sampling effects’ refers to an increased probability of including highly productive dominant species in more diverse communities. Our study suggested that a 1% diversity loss corresponds to on average 0.35 (0.04 – 1) % productivity loss. This result was consistent with the findings from Costanza et al. (2007), that a 1% change in diversity in warm ecoregions corresponds to a 0.173% change in productivity based on multiple regression analysis at the ecoregion scale in North America. Our study further suggested productivity could increase monotonically with diversity as $P' \sim D'^{\vartheta}$ (ϑ=0.34 in the study), as approximately 50 and 80% of productivity was still maintained at 15% and 50% of pristine species richness, respectively (Figure 17). The result of ϑ was consistent with that reported in other studies, ranging from 0.1 to 0.5 in algae, grasses, shrubs and trees (Liang et al., 2016, Duffy et al., 2017, Chen et al., 2018).

However, it should be noted that the present quantitative diversity-productivity relationships were derived from evidence in terrestrial experiments. While our study showed similar quantitative diversity-productivity patterns in aquatic realms (freshwater, transitional and marine) and observational studies (Figure A1 in Appendices), uncertainties remain. For example, compared to terrestrial systems, aquatic systems are considered more complex due to multitrophic interactions, faster biological processes, greater propagule and material exchange, and often steeper physical and chemical gradients (Giller et al., 2004, Gamfeldt et al., 2015, Daam et al., 2019). As a result, the direct extrapolation of conclusions on diversity effects on productivity from terrestrial experiments might be limited. Besides, positive concave-up diversity-productivity patterns (i.e. exponential) were reported in two large-scale observational studies on deep-sea nematodes and coral reef fishes (Danovaro et al., 2008, Mora et al., 2011). The loss of species is likely to affect the functioning of natural ecosystems more than would be expected from manipulation experiments (Mora et al., 2014). Therefore, given the differences between terrestrial and aquatic ecosystems and differences between experimental and observational studies, further study is still needed to improve our understanding of the mechanisms behind the diversity-productivity relationships across a range of ecosystems, or diversity-ecosystem functioning relationships in general.

Productivity-ES value relationship. The differences in ES values between biomes could be generally explained by the differences in productivity, with higher productivity resulting in higher ES values (this study and others, e.g. Egoh et al. (2008)). Productivity as a proxy for ESs could therefore facilitate and simplify quantitative assessments of ESs, since productivity can be measured through remote sensing over space and time (Costanza et al., 2017). However, we consider our productivity-ES relationship as a necessary but still highly uncertain step in the approach (note the logarithmic axes for both variables in Figure 18). The total ES value for each biome on average varied two orders of magnitude due to the heterogeneity of original data in terms of valuation methods, ES terminologies, and socio-economic characteristics in different locations and periods (De Groot et al., 2012). Besides, for most biomes, less than half of the total number of services (potentially 22 recognised services) were valued (De Groot et al., 2012). Consequently, the total ES value shown in Figure 18 is an underestimate of the economic importance of each biome/ecosystem. Moreover, the economic impacts of polluted sediments were estimated based on the average ES value provided by estuarine or freshwater ecosystems (lakes/rivers, estuaries, and swamps/floodplains). As sediments make up the bottom of these ecosystems, we envision that individual case studies (i.e. the original ES value) considered the essential ecosystem functions of sediments (e.g. habitat provision, flood protection). Nevertheless, in the absence of total ES value specifically for sediments, it is recommended to understand the broad roles of sediments as essential and dynamic components in ecosystems, and to evaluate the ecological benefits of sediments.

To date, ES valuation tends to focus on individual estimates of specific ESs value for a particular biome or ecosystem at local or regional scales for uses such as urban land use planning and specific policy analysis. The individual ES estimates for each biome may reflect the interdependencies among ESs, biome types and valuation methods (Schild et al., 2018). On the other hand, the aggregation of ES values for (global) ecosystems or biomes is also necessary, especially in the case of raising awareness in decision-making processes where trade-offs exist (Costanza et al., 2017). The aggregation of ES values is free from data limitations (e.g. explicit information on ecological and socioeconomic contexts), and is feasible to explore overarching principles. As such, the individual estimates for specific ESs at a local scale and the overall aggregated estimates to a larger scale could supplement each other, allowing for a more comprehensive understanding and assessment on importance of nature to human wellbeing.

Overall, 1% of msPAF(HC50) was estimated to correspond to on average 0.5 (0.05-1.4) % of total ES loss. As our study is the first to assess chemical pollution impacts on ES values, a direct comparison of our methodology and results with other studies is difficult. However, ongoing studies corroborate that approximately one-third of the variability in the ecological status of European surface waters can be attributed to chemical mixtures (Posthuma et al., 2019a). In terms of the magnitude of adverse effects of chemical pollution on ecosystem health, our results are similar to those from Posthuma et al. (2019a). Our methodology could potentially serve as an additional risk assessment tool for informed decisions on water quality management, as the economic outcome is understandable to policymakers given the practical decision context.

4.3 Recommendations and outlook

In the present study, we analysed similarities and discrepancies between chemical, toxicological and ecological measurements and estimates of sediment pollution. These apparent inconsistencies have been theoretically attributed to the limited number of sites, substances, physical-chemical conditions, species, and endpoints covered so far (Chapter 1). From our analysis we conclude that:

1. **Data collection**. Covering more samples, regions, water types, countries and species did not improve correlations.

2. **Data treatment**. Use of recent statistical techniques did not improve correlations.

3. **Chemical modelling**. Estimations of concentrations in (pore-)water, using transfer functions rather than standard correction of sediment did not substantially improve relationships for the data set investigated.

4. **Ecotoxicological modelling**. About 40-90% of the toxicity observed in **single-species lab assays** could be attributed to chemicals regularly monitored. The remaining differences (<10%) are likely caused by a) unidentified substances, such as organophosphates, b) differences in bioavailability and toxicity due to divergent physical-chemical conditions. For the latter, we showed that explained variability increased substantially (from 26% to 90%) by a refined speciation analysis and adaptation of LC50 values, most prominently for chromium, organotin, nitrogen and phosphor. Based on concentrations monitored, we calculated about 20-40% of the species to be affected by substances. As earlier attempts are in the same order, increasing the number of substances with toxicity values apparently did not make a difference. While we could not confirm correlations between PAF and species richness in **multi-species field surveys**, other studies showed estimated and measured fraction of species affected to be proportional to each other. Hence, we proceeded by providing, for the first time in chemical risk assessment, an outline for subsequently relating PAF to diversity, productivity and **ecosystem services**.

Recommendations. To cost-effectively reduce emissions and remediate polluted sediments, one needs to know the substances and sites that contribute most to the fraction of individuals and species affected. In the present study, we developed and applied models to set the right priorities using chemical, toxicological and ecological monitoring across hundreds of sites across two countries. Based on this study, we recommend to:

1. increase the number of **chemical substances** analysed and **possibly** the number of **physical-chemical characteristics** in monitoring programs. In particular, chromium, organotin and organophosphates as well as nitrogen might be included, and more should be included if additional tests confirm their increased contribution to effects. The physical-chemical characteristics measured did not improve relationships between concentrations and effects substances. However, additional characteristics not measured but demonstrated to be important in transfer functions might improve explanations.

2. **identify** the **locally** most problematic substances and sites;

3. cautiously **extrapolate concentrations of chemicals** to **ecosystem services**, empirically underpinning the steps outlined;

4. **assess** water and sediment quality by implementing our approach in analyses tools used in water management.

Management. To facilitate implementation of these recommendations by water management, the website

https://www.ru.nl/environmentalscience/research/themes-0/human-environmental-risk-assessment-hera/models/

provides all underlying data, (beta-versions of) models used, scientific papers, links to related activities (e.g., on water rather than sediment) and videos, so far used in various projects. Specific information on the application in Sullied Sediment is available at

https://www.ru.nl/environmentalscience/research/themes-0/human-environmental-risk-assessment-hera/models/societal-applications-us/sullied-sediments/

We have organised and participated in workshops involving different stakeholders and assist in application and implementation by end-users.

Research. The above-mentioned suggestions for research will be addressed in programmes for the SIMPLEBOX/TREAT and OMEGA models linking chemical emissions to ecological and health effects (See same websites).

5. Conclusions

The North Sea region is one of the most densely populated areas worldwide, encompassing catchments of several large rivers. Sediment pollution has become problematic for navigation, nature development and other interventions in this region. Over the years, risks have been assessed in different ways. Well-standardised chemical detection techniques allow comparison across systems. By contrast, toxicological assays are not routinely applied, involve region-specific testing procedures and include a few species only. Ecological surveys differ even more across regions and over time. Consequently, we aimed to compare and interpret chemical, toxicological and ecological monitoring across countries, authorities and systems based on frequently used modelling tools linking chemical concentrations to biological effects.

