Simulation-based assessment of the impact of fertiliser and herbicide application on freshwater ecosystems at the Three Gorges Reservoir in China

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HIGHLIGHTS

- Aquatic food webs of a Three Gorges Reservoir tributary are simulated using AQUATOX.
- Impacts of high nutrient inflows from agriculture are low by dilution.
- Potential risks from propanil via edible fish consumption cannot be excluded.

GRAPHICAL ABSTRACT
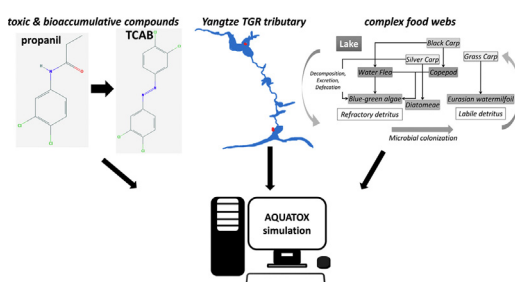
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ABSTRACT

Dams have profound impacts on river ecosystems, amongst them inundation of land, altered dynamics of the water body or uprising reservoir backwaters influencing tributary or upstream river sections. Along the outstandingly ecologically important Yangtze River in China, the Three Gorges Reservoir (TGR) is the largest project, covering an area of 1080 km^2. From the beginning, the dam-project came in for criticism on increasing environmental risks due to sub-merging former industrial and urban areas.

We simulated dynamics of biotic and abiotic components of the TGR ecosystem (trophic guilds of aquatic organisms, hydrodynamics, nutrients), as well as the behaviour of the herbicidal substance propanil and its metabolites 3,4-Dichloroaniline (DCA) and 3,3′,4,4′-tetrachloroazoxybenzene (TCAB). A modelling environment, provided by the AQUATOX software, was adapted to the specific situation at a tributary reach to the Yangtze river 'Daning River'. As the simulated food web contained several interconnected trophic levels, a significant biomagnification of metabolites was demonstrated by our simulation studies. In particular, newly emerging stagnant downstream sections of tributaries exhibited high probabilities due to accumulating pesticides from upstream sources.

The common problem of algal blooms in the TGR-region was addressed by dose-response simulation experiments with essential nutrients. Impacts on structure and abundance of populations of aquatic organisms were shown. However, even high nutrient loads resulted in only slight changes of densities of organisms of all trophic levels. Nevertheless, the probabilities for large-scale algal blooms affecting drinking water quality were considered low because of high flow velocities and discharge rates towards the Yangtze River.

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We see high potential of simulation-based assessments that provide information for risk managers dealing with whole catchment areas. They are put in the position to differentiate the magnitude of impacts of various factors and decide about the most effective remediation measures.

1. Introduction

1.1. The ecosystems of the Three Gorges Reservoir after impoundment

The Yangtze River (Chang Jiang) with a length of 6300 km is the longest river in China. The middle course of 950 km in length covering a drainage area of 680,000 km^2 (Chen et al., 2010) strides across an economically prospering region in the province of Chongqing (30 million residents since the year 2015 (NBS, 2018)), with the city of Chongqing as the major fast growing economic centre and river port (Fu et al., 2010). The developing economy needs energy and safe transportation of goods throughout the whole year. For reasons of hydroelectric power production, flood prevention and navigability, numerous dams were built at the Yangtze River. Amongst them, the Three Gorges Reservoir (TGR) is the largest, covering an area of 1080 km^2. Further, the Yangtze basin has an outstanding ecological importance for China's freshwater ecosystems. It bears one of the highest diversity with 361 fish species, of which 177 are endemic and about one third is found on the list of endangered species of China (Xie, 2003). Large dams worldwide cause profound changes to the original river ecosystems. This is due to a variety of impacts, amongst them inundation of land, altered dynamics of the water body or uprising reservoir backwaters influencing tributary or upstream river sections (Dorcey, 1997). Altered land use (e.g. towards intensification of agriculture) can result in high loads of nutrients due to excess fertiliser or pesticide use on the fewer remaining cultivable areas after inundation. An intensification was foreseen for the TGR during the planning phase (Luk and Whitney, 1993) and e.g. the per capita cropland increased already during the impoundment phase (Fu et al., 2010). The use of fertilisers in the Three Gorges region increased greatly in the last decade (Sun et al., 2013). In order to analyse different patterns of nutrient loads, nitrogen (as nitrate, diversifying into the relevant nitrogen species via nitrification and denitrification processes) and phosphate as well as a combined pollution by nitrate and phosphate was simulated. In China nowadays, the excess use of water and fertilisers in rice cultures very often had led to ineffective conversion into biomass and further surface runoff into the adjacent water bodies could occur (Liang et al., 2013). Increasing use intensification should be brought into agreement with the conservation of the ecosystem services provided by the river. From the beginning, the dam-project came in for criticism on increasing environmental risks due to inundation of former industrial and urban areas. The special thing of study area was a unique hydrodynamic situation at the mouth of the Daning River where a huge eddy formation marked by long residence time of Wushan Lake water was formed.