Monitoring data were obtained from programs carried out in Flanders and the Netherlands. Based on different approaches, we converted total sediment concentrations to pore water levels. We subsequently translated water concentrations to effects using a database on median effect concentrations (LC50, EC50 and HC50) of 12836 chemicals. The sum of the toxic units $TU = \Sigma C/LC50$ of all substances for a given species was calculated and compared to measured survival in lab assays, indicating that 40-90% of the toxicity could be explained by the substances identified. The explained variation increased from 20% to 90% by fitting chromium, tin, ammonia and phosphate availability and toxicity to field data. We also computed the multi-substance Potentially Affected Fraction at the HC50 level (msPAF(HC50)) and compared this to measured macrofauna abundance from field surveys. For the first time, chemical concentrations were subsequently extrapolated to diversity, productivity and ecosystem services. Based on this study we recommend to 1) add other sediment characteristics and chemical substances to monitoring programmes and to use our models for 2) selecting problematic substances and hotspots, 3) extrapolating to diversity, productivity and ecosystems services providing additional empirical underpinning 4) implement our approach in tools for water and sediment quality assessment based on monitoring data. Implementation of these recommendations is supported by outreach involving end-users and by addressing model improvement in our SIMPLEBOX/TREAT and OMEGA research programs.

6. References

Abbasi, T., Kannadasan, T. & Abbasi, S. A. 2009. A study of the impact of acid rain on chromium toxicity. *International Journal of Environmental Studies,* 66**,** 765–771.

Ankley, G. T., Schubauerberigan, M. K. & Monson, P. D. 1995. Influence of pH and hardness on toxicity of ammonia to the amphipod Hyalella azteca. *Canadian Journal of Fisheries and Aquatic Sciences,* 52**,** 2078-2083.

Apitz, S. E. 2012. Conceptualizing the role of sediment in sustaining ecosystem services: Sediment-ecosystem regional assessment (SEcoRA). *Science of The Total Environment,* 415**,** 9-30.

Ardestani, M. M., Van Straalen, N. M. & Van Gestel, C. A. 2014. Uptake and elimination kinetics of metals in soil invertebrates: a review. *Environmental Pollution,* 193**,** 277-295.

Arenas, F., Rey, F. & Pinto, I. S. 2009. Diversity effects beyond species richness: evidence from intertidal macroalgal assemblages. *Marine Ecology Progress Series,* 381**,** 99-108.

ASTM 1997. Standard test methods for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates. E1706-95b. ASTM annual book of standards, Vol. 11.05, American Society for Testing and Materials, Philadelphia, PA, pp. 1138-1220.

Backhaus, T., Snape, J. & Lazorchak, J. 2012. The impact of chemical pollution on biodiversity and ecosystem services: the need for an improved understanding. *IEAM-Integrated Environmental Assessment and Management,* 8**,** 575.

Balvanera, P., Pfisterer, A. B., Buchmann, N., He, J. S., Nakashizuka, T., Raffaelli, D. & Schmid, B. 2006. Quantifying the evidence for biodiversity effects on ecosystem functioning and services. *Ecology Letters,* 9**,** 1146-1156.

Batley G.E., Stahl R.G., Babut M.P., Bott T.L., Clark J.R., Field L.J., Ho K.T., Mount D.R., Swartz R.C., Tessier A. 2005. Scientific underpinnings of sediment quality guidelines. Pellston Workshop on Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments, SETAC Press: 39-119Berry, W. J., Boothman, W. S., Serbst, J. R. & Edwards, P. A. 2004. Predicting the toxicity of chromium in sediments. *Environmental Toxicology and Chemistry,* 23**,** 2981-2992.

Besser, J. M., Brumbaugh, W. G., Kemble, N. E., May, T. W. & Ingersoll, C. G. 2004. Effects of sediment characteristics on the toxicity of chromium(III) and chromium(VI) to the amphipod, Hyalella azteca. *Environmental Science & Technology,* 38**,** 6210-6216.

Beyer, W. N. M., J.P. 2011. *Environmental Contaminants in Biota: Interpreting Tissue Concentrations*, CRC Press.

Birks, H. J. B., Lotter, A. F., Juggins, S. & Smol, J. P. 2012. *Tracking environmental change using lake sediments: data handling and numerical techniques*, Springer Science & Business Media.

Blunden, S. J. H., L.A.; Smith, P.J. 1984. The environmental chemistry of organotin compounds. *Environmental Chemistry,* 3**,** 49-77.

Bolin, B., Degens, E. T., Kempe, S. & Ketner, P. 1979. Global carbon cycle: SCOPE 13. John Wiley and Sons, New York, NY.

Bootsma, H. P. & Vink, J. P. M. 2016. Simple equations for the calculation of free metal ion activities in surface waters. Deltares report 1210758, Utrecht, The Netherlands.

Borgmann, U., Couillard, Y., Doyle, P. & Dixon, D. G. 2005. Toxicity of sixty-three metals and metalloids to Hyalella azteca at two levels of water hardness. *Environmental Toxicology and Chemistry,* 24**,** 641-652.

Boyer, K. E., Kertesz, J. S. & Bruno, J. F. 2009. Biodiversity effects on productivity and stability of marine macroalgal communities: the role of environmental context. *Oikos,* 118**,** 1062-1072.

Brouwer, R., Brander, L., Kuik, O., Papyrakis, E. & Bateman, I. 2013. A synthesis of approaches to assess and value ecosystem services in the EU in the context of TEEB. *VU University Amsterdam*.

Bruno, J. F., Boyer, K. E., Duffy, J., Lee, S. C. & Kertesz, J. S. 2005. Effects of macroalgal species identity and richness on primary production in benthic marine communities. *Ecology Letters,* 8**,** 1165-1174.

Bullock, J. M., Pywell, R. F., Burke, M. J. & Walker, K. J. 2001. Restoration of biodiversity enhances agricultural production. *Ecology Letters,* 4**,** 185-189.

Caldeira, M. C., Ryel, R. J., Lawton, J. H. & Pereira, J. S. 2001. Mechanisms of positive biodiversity–production relationships: insights provided by δ13C analysis in experimental Mediterranean grassland plots. *Ecology Letters,* 4**,** 439-443.

Callaway, J. C., Sullivan, G. & Zedler, J. B. 2003. Species‐rich plantings increase biomass and nitrogen accumulation in a wetland restoration experiment. *Ecological Applications,* 13**,** 1626-1639.

Cardinale, B. J., Srivastava, D. S., Duffy, J. E., Wright, J. P., Downing, A. L., Sankaran, M. & Jouseau, C. 2006. Effects of biodiversity on the functioning of trophic groups and ecosystems. *Nature,* 443**,** 989.

Chapman, P. M. 1989. Current approaches to developing sediment quality criteria. *Environmental Toxicology and Chemistry: An International Journal,* 8**,** 589-599.

Chapman, P. M. 1990. The sediment quality triad approach to determining pollution-induced degradation. *Science of The Total Environment,* 97**,** 815-825.

Chapman, P. M. & Mcdonald, B. G. 2005. Using the sediment quality triad (SQT) in ecological risk assessment. *Small-scale freshwater toxicity investigations.* Springer.

Chen, S., Wang, W., Xu, W., Wang, Y., Wan, H., Chen, D., Tang, Z., Tang, X., Zhou, G. & Xie, Z. 2018. Plant diversity enhances productivity and soil carbon storage. *Proceedings of the National Academy of Sciences,* 115**,** 4027-4032.

Chovanec, P., Sparacino-Watkins, C., Zhang, N., Basu, P. & Stolz, J. F. 2012. Microbial reduction of chromate in the presence of nitrate by three nitrate respiring organisms. *Frontiers in Microbiology,* 3.

Costanza, R., D'arge, R., De Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., O'neill, R. V. & Paruelo, J. 1997. The value of the world's ecosystem services and natural capital. *Nature,* 387**,** 253.

Costanza, R., D’arge, R., De Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., O’neill, R. V. & Paruelo, J. 1998. The value of ecosystem services: putting the issues in perspective. *Ecological Economics,* 25**,** 67-72.

Costanza, R., De Groot, R., Braat, L., Kubiszewski, I., Fioramonti, L., Sutton, P., Farber, S. & Grasso, M. 2017. Twenty years of ecosystem services: how far have we come and how far do we still need to go? *Ecosystem Services,* 28**,** 1-16.

Costanza, R., De Groot, R., Sutton, P., Van Der Ploeg, S., Anderson, S. J., Kubiszewski, I., Farber, S. & Turner, R. K. 2014. Changes in the global value of ecosystem services. *Global Environmental Change,* 26**,** 152-158.

Costanza, R., Fisher, B., Mulder, K., Liu, S. & Christopher, T. 2007. Biodiversity and ecosystem services: A multi-scale empirical study of the relationship between species richness and net primary production. *Ecological Economics,* 61**,** 478-491.

Crommentuijn, T., Polder, M. & Van De Plassche, E. J. 1997. Maximum permissible concentrations and negligible concentrations for metals, taking background concentrations into account.

Crommentuijn, T. P., M.D.; Van De Plassche, E.J. 1997. Maximum Permissible Concentrations and Negligible Concentrations for metals, taking background concentrations into account. Bilthoven, the Netherlands: National Institute of Public Health and the Environment.

Daam, M. A., Teixeira, H., Lillebø, A. I. & Nogueira, A. J. 2019. Establishing causal links between aquatic biodiversity and ecosystem functioning: Status and research needs. *Science of The Total Environment,* 656**,** 1145-1156.

Danovaro, R., Gambi, C., Dell'anno, A., Corinaldesi, C., Fraschetti, S., Vanreusel, A., Vincx, M. & Gooday, A. J. 2008. Exponential decline of deep-sea ecosystem functioning linked to benthic biodiversity loss. *Current Biology,* 18**,** 1-8.

De Bruijn, J. H. M. & Denneman, C. a. J. 1992. Achtergrondgehalten van negen sporen-metalen in oppervlaktewater, grondwater en grond van Nederland.

De Castro-Català, N., Kuzmanovic, M., Roig, N., Sierra, J., Ginebreda, A., Barceló, D., Pérez, S., Petrovic, M., Picó, Y. & Schuhmacher, M. 2016. Ecotoxicity of sediments in rivers: Invertebrate community, toxicity bioassays and the toxic unit approach as complementary assessment tools. *Science of The Total Environment,* 540**,** 297-306.

De Deckere, E., De Cooman, W., Florus, M. & Devroede-Vanderlinden, M. 2000. Handboek voor de karakterisatie van de bodems van de Vlaamse waterlopen, volgens de Triade, 2de versie (Guidance document for characterisation of Flemish waters according to the Triad, 2nd version–in Dutch). *Ministerie van de Vlaamse Gemeenschap, AMINAL/afdeling Water, Brussel*.

De Deckere, E., De Cooman, W., Leloup, V., Meire, P., Schmitt, C. & Peter, C. 2011. Development of sediment quality guidelines for freshwater ecosystems. *Journal of Soils and Sediments,* 11**,** 504-517.

De Groot, R., Brander, L., Van Der Ploeg, S., Costanza, R., Bernard, F., Braat, L., Christie, M., Crossman, N., Ghermandi, A. & Hein, L. 2012. Global estimates of the value of ecosystems and their services in monetary units. *Ecosystem Services,* 1**,** 50-61.

De Lange, H. J., De Jonge, J., Den Besten, P. J., Oosterbaan, J. & Peeters, E. T. H. M. 2004. Sediment pollution and predation affect structure and production of benthic macroinvertebrate communities in the Rhine–Meuse delta, The Netherlands. *Journal of the North American Benthological Society,* 23**,** 557-579.

De Vries, P., Smit, M. G., Van Dalfsen, J. A., De Laender, F. & Karman, C. C. 2010. Consequences of stressor‐induced changes in species assemblage for biodiversity indicators. *Environmental Toxicology and Chemistry,* 29**,** 1868-1876.

De Zwart, D. & Posthuma, L. 2005. Complex mixture toxicity for single and multiple species: Proposed methodologies. *Environmental Toxicology and Chemistry,* 24**,** 2665-2676.

Del Grosso, S., Parton, W., Stohlgren, T., Zheng, D., Bachelet, D., Prince, S., Hibbard, K. & Olson, R. 2008. Global potential net primary production predicted from vegetation class, precipitation, and temperature. *Ecology,* 89**,** 2117-2126.

Delgado-Baquerizo, M., Maestre, F. T., Reich, P. B., Jeffries, T. C., Gaitan, J. J., Encinar, D., Berdugo, M., Campbell, C. D. & Singh, B. K. 2016. Microbial diversity drives multifunctionality in terrestrial ecosystems. *Nature Communications,* 7**,** 10541.

Den Besten, P., Schmidt, C., Ohm, M., Ruys, M., Van Berghem, J. & Van De Guchte, C. 1995. Sediment quality assessment in the delta of rivers Rhine and Meuse based on field observations, bioassays and food chain implications. *Journal of Aquatic Ecosystem Health,* 4**,** 257-270.

Den Besten, P. J., De Deckere, E., Babut, M. P., Power, B., Delvalls, T. A., Zago, C., Oen, A. M. & Heise, S. 2003. Biological effects-based sediment quality in ecological risk assessment for European waters. *Journal of Soils and Sediments,* 3**,** 144.

Dimitrakopoulos, P. G. & Schmid, B. 2004. Biodiversity effects increase linearly with biotope space. *Ecology Letters,* 7**,** 574-583.

Downing, A. L. & Leibold, M. A. 2002. Ecosystem consequences of species richness and composition in pond food webs. *Nature,* 416**,** 837.

Duffy, J. E., Godwin, C. M. & Cardinale, B. J. 2017. Biodiversity effects in the wild are common and as strong as key drivers of productivity. *Nature,* 549**,** 261.

Duffy, J. E., Lefcheck, J. S., Stuart-Smith, R. D., Navarrete, S. A. & Edgar, G. J. 2016. Biodiversity enhances reef fish biomass and resistance to climate change. *Proceedings of the National Academy of Sciences,* 113**,** 6230-6235.

Duffy, J. E., Macdonald, K. S., Rhode, J. M. & Parker, J. D. 2001. Grazer diversity, functional redundancy, and productivity in seagrass beds: an experimental test. *Ecology,* 82**,** 2417-2434.

Dukes, J. S. 2001. Productivity and complementarity in grassland microcosms of varying diversity. *Oikos,* 94**,** 468-480.

Durand-Huiting, A. M. 2001. Technische documentatie OMEGA123 en OMEGA45. Werkdocument 99-174X, Institute for Inland Water Management and Waste Water Treatment RIZA, Lelystad, the Netherlands.

Durand-Huiting, A. M. 2004. Handleiding en achtergronden OMEGA 6.0. Werkdocument 2004.132X, Institute for Inland Water Management and Waste Water Treatment RIZA, Lelystad, the Netherlands.

Egoh, B., Reyers, B., Rouget, M., Richardson, D. M., Le Maitre, D. C. & Van Jaarsveld, A. S. 2008. Mapping ecosystem services for planning and management. *Agriculture, Ecosystems & Environment,* 127**,** 135-140.

Emmett Duffy, J., Paul Richardson, J. & Canuel, E. A. 2003. Grazer diversity effects on ecosystem functioning in seagrass beds. *Ecology letters,* 6**,** 637-645.

Engelhardt, K. A. & Kadlec, J. A. 2001. Species traits, species richness and the resilience of wetlands after disturbance. *Journal of Aquatic Plant Management,* 39**,** 36-39.

Engelhardt, K. A. & Ritchie, M. E. 2001. Effects of macrophyte species richness on wetland ecosystem functioning and services. *Nature,* 411**,** 687.

Fang, L. P., Borggaard, O. K., Christensen, J. H., Holm, P. E. & Hansen, H. C. B. 2012. Adsorption of mono- and di-butyltin by a wheat charcoal: pH effects and modeling. *Chemosphere,* 89**,** 863-868.

Fent, K. 1996. Ecotoxicology of organotin compounds. *Critical Reviews in Toxicology,* 26**,** 3-117.

Fridley, J. D. 2002. Resource availability dominates and alters the relationship between species diversity and ecosystem productivity in experimental plant communities. *Oecologia,* 132**,** 271-277.

Fridley, J. D. 2003. Diversity effects on production in different light and fertility environments: an experiment with communities of annual plants. *Journal of Ecology,* 91**,** 396-406.

Gamfeldt, L., Hillebrand, H. & Jonsson, P. 2005. Species richness changes across two trophic levels simultaneously affect prey and consumer biomass. *Ecology Letters,* 8**,** 696-703.

Gamfeldt, L., Lefcheck, J. S., Byrnes, J. E., Cardinale, B. J., Duffy, J. E. & Griffin, J. N. 2015. Marine biodiversity and ecosystem functioning: what's known and what's next? *Oikos,* 124**,** 252-265.

Gamfeldt, L., Snäll, T., Bagchi, R., Jonsson, M., Gustafsson, L., Kjellander, P., Ruiz-Jaen, M. C., Fröberg, M., Stendahl, J. & Philipson, C. D. 2013. Higher levels of multiple ecosystem services are found in forests with more tree species. *Nature Communications,* 4**,** 1340.

Giller, P., Hillebrand, H., Berninger, U. G., O. Gessner, M., Hawkins, S., Inchausti, P., Inglis, C., Leslie, H., Malmqvist, B. & T. Monaghan, M. 2004. Biodiversity effects on ecosystem functioning: emerging issues and their experimental test in aquatic environments. *Oikos,* 104**,** 423-436.

Grace, J. B., Anderson, T. M., Seabloom, E. W., Borer, E. T., Adler, P. B., Harpole, W. S., Hautier, Y., Hillebrand, H., Lind, E. M. & Pärtel, M. 2016. Integrative modelling reveals mechanisms linking productivity and plant species richness. *Nature,* 529**,** 390.

Griffin, J. N., Méndez, V., Johnson, A. F., Jenkins, S. R. & Foggo, A. 2009. Functional diversity predicts overyielding effect of species combination on primary productivity. *Oikos,* 118**,** 37-44.

Haddad, H. H. 2012. The Effect of Heavy Metals Cadimium, Chromium and Iron Accumulation in Human Eyes. *American Journal of Analytical Chemistry,* 3**,** 710-713.

Harvey, E., Séguin, A., Nozais, C., Archambault, P. & Gravel, D. 2013. Identity effects dominate the impacts of multiple species extinctions on the functioning of complex food webs. *Ecology,* 94**,** 169-179.

Hassan, S. M. & Garrison, A. W. 1996. Distribution of chromium species between soil and porewater. *Chemical Speciation and Bioavailability,* 8**,** 85-103.

He, J.-S., Wolfe-Bellin, K. S., Schmid, B. & Bazzaz, F. 2005. Density may alter diversity–productivity relationships in experimental plant communities. *Basic and Applied Ecology,* 6**,** 505-517.

Hector, A., Schmid, B., Beierkuhnlein, C., Caldeira, M., Diemer, M., Dimitrakopoulos, P., Finn, J., Freitas, H., Giller, P. & Good, J. 1999. Plant diversity and productivity experiments in European grasslands. *Science,* 286**,** 1123-1127.

Hendriks, A. J., Traas, T. P. & Huijbregts, M. a. J. 2005. Critical Body Residues Linked to Octanol−Water Partitioning, Organism Composition, and LC50 QSARs: Meta-analysis and Model. *Environmental Science & Technology,* 39**,** 3226-3236.

Hendriks, A. J. & Van De Guchte, K. 1997. Optimal modeling and monitoring in ecotoxicological assessments: Choosing instruments for applied research and management with examples from the Rhine - Meuse delta. *Environmental Toxicology and Water Quality: An International Journal,* 12**,** 321-333.

Hendriks, A. J., Van Der Linde, A., Cornelissen, G. & Sijm, D. T. 2001. The power of size. 1. Rate constants and equilibrium ratios for accumulation of organic substances related to octanol-water partition ratio and species weight. *Environmental Toxicology and Chemistry: An International Journal,* 20**,** 1399-1420.

Hendriks, A. J. & Van Straalen, N. M. 2019. 5.5 Population models. *Environmental Toxicology, an open online textbook.*

Henriksen, K., Rasmussen, M. B. & Jensen, A. 1983. Effect of Bioturbation on Microbial Nitrogen Transformations in the Sediment and Fluxes of Ammonium and Nitrate to the Overlaying Water. *Ecological Bulletins***,** 193-205.

Hin, J., Osté, L. & Schmidt, C. 2010. Guidance document for sediment assessment: methods to determine to what extent the realization of water quality objectives of a water system is impeded by contaminated sediments. *Dutch Ministry of Infrastructure and the Environment–DG Water*.

Hoeks, S., Huijbregts, M. A., Douziech, M., Jan Hendriks, A. & Oldenkamp, R. 2020. Mean Species Abundance as a Measure of Ecotoxicological Risk. *Environmental Toxicology and Chemistry*.

Hooper, D. U. & Vitousek, P. M. 1997. The effects of plant composition and diversity on ecosystem processes. *Science,* 277**,** 1302-1305.

Hu, Y. T., Chen, N., Li, M., Feng, C. P. & Liu, T. 2019. Insights into simultaneous microbial chromium and nitrate reduction: inhibitory effects and molecular mechanisms. *Journal of Chemical Technology and Biotechnology,* 94**,** 2589-2596.

Hunziker, R. W., Escher, B. I. & Schwarzenbach, R. P. 2001. pH dependence of the partitioning of triphenyltin and tributyltin between phosphatidylcholine liposomes and water. *Environmental Science & Technology,* 35**,** 3899-3904.

ISO 14371 2012. Water quality - Determination of fresh water sediment toxicity to Heterocypris incongruens (Crustacea, Ostracoda).

Jing, X., Sanders, N. J., Shi, Y., Chu, H., Classen, A. T., Zhao, K., Chen, L., Shi, Y., Jiang, Y. & He, J.-S. 2015. The links between ecosystem multifunctionality and above-and belowground biodiversity are mediated by climate. *Nature Communications,* 6**,** 8159.

Karanovic, I. 2012. *Recent Freshwater Ostracods of the World: Crustacea, Ostracoda, Podocopida,* Heidelberg, Springer.

Karickhoff, S. W., Brown, D. S. & Scott, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research,* 13**,** 241-248.

Kenkel, N., Kenkel, N., Peltzer, D., Peltzer, D., Baluta, D., Baluta, D., Pirie, D. & Pirie, D. 2001. Increasing plant diversity does not influence productivity: empirical evidence and potential mechanisms. *Community Ecology,* 1**,** 165-170.

Kim, S., Thiessen, P. A., Bolton, E. E., Chen, J., Fu, G., Gindulyte, A., Han, L., He, J., He, S. & Shoemaker, B. A. 2016. PubChem substance and compound databases. *Nucleic Acids Research,* 44**,** D1202-D1213.

Knoben, R., Beek, M. & Durand, A. 1998. Application of species sensitivity distributions as ecological risk assessment tool for water management. *Journal of Hazardous Materials,* 61**,** 203-207.

Knoben, R. & Snijders, J. 2010. *Instructie voor het omgaan met normoverschrijdingen van metalen en andere microverontreinigingen in oppervlaktewater*, Royal Haskoning.

Laane, R., Van De Meent, D., De Voogt, P., Parsons, J., Hendriks, J. & Van Gils, J. 2011. Modeling organic compounds in the estuarine and coastal environment.

Langenheder, S., Bulling, M. T., Solan, M. & Prosser, J. I. 2010. Bacterial biodiversity-ecosystem functioning relations are modified by environmental complexity. *PloS One,* 5**,** e10834.

Lanta, V. & Lepš, J. 2006. Effect of functional group richness and species richness in manipulated productivity–diversity studies: a glasshouse pot experiment. *Acta Oecologica,* 29**,** 85-96.

Lee, J. H., Landrum, P. F., Field, L. J. & Koh, C. H. 2001. Application of a sigmapolycyclic aromatic hydrocarbon model and a logistic regression model to sediment toxicity data based on a species-specific, water-only LC50 toxic unit for Hyalella azteca. *Environmental Toxicology and Chemistry,* 20**,** 2102-13.

Li, M. L., Costello, D. M. & Burton, G. A. 2012. Interactive effects of phosphorus and copper on Hyalella azteca via periphyton in aquatic ecosystems. *Ecotoxicology and Environmental Safety,* 83**,** 41-46.

Liang, J., Crowther, T. W., Picard, N., Wiser, S., Zhou, M., Alberti, G., Schulze, E.-D., Mcguire, A. D., Bozzato, F. & Pretzsch, H. 2016. Positive biodiversity-productivity relationship predominant in global forests. *Science,* 354**,** aaf8957.

Loreau, M., Naeem, S., Inchausti, P., Bengtsson, J., Grime, J., Hector, A., Hooper, D., Huston, M., Raffaelli, D. & Schmid, B. 2001. Biodiversity and ecosystem functioning: current knowledge and future challenges. *Science,* 294**,** 804-808.

Maas, J., Van De Guchte, C. & Kerkum, F. 1993. Methods for the assessment of contaminated sediments according to the Triad approach. Report 93.027, Institute for Inland Water Management and Waste Water Treatment (RIZA), Lelystad, The Netherlands (in Dutch), 74pp.

Mackay, D., Shiu, W., Ma, K. & Lee, S. 2006. *Handbook of physical-chemical properties and enviornmental fate for organic chemicals,* Boca Raton, USA, CRC Press Inc.

Maestre, F. T., Quero, J. L., Gotelli, N. J., Escudero, A., Ochoa, V., Delgado-Baquerizo, M., García-Gómez, M., Bowker, M. A., Soliveres, S. & Escolar, C. 2012. Plant species richness and ecosystem multifunctionality in global drylands. *Science,* 335**,** 214-218.

Malaj, E., Peter, C., Grote, M., Kühne, R., Mondy, C. P., Usseglio-Polatera, P., Brack, W. & Schäfer, R. B. 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. *Proceedings of the National Academy of Sciences,* 111**,** 9549-9554.

Meador, J. P. 2000. Predicting the fate and effects of tributyltin in marine systems: Section IV. Bioaccumulation A. Tissue-Water Partitioning. *In:* WARE, G. W. (ed.) *Reviews of Environmental Contamination and Toxicology* New York, USA: Springer.

Mellinger, M. V. & Mcnaughton, S. 1975. Structure and function of successional vascular plant communities in central New York. *Ecological Monographs,* 45**,** 161-182.

Merrington, G., Peters, A. & Schlekat, C. E. 2016. Accounting for metal bioavailability in assessing water quality: A step change? *Environmental Toxicology and Chemistry,* 35**,** 257-265.

Mikola, J., Salonen, V. & Setälä, H. 2002. Studying the effects of plant species richness on ecosystem functioning: does the choice of experimental design matter? *Oecologia,* 133**,** 594-598.

Millennium Ecosystem Assessment 2005. *Ecosystems and human well-being*, Island press Washington, DC.

Mohamed, M., Mohamed, A. & Shoukry, M. M. 2001. Interaction of diphenyltin(IV) dichloride with some selected bioligands. *Chemical & Pharmaceutical Bulletin,* 49**,** 253-257.

Mora, C., Aburto-Oropeza, O., Bocos, A. A., Ayotte, P. M., Banks, S., Bauman, A. G., Beger, M., Bessudo, S., Booth, D. J. & Brokovich, E. 2011. Global human footprint on the linkage between biodiversity and ecosystem functioning in reef fishes. *PLoS Biology,* 9**,** e1000606.

Mora, C., Danovaro, R. & Loreau, M. 2014. Alternative hypotheses to explain why biodiversity-ecosystem functioning relationships are concave-up in some natural ecosystems but concave-down in manipulative experiments. *Scientific Reports,* 4**,** 5427.

Mori, A. S. 2018. Environmental controls on the causes and functional consequences of tree species diversity. *Journal of Ecology,* 106**,** 113-125.

Mulder, C., Uliassi, D. & Doak, D. 2001. Physical stress and diversity-productivity relationships: the role of positive interactions. *Proceedings of the National Academy of Sciences,* 98**,** 6704-6708.

Naeem, S., Hahn, D. R. & Schuurman, G. 2000. Producer–decomposer co-dependency influences biodiversity effects. *Nature,* 403**,** 762.

Naeem, S., Naeem, S., Thompson, L. J., Lawler, S. P., Lawton, J. H. & Woodfin, R. M. 1995. Empirical evidence that declining species diversity may alter the performance of terrestrial ecosystems. *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences,* 347**,** 249-262.

Norberg, J. 2000. Resource-niche complementarity and autotrophic compensation determines ecosystem-level responses to increased cladoceran species richness. *Oecologia,* 122**,** 264-272.

O'gorman, E. J., Enright, R. A. & Emmerson, M. C. 2008. Predator diversity enhances secondary production and decreases the likelihood of trophic cascades. *Oecologia,* 158**,** 557-567.

Oecd 1984. OECD guideline for testing of chemicals 201: Alga, growth inhibition test. Paris, France: Organisation of Economic Cooperation and Development.

Oguma, A. Y. & Klerks, P. L. 2020. Comparisons Between Laboratory Sediment Toxicity Test Results and Assessment of Benthic Community Changes for a Lake with Mild Metal Contamination. *Archives of Environmental Contamination and Toxicology,* 78**,** 106-116.

Palmer, C. D. P., R.W. 1994. Natural Attenuation of Hexavalent Chromium in Groundwater and Soils. EPA.

Panda, S. K. C., S. 2005. Chromium stress in plants. *Brazilian Journal of Plant Physiology,* 17**,** 95-102.

Parmentier, K. F., Verhaegen, Y. a. M., De Witte, B., Hoffman, S., Delbare, D. H., Roose, P. M., Hylland, K. D., Burgeot, T., Smagghe, G. J. & Cooreman, K. 2019. Tributyltin: a Bottom-up Regulator of the Crangon crangon Population? *Frontiers in Marine Science,* 6**,** 633.

Pfisterer, A. B. & Schmid, B. 2002. Diversity-dependent production can decrease the stability of ecosystem functioning. *Nature,* 416**,** 84.

Poorter, L., Van Der Sande, M., Thompson, J., Arets, E., Alarcón, A., lvarez‐Sánchez, J., Ascarrunz, N., Balvanera, P., Barajas‐Guzmán, G. & Boit, A. 2015. Diversity enhances carbon storage in tropical forests. *Global Ecology and Biogeography,* 24**,** 1314-1328.

Posthuma L, De Zwart D, Osté L, Van Der Oost R & J, P. 2016a. Ecologische Sleutelfactor Toxiciteit. Deel 1: Methode voor het in beeld brengen van de effecten van giftige stoffen in oppervlaktewater. *STOWA rapport.*

Posthuma L, De Zwart D, Van Der Oost R & J, P. 2016b. Ecologische Sleutelfactor Toxiciteit. Deel 3: Technische handleiding en tips Esf-toxiciteit chemie tool. *STOWA rapport.*

Posthuma, L., Brack, W., Van Gils, J., Focks, A., Müller, C., De Zwart, D. & Birk, S. 2019a. Mixtures of chemicals are important drivers of impacts on ecological status in European surface waters. *Environmental Sciences Europe,* 31**,** 71.

Posthuma, L. & De Zwart, D. 2012. Predicted mixture toxic pressure relates to observed fraction of benthic macrofauna species impacted by contaminant mixtures. *Environmental Toxicology and Chemistry,* 31**,** 2175-2188.

Posthuma, L., De Zwart, D., Keijzers, R. & Postma, J. 2016. Ecologische Sleutelfactor Toxiciteit. Deel 2: Kalibratie: toxische druk en ecologische effecten op macrofauna. *STOWA rapport.*

Posthuma, L., Van Gils, J., Zijp, M. C., Van De Meent, D. & De Zwart, D. 2019b. Species sensitivity distributions for use in environmental protection, assessment, and management of aquatic ecosystems for 12 386 chemicals. *Environmental Toxicology and Chemistry,* 38**,** 905-917.

Posthuma, L., Zijp, M. C., De Zwart, D., Van De Meent, D., Globevnik, L., Koprivsek, M., Focks, A., Van Gils, J. & Birk, S. 2020. Chemical pollution imposes limitations to the ecological status of European surface waters. *Scientific Reports,* 10**,** 14825.

Postma, J. F. & Den Besten, P. 2001. *Biotisch effectonderzoek Sliedrechtse Biesbosch: nader onderzoek waterbodemkwaliteit*, Directoraat-Generaal Rijkswaterstaat, RIZA Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling.

Pusceddu, A., Gambi, C., Corinaldesi, C., Scopa, M. & Danovaro, R. 2014. Relationships between meiofaunal biodiversity and prokaryotic heterotrophic production in different tropical habitats and oceanic regions. *PLoS One,* 9**,** e91056.

Reinhold-Dudok, H. & Den Besten, H. P. 1999. The relation between macroinvertebrate assemblages in the Rhine-Meuse delta (The Netherlands) and sediment quality. *Aquatic Ecosystem Health & Management,* 2**,** 19-38.

Reynolds, M. & Zhitkovich, A. 2007. Cellular vitamin C increases chromate toxicity via a death program requiring mismatch repair but not p53. *Carcinogenesis,* 28**,** 1613-1620.

Rifkin, E. G., P.; Bouwer, E. 2004. Chromium and Sediment Toxicity. *Environmental Science & Technology***,** 267-271.

Rosales, R. M., Faz, A., Gomez-Garrido, M., Munoz, M. A., Murcia, F. J., Gonzalez, V. & Acosta, J. A. 2017. Geochemical speciation of chromium related to sediments properties in the riverbed contaminated by tannery effluents. *Journal of Soils and Sediments,* 17**,** 1437-1448.

Ruiz‐Benito, P., Gómez‐Aparicio, L., Paquette, A., Messier, C., Kattge, J. & Zavala, M. A. 2014. Diversity increases carbon storage and tree productivity in S panish forests. *Global Ecology and Biogeography,* 23**,** 311-322.

Sangwan, P., Kumar, V., Gulati, D. & Joshi, U. N. 2015. Interactive effects of salicylic acid on enzymes of nitrogen metabolism in clusterbean (Cyamopsis tetragonoloba L.) under chromium(VI) toxicity. *Biocatalysis and Agricultural Biotechnology,* 4**,** 309-314.

Schild, J. E., Vermaat, J. E. & Van Bodegom, P. M. 2018. Differential effects of valuation method and ecosystem type on the monetary valuation of dryland ecosystem services: A quantitative analysis. *Journal of Arid Environments,* 159**,** 11-21.

Schoorl, M., Hollander, A. & Van De Meent, D. 2015. SimpleBox 4.0: A multimedia mass balance model for evaluating the fate of chemical substances. RIVM Report 2015-0161. National Institute for Public Health and the Environment, Bilthoven, The Netherlands.

Shoukry, M. M., Al-Alousi, A. & Tarek, S. M. 2014. Diorganotin(IV) Complexes with Methionine Methyl Ester. Equilibria and Displacement by DNA Constituents. *South African Journal of Chemistry-Suid-Afrikaanse Tydskrif Vir Chemie,* 67**,** 94-98.

Small, C. & Cohen, J. 2004. Continental physiography, climate, and the global distribution of human population. *Current Anthropology,* 45**,** 269-277.

Spehn, E., Hector, A., Joshi, J., Scherer-Lorenzen, M., Schmid, B., Bazeley-White, E., Beierkuhnlein, C., Caldeira, M., Diemer, M. & Dimitrakopoulos, P. 2005. Ecosystem effects of biodiversity manipulations in European grasslands. *Ecological Monographs,* 75**,** 37-63.

Sprague, J. B. 1970. Measurement of pollutant toxicity to fish. II. Utilizing and applying bioassay results. *Water Research,* 4**,** 3-32.

Stadnicka, J., Schirmer, K. & Ashauer, R. 2012. Predicting concentrations of organic chemicals in fish by using toxicokinetic models. *Environmental Science & Technology,* 46**,** 3273-3280.

Staniszewska, M., Radke, B., Namiesnik, J. & Bolalek, J. 2008. Analytical methods and problems related to the determination of organotin compounds in marine sediments. *International Journal of Environmental Analytical Chemistry,* 88**,** 747-774.

Stevens, M. H. H. & Carson, W. P. 2001. Phenological complementarity, species diversity, and ecosystem function. *Oikos,* 92**,** 291-296.

Strand, J. & Jacobsen, J. A. 2005. Accumulation and trophic transfer of organotins in a marine food web from the Danish coastal waters. *Science of the Total Environment,* 350**,** 72-85.

Symstad, A. J., Tilman, D., Willson, J. & Knops, J. M. 1998. Species loss and ecosystem functioning: effects of species identity and community composition. *Oikos***,** 389-397.

Takeno, N. 2005. Atlas of Eh-pH diagrams - Intercomparison of thermodynamic databases. *Geological Survey of Japan Open File Report No.419.* National Institute of Advanced Industrial Science and Technology - Research Center for Deep Geological Environments.

Thompson, P. L., Davies, T. J. & Gonzalez, A. 2015. Ecosystem functions across trophic levels are linked to functional and phylogenetic diversity. *PLoS One,* 10**,** e0117595.

Thunnissen, N. W., Geurts, K. A. G. & Hendriks, A. J. in preparation. The impact of imidacloprid and thiacloprid on the mean species abundance in aquatic ecosystems.

Tilman, D., Knops, J., Wedin, D., Reich, P., Ritchie, M. & Siemann, E. 1997. The influence of functional diversity and composition on ecosystem processes. *Science,* 277**,** 1300-1302.

Tilman, D., Wedin, D. & Knops, J. 1996. Productivity and sustainability influenced by biodiversity in grassland ecosystems. *Nature,* 379**,** 718.

Traas, T. P., Janse, J. H., Van Den Brink, P. J., Brock, T. C. & Aldenberg, T. 2004. A freshwater food web model for the combined effects of nutrients and insecticide stress and subsequent recovery. *Environmental Toxicology and Chemistry: An International Journal,* 23**,** 521-529.

Troumbis, A. Y., Dimitrakopoulos, P. G., Siamantziouras, A. S. D. & Memtsas, D. 2000. Hidden diversity and productivity patterns in mixed Mediterranean grasslands. *Oikos,* 90**,** 549-559.

Troumbis, A. Y. & Memtsas, D. 2000. Observational evidence that diversity may increase productivity in Mediterranean shrublands. *Oecologia,* 125**,** 101-108.

Tylianakis, J. M., Rand, T. A., Kahmen, A., Klein, A.-M., Buchmann, N., Perner, J. & Tscharntke, T. 2008. Resource heterogeneity moderates the biodiversity-function relationship in real world ecosystems. *PLoS Biology,* 6**,** e122.

U.S. EPA. 2019. *ECOTOX Database* [Online]. Available: http://cfub.epa.gov/ecotox/ [Accessed February 13, 2020.

Van De Guchte, C. 1992. The sediment quality triad: an integrated approach to assess contaminated sediments. *River Water Quality. Ecological Assessment and Control. ECSC EEC EAEC, Brussels Luxembourg***,** 425.

Van Der Kooij, L., Van De Meent, D., Van Leeuwen, C. & Bruggeman, W. 1991. Deriving quality criteria for water and sediment from the results of aquatic toxicity tests and product standards: application of the equilibrium partitioning method. *Water Research,* 25**,** 697-705.

Van Ruijven, J. & Berendse, F. 2003. Positive effects of plant species diversity on productivity in the absence of legumes. *Ecology Letters,* 6**,** 170-175.

Van Ruijven, J. & Berendse, F. 2005. Diversity–productivity relationships: initial effects, long-term patterns, and underlying mechanisms. *Proceedings of the National Academy of Sciences,* 102**,** 695-700.

Vannevel, R., Brosens, D., De Cooman, W., Gabriels, W., Lavens, F., Mertens, J. & Vervaeke, B. 2018. The inland water macro-invertebrate occurrences in Flanders, Belgium. *ZooKeys***,** 117.

Verhaegen, Y. 2012. *Mode of action, concentrations and effects of tributyltin in common shrimp Crangon crangon.* Ghent University.

Verschoor, A. J., Vijver, M. G. & Vink, J. P. 2017. Refinement and cross-validation of nickel bioavailability in PNEC-Pro, a regulatory tool for site-specific risk assessment of metals in surface water. *Environmental Toxicology and Chemistry,* 36**,** 2367-2376.

Viamajala, S., Peyton, B. M., Apel, W. A. & Petersen, J. N. 2002. Chromate/nitrite interactions in Shewanella oneidensis MR-1: Evidence for multiple hexavalent chromium [Cr(VI)] reduction mechanisms dependent on physiological growth conditions. *Biotechnology and Bioengineering,* 78**,** 770-778.

Vilà, M., Carrillo-Gavilán, A., Vayreda, J., Bugmann, H., Fridman, J., Grodzki, W., Haase, J., Kunstler, G., Schelhaas, M. & Trasobares, A. 2013. Disentangling biodiversity and climatic determinants of wood production. *PloS One,* 8**,** e53530.

Vilà, M., Vayreda, J., Gracia, C. & Ibáñez, J. J. 2003. Does tree diversity increase wood production in pine forests? *Oecologia,* 135**,** 299-303.

Vink, J. & Hendriks, J. 1999. RIZA: zware metalen wel degelijk een ecotoxologisch risico. *H2O***,** 38-45.

Vink, J. P. 2009. The origin of speciation: Trace metal kinetics over natural water/sediment interfaces and the consequences for bioaccumulation. *Environmental Pollution,* 157**,** 519-527.

Vlm 2019. EINDRAPPORT "MILIEUKUNDIG EN ECONOMISCH VERANTWOORD FOSFORGEBRUIK". APLM/2014/3 in opdracht van VLM /29.01.2019.

Von Der Heyden, C. & New, M. 2004. Sediment chemistry: a history of mine contaminant remediation and an assessment of processes and pollution potential. *Journal of Geochemical Exploration,* 82**,** 35-57.

VROM 2007. Regeling bodemkwaliteit. Den Haag.

Wang, S. & Choi, J. H. 2013. Simulating fate and transport of chromium in saturated sediments. *Applied Mathematical Modelling,* 37**,** 102-111.

Wardle, D. A. 2016. Do experiments exploring plant diversity–ecosystem functioning relationships inform how biodiversity loss impacts natural ecosystems? *Journal of Vegetation Science,* 27**,** 646-653.

Watson, J. V., Liang, J., Tobin, P. C., Lei, X., Rentch, J. S. & Artis, C. E. 2015. Large-scale forest inventories of the United States and China reveal positive effects of biodiversity on productivity. *Forest Ecosystems,* 2**,** 22.

Weis, J. J., Madrigal, D. S. & Cardinale, B. J. 2008. Effects of algal diversity on the production of biomass in homogeneous and heterogeneous nutrient environments: a microcosm experiment. *PLoS One,* 3**,** e2825.

Whittaker, R. 1975. Communities and ecosystems, 2nd edn Macmillan Publishing Company. *New York, NY*.

Wilbur, S. a. H. F., M.; Yu, D.; Tencza, B., Ingerman, L.; Klotzbach, J. James, S. 2012. Toxicological Profile for Chromium. *Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles*.

Wilsey, B. J. & Polley, H. W. 2004. Realistically low species evenness does not alter grassland species-richness–productivity relationships. *Ecology,* 85**,** 2693-2700.

Wilsey, B. J. & Potvin, C. 2000. Biodiversity and ecosystem functioning: importance of species evenness in an old field. *Ecology,* 81**,** 887-892.

Yavuzatmaca, M., Kulkoyluoglu, O., Yilmaz, O. & Akdemir, D. 2017. On the Relationship of Ostracod Species (Crustacea) to Shallow Water Ion and Sediment Phosphate Concentration Across Different Elevational Range (Sinop, Turkey). *Turkish Journal of Fisheries and Aquatic Sciences,* 17**,** 1333-1346.

Yu, N., Chen, S. M., Li, E. C., Chen, J. Y. & Chen, L. Q. 2009. Tolerance of Physocypria kraepelini (Crustacean, Ostracoda) to water-borne ammonia, phosphate and pH value. *Journal of Environmental Sciences,* 21**,** 1575-1580.

Zhang, C., Yu, Z. G., Zeng, G. M., Jiang, M., Yang, Z. Z., Cui, F., Zhu, M. Y., Shen, L. Q. & Hu, L. 2014. Effects of sediment geochemical properties on heavy metal bioavailability. *Environment International,* 73**,** 270-281.

Zhang, Q.-G. & Zhang, D.-Y. 2006. Resource availability and biodiversity effects on the productivity, temporal variability and resistance of experimental algal communities. *Oikos,* 114**,** 385-396.

Zhang, Q., Buyantuev, A., Li, F. Y., Jiang, L., Niu, J., Ding, Y., Kang, S. & Ma, W. 2017. Functional dominance rather than taxonomic diversity and functional diversity mainly affects community aboveground biomass in the Inner Mongolia grassland. *Ecology and Evolution,* 7**,** 1605-1615.

Zhang, Y., Chen, H. Y. & Reich, P. B. 2012. Forest productivity increases with evenness, species richness and trait variation: a global meta‐analysis. *Journal of Ecology,* 100**,** 742-749.

Zimmerman, E. K. & Cardinale, B. J. 2014. Is the relationship between algal diversity and biomass in North American lakes consistent with biodiversity experiments? *Oikos,* 123**,** 267-278.

7. › Acknowledgements

‘Sullied Sediments’ has been has been co-funded by the European Regional Development Fund through the Interreg VB North Sea Region Programme with a grant of 2.043.413 euros with equivalent match funding from the partners involved. The project partnership includes public, private and third sector organisations based in the United Kingdom, Germany, Belgium and the Netherlands

We thank Flanders Environment Agency (VMM) and Ecofide for access to their databases and reports. Requests for raw data provided by these organisations are to be directed to Ward de Cooman and Jaap Postma. Curated and treated data are stored according to Radboud University guidelines and available in the repository link.

Interreg
North Sea Region
European Regional Development Fund

EUROPEAN UNION

8. Partners

The Sullied Sediments project partnership comprises 13 project beneficiaries:

Canal and River Trust (UK)
East Riding of Yorkshire Council (UK)
Ecossa (Germany)
Hamburg Port Authority (Germany)
Hamburg University of Applied Sciences (Germany)
Institut Dr Nowak (Germany)
Openbare Vlaamse Afvalstoffenmaatschappij (Belgium)
Radboud University (The Netherlands)
Socotec UK Ltd (UK)
University of Antwerp (Belgium)
University of Hull (UK)
University of Leeds (UK)
Vlaamse Milieumaatschappij (Belgium)

The partnership also receives expert advice from 12 strategic partners who form our Advisory Group:

East and North Yorkshire Waterways Partnership (UK)
Elbe Habitat Foundation (Germany)
Environment Agency (UK)
Federal Institute of Hydrology (Germany)
Foundation for Applied Water Research (Europe)
Hamburg Ministry of the Environment and Energy (Germany)
Northumbrian Water (UK)
River Hull Board (UK)
Sediment European Network Steering Group (European)
Thames Water (UK)
Vlakwa (water research consultancy) (Belgium)
Yorkshire Water (UK)

9. › Contact us

For more information about this publications, please contact:

Visit our webspace: www.northsearegion.eu/sullied-sediments

Follow us on Twitter: @SulliedSediment

Join our blog: www.sulliedsediments.wordpress.com/

✉ Join our blog: www.sulliedsediments.wordpress.com/

10. Appendices/Supporting info

Tables

Table A1. Toxicity data applied in the present study[a].

Chemical	TMoA	EC50 (μg/L)[b]	β
Cd	Cadmium	2.91	1.13
Hg	Mercury	2.26	0.98
Cu	Copper	2.26	0.70
Ni	Nickel	3.38	1.17
Pb	Lead	3.55	0.78
Zn	Zinc	3.22	0.78
Cr	Chromium	3.89	1.09
As	Arsenic	3.39	0.86
Ace	PAH	2.96	0.44
Acy	PAH	3.20	0.70
Ant	PAH	1.27	0.81
B(a)P	PAH	1.48	0.70
B(a)A	PAH	0.57	0.70
B(b)F	PAH	0.62	0.70
B(ghi)P	PAH	-0.33	0.70
B(k)F	PAH	0.97	0.70
Chr	PAH	3.10	0.70
Db(a,h)A	PAH	0.04	0.70
Phen	PAH	2.67	0.45
Flah	PAH	2.13	1.02
Flu	PAH	3.38	0.78
INP	PAH	1.08	0.70
Naph	PAH	3.62	0.48
Pyr	PAH	1.95	0.70
DDD	OCP	1.29	1.22
DDE	OCP	1.92	1.44
DDT	OCP	1.40	1.09
Dieldrin	OCP	1.37	1.03
Endrin	OCP	0.48	1.03
Aldrin	OCP	1.72	1.11
Endosulfan I	OCP	0.85	1.60
α -HCH	OCP	3.14	0.43
β-HCH	OCP	2.93	0.35
Lindane	OCP	2.07	1.05
HCBD	OCP	2.61	0.52
Heptachlor	OCP	1.39	0.94
Telodrin	OCP	3.35	0.70
HCB	OCP	2.90	1.50
PeCBz	OCP	2.99	0.71
PCB101	PCB	1.44	0.76
PCB118	PCB	1.44	0.76
PCB138	PCB	1.44	0.76

PCB153	PCB	0.11	0.70
PCB180	PCB	1.44	0.76
PCB28	PCB	2.20	0.70
PCB52	PCB	1.48	0.70

[a] TMoA= toxic mode of action, PAH= polycyclic aromatic hydrocarbons, OCP= organochlorine pesticides, PCB= polychlorinated biphenyls.

[b] Values are log-transformed.

Table A2. Experimental evidence for relationships between diversity and productivity in terrestrial ecosystems.

Reference	Ecosystem type	Type of diversity	Ecosystem property measured	Biomass/ productivity	Direction	Function form
Bullock et al. (2001)	Grassland	Species richness	Hay production	Biomass	Positive	Linear
Hooper and Vitousek (1997)	Grassland	Functional group richness	Aboveground biomass	Biomass	Positive	Log-linear
Dukes (2001)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	M-M
Mulder et al. (2001)	Forest	Species richness	Aboveground biomass	Biomass	0	-
Symstad et al. (1998)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	M-M
Kenkel et al. (2001)	Grassland	Species richness	Aboveground biomass	Biomass	0	-
Naeem et al. (1995)	Grassland	Species richness	Mean biomass	Biomass	Positive	Log-linear
Tilman et al. (1996)	Grassland	Species richness	Total plant cover (%)	Biomass	Positive	M-M
Troumbis et al. (2000)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Fridley (2002)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Stevens and Carson (2001)	Grassland	Species richness	Total plant cover (%)	Biomass	Positive	-
Wilsey and Potvin (2000)	Grassland	Species richness	Total biomass	Biomass	Positive	Linear
Tilman et al. (1997)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	M-M
Tilman et al. (1997)	Grassland	Functional group richness	Aboveground biomass	Biomass	Positive	M-M
Fridley (2003)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Mikola et al. (2002)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Linear
Van Ruijven and Berendse (2003)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
van Ruijven and Berendse (2005)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Caldeira et al. (2001)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	-
He et al. (2005)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Linear
He et al. (2005)	Grassland	Species richness	Total biomass	Biomass	Positive	Linear
Pfisterer and Schmid (2002)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Callaway et al. (2003)	Ruderal/salt marsh	Species richness	Total biomass	Biomass	Positive	Linear
Hector et al. (1999)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Hector et al. (1999)	Grassland	Functional group richness	Aboveground biomass	Biomass	Positive	Linear
Dimitrakopoulos and Schmid (2004)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	Log-linear
Lanta and Lepš (2006)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	-
Lanta and Lepš (2006)	Grassland	Functional richness	Aboveground biomass	Biomass	Positive	-
Spehn et al. (2005)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	-
Spehn et al. (2005)	Grassland	Functional group richness	Aboveground biomass	Biomass	Positive	-

Mellinger and McNaughton (1975)	Grassland	Species richness	Total net productivity	Biomass	0	-
Wilsey and Polley (2004)	Grassland	Species richness	Aboveground biomass	Biomass	Positive	-

Table A3. Experimental evidence for relationships between biodiversity and productivity in aquatic ecosystems.

Reference	Ecosystem function	Specific taxon	Type of diversity	Ecosystem property measured	Biomass/ productivity	Direction	Function form
Arenas et al. (2009)	Primary production	Macroalgae	Species richness	Max NPP	Productivity	Positive	Log-linear
Bruno et al. (2005)	Primary production	Macroalgae	Species richness	Algal biomass	Biomass	Positive	M-M
Boyer et al. (2009)	Primary production	Macroalgae	Species richness	Algal biomass	Biomass	Positive	-
Griffin et al. (2009)	Primary production	Macroalgae	Functional group richness	Net primary productivity	Productivity	Positive	Linear
Engelhardt and Ritchie (2001)	Primary production	Macrophyte	Species richness	Algal biomass	Biomass	Positive	M-M
Weis et al. (2008)	Primary production	Algae	Species richness	Algal biomass	Biomass	Positive	-
Naeem et al. (2000)	Primary production	Algae	Species richness	Algal biomass	Biomass	Positive	Linear
Downing and Leibold (2002)	Primary production	Trophic structure	Species richness	Phytoplankton biomass	Biomass	Positive	M-M
Engelhardt and Kadlec (2001)	Primary production	Macrophyte	Species richness	Aboveground biomass	Biomass	Positive	-
Gamfeldt et al. (2005)	Primary production	Algae	Species richness	Algal biomass	Biomass	0	No
Zhang and Zhang (2006)	Primary production	Algae	Species richness	Algal biomass	Biomass	0	No
Harvey et al. (2013)	Secondary production	Benthic macrofauna	Functional group richness	Macroalgae consumption	Biomass	Positive	M-M
Langenheder et al. (2010)	Secondary production	Prokaryotes	Species richness	Metabolic activity (substrate oxidation)	Productivity	Positive	M-M
Pusceddu et al. (2014)	Secondary production	Benthic meiofauna	Species richness	Prokaryotic heterotrophic production	Productivity	Positive	Linear
Emmett Duffy et al. (2003)	Secondary production	Grazer	Species richness	Grazer biomass	Biomass	Positive	Linear
Norberg (2000)	Secondary production	Zooplankton	Species richness	phytoplankton per capita	Productivity	0	No
Duffy et al. (2001)	Secondary production	Grazer	Species richness	Eelgrass biomass	Biomass	0	No
Duffy et al. (2001)	Secondary production	Grazer	Species richness	Epiphyte biomass	Biomass	0	No

O'Gorman et al. (2008)	Secondary production	Benthic macrofauna	Species richness	Total invertebrate biomass	Biomass	Positive	-

Table A4. Observational evidence for relationships between biodiversity and productivity.

Reference	Ecosystem type	Specific taxon	Type of diversity	Ecosystem property measured	Biomass/ productivity	Direction	Effect form
Danovaro et al. (2008)	Marine (deep sea)	Benthic meiofauna (Nematode)	Functional richness	Prokaryote C production	Productivity	Positive	Power (b>1)
Danovaro et al. (2008)	Marine (deep sea)	Benthic meiofauna (Nematode)	Functional richness	Faunal Biomass	Biomass	Positive	Power (b>1)
Duffy et al. (2016)	Marine	Reef fish	Species richness	Fish biomass	Biomass	Positive	Power (0<b<1)
Mora et al. (2011)	Marine	Reef fish	Functional richness	Standing biomass	Biomass	Positive	Power (b>1)
Thompson et al. (2015)	Lake (temperate)	Zooplankton	Functional richness	Zooplankton biomass	Biomass	Positive	Log-linear
Thompson et al. (2015)	Lake (temperate)	Zooplankton	Species richness	Zooplankton biomass	Biomass	Positive	Unimodal
Zimmerman and Cardinale (2014)	Lake (temperate)	Phytoplankton	Species richness	Total algal biomass	Biomass	Positive	Power (0<b<1)
Troumbis and Memtsas (2000)	Shrubland	Cistus shrublands	Species richness	Total biomass	Biomass	Positive	Linear
Gamfeldt et al. (2013)	Forest (temperate)	Tree	Species richness	Tree biomass production	Productivity	Positive	Unimodal
Grace et al. (2016)	Grassland	Herbaceous plants	Species richness	Above-ground productivity	Productivity	Positive	Power (0<b<1)
Jing et al. (2015)	Grassland (alpine)	Plants	Species richness	Ecosystem multifunctionality index	-	Positive	Log-linear
Maestre et al. (2012)	Dryland	Plants	Species richness	Ecosystem multifunctionality index	-	Positive	-
Ruiz-Benito et al. (2014)	Forest (temperate)	Tree	Functional richness	Tree productivity	Productivity	Positive	M-M
Tylianakis et al. (2008)	Grassland	Plants	Species richness	Belowground biomass	Biomass	Positive	Linear
Vilà et al. (2013)	Forest	Tree	Species richness	Wood production	Productivity	Positive	-
Watson et al. (2015)	Forest	Tree	Species richness	Stand productivity	Productivity	Positive	M-M
Zhang et al. (2012)	Forest	Tree	Species richness	Ln (effect size)	Productivity	Positive	M-M
Poorter et al. (2015)	Forest (Tropical)	Tree	Species richness	Aboveground biomass	Biomass	Positive	Linear

Delgado-Baquerizo et al. (2016)	Dryland	Bacteria	Species richness	Ecosystem multifunctionality index	-	Positive	Linear
Delgado-Baquerizo et al. (2016)	Dryland	Fungi	Species richness	Ecosystem multifunctionality index	-	Positive	Linear
Zhang et al. (2017)	Grassland	Vascular plants	Species richness	Aboveground biomass	Biomass	Positive	Linear
Zhang et al. (2017)	Grassland	Vascular plants	Functional richness	Aboveground biomass	Biomass	Positive	Linear
Vilà et al. (2003)	Forest	Tree	Species richness	Wood production	Productivity	0	-
Mellinger and McNaughton (1975)	Forest	Tree	Species richness	Total net productivity	Productivity	0	-

Table A5. Summary of total monetary values of ecosystem services per biome reported in literatures (values in 2007\$ ha^{-1}yr^{-1})

	Costanza et al. (1997)	De Groot et al. (2012)	Costanza et al. (2014)
Open ocean	347.76 (1,8,11,13-14,17)	491 (2,13-16)	660 (2,8,11,13-16)
Estuaries	31508.16 (3,8,11-14,16-17)	28917 (2,6,12-17)	28917 (2,6,12-17)
Seagrass/Algae beds	26225.52 (8,14)	28917 (2,6,12-17)	28917 (2,6,12-17)
Coral reefs	8383.5 (3,9,11-14,16-17)	352915 (2,3,6,9,12-17)	352249 (2,3,6,9,11-17)
Shelf	2221.8 (8,11,13-14,17)	2221.8 (8,11,13-14,17)	2221.8 (8,11,13-14,17)
Lakes/Rivers	11727.24 (4,5,9,13,16)	4267 (5,13,16)	12512 (4,5,9,13,16)
Tropical forest	2769.66 (2-9,13-17)	5264 (1-3,5,8,10-16)	5382 (1-17)
Temperate/Boreal forest	416.76 (2,4,7,9,11,13-14,16-17)	3013 (2,5,8,11-14,16-17)	3137 (2,4-5,7-9,11-14,16-17)
Grass/Rangelands	320.16 (1-2,4,6-7,9-11,13,15-16)	2871 (2,5,6,9,12-17)	4166 (1-2,4-7,9-17)
Tidal marsh/Mangroves	13786.2 (3,9,12-14,16)	193845 (2-3,5-6,8-9,12-16)	193845 (2-3,5-6,8-9,12-16)
Swamps/Floodplains	27020.4 (1,3-5,9,12-14,16-17)	25682 (2-6,8-9,11-17)	25682 (2-6,8-9,11-17)

Numbers in parentheses show the ecosystem services included in respective study: 1=gas regulation, 2= climate regulation, 3=disturbance regulation, 4=water regulation, 5=water supply, 6=erosion control, 7=soil formation, 8=nutrient cycling, 9=waste treatment, 10=pollination, 11=biological control, 12=habitat/refugia, 13=food production, 14=raw materials, 15=genetic resources, 16=recreation, 17=cultural.

Table A6. Mean values of productivity per unit area per biome reported in literatures (values in kg/m^2/yr).

	Whittaker (1975)	Bolin et al. (1979)	Chen et al. (2018)	Del Grosso et al. (2008)	(Mori (2018))
Open ocean	0.125	0.125			
Estuaries	1.5	1.5			
Seagrass/Algae beds	2.5	2			
Coral reefs	2.5	1			
Shelf	0.36	0.36			
Lakes/Rivers	0.25	0.4			
Tropical forest	1.9	2	2.35	0.87	
Temperate/Boreal forest	1.1	1	1.14	0.55	1.06
Grass/Rangelands	0.6	0.8			
Tidal marsh/Mangroves	2	3			
Swamps/Floodplains	2	3.5			
Cropland	0.65				

Figures

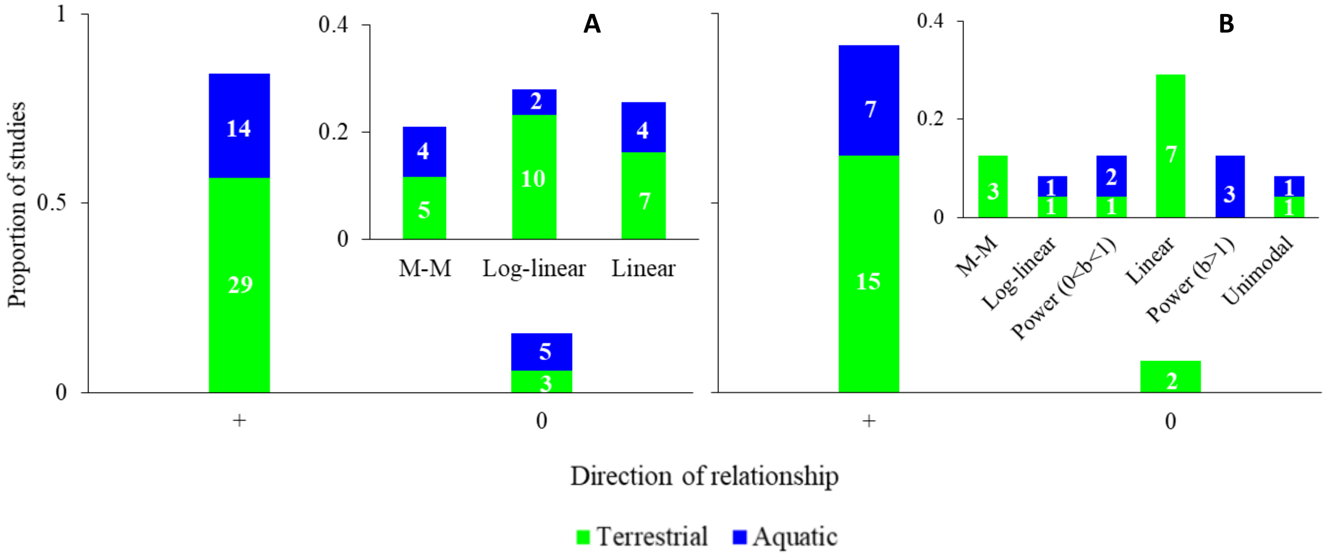


Figure A1 Proportions of studies with positive (+) and neutral (0) diversity effects on biomass production in terrestrial (green) and aquatic (blue) ecosystems based on experimental (A) and observational studies (B) listed in Table A2-A4 in Appendices. Insets show proportions of studies with different mathematical function forms of the diversity-productivity relationship in experimental (A) and observational studies (B) respectively. M-M represents the Michaelis-Menten function. Numbers inside bars represent the number of studies in each category.