1.2. The concept of integrated ecosystem modelling

We described the subject of our studies that we conducted at the Yangtze TGR, the problems after impounding of the new reservoir and the conceptual approach of an integrated ecosystem modelling of micropollutant impacts in several previous studies (Floehr et al., 2013; Floehr et al., 2015; Scholz-Starke et al., 2013; Fig. 1). The way forward that we describe by this contribution the final implementation of the information from all available sources of the contextual Yangtze - project, and additionally demonstrate the feasibility and ecological validity of our model calibration.

We simulated the dynamics of biotic and abiotic components of the TGR ecosystem, as well as the behaviour of propanil and closely related and highly relevant metabolites, which has been widely used in this region as herbicide. The relevance of this compound was exposed by Xiao et al. (2016) and supported by sales and marketing numbers and literature (e.g. Zhang, 2003). Specifically, the last stretch of the Daning River before the confluence with the Yangtze River at the city of Wushan, Eastern China, was analysed. The stretch was divided into ten segments of alternating flowing and stagnating waters (Scholz-Starke et al., 2013). The area belongs to the Three Gorges Reservoir and is impacted by a very large water fluctuation of 30 m within a year (winter high tide, summer low tide). Fluctuation bears many problems, amongst which we focused on the likely runoff from agricultural fields. A further focus of our work applied to the fact that after the impoundment of the reservoir, large zones of formerly fast running waters slowed down from 2 to 3 meter flow velocity per second to <0.05 to 1.5 m/s on average or became stagnant (Chen et al., 2005; Wang et al., 2009). Consequently, the residence time of the water increased and thus the probability of bioaccumulation processes to biota taking place increased. The loads of micropollutants at tributary rivers and the main stream of the Yangtze in the TGR region could be assumed as particularly high under the newly inverted water level patterns (high water levels during winter dry season, and low water levels during the rainy season) after impoundment (Floehr et al., 2013).

1.3. The AQUATOX ecosystem model

We used the complex, process-based, mechanistic ecosystem model AQUATOX in an integrative model approach. The AQUATOX model environment was originally developed to support environmental risk assessments under the responsibility of the US Environmental Protection Agency (Park and Clough, 2010). The model was used to predict fate and behaviour of chemicals or nutrients and to describe the impact of risk management options (Park et al., 2008) and successfully applied recently for the prospective risk assessment of chemicals (e.g. by Lombardo et al., 2015).

We described our conceptual approach to calibrate the model in a previous paper (Scholz-Starke et al. (2013) and Fig. 2). There was indication for the usefulness of combining predictive modelling techniques with biological assessments to support decisions on future management measures that should protect the aquatic ecosystem at the TGR (McKnight et al., 2012). The paper describes the data that was used to adapt the AQUATOX simulation environment to the situation at the Daning River from the Dachang Lake to the Wushan Lake (Fig. 3). The exposure to the herbicidal model substance propanil (*module EXM*) was estimated by analysing the land-use patterns nearby the ten tributary segments of the Daning River (global land cover map by European Space Agency, Arino et al., 2012), assuming that areas classified as irrigated croplands in this region would get overuse-rates of common pesticides. Exposure calculations taken from the European standard risk assessment for pesticides provided the predicted environmental concentrations (PEC) that the water bodies initially received (PEC$_{initial}$). Physico-chemical and morphological parameters of the water bodies were partly leant against measurements derived from the literature and Geographical Information Systems (GIS) or left to the transformations implemented in AQUATOX (e.g. organic matter cycling, *modules SDM and HDM*). Since propanil was actually registered in China and Europe for herbicidal use at that time, plenty of information on its effects on aquatic organisms was available (Ministry of Health of Italy, 2006). The parent compound showed moderate toxicity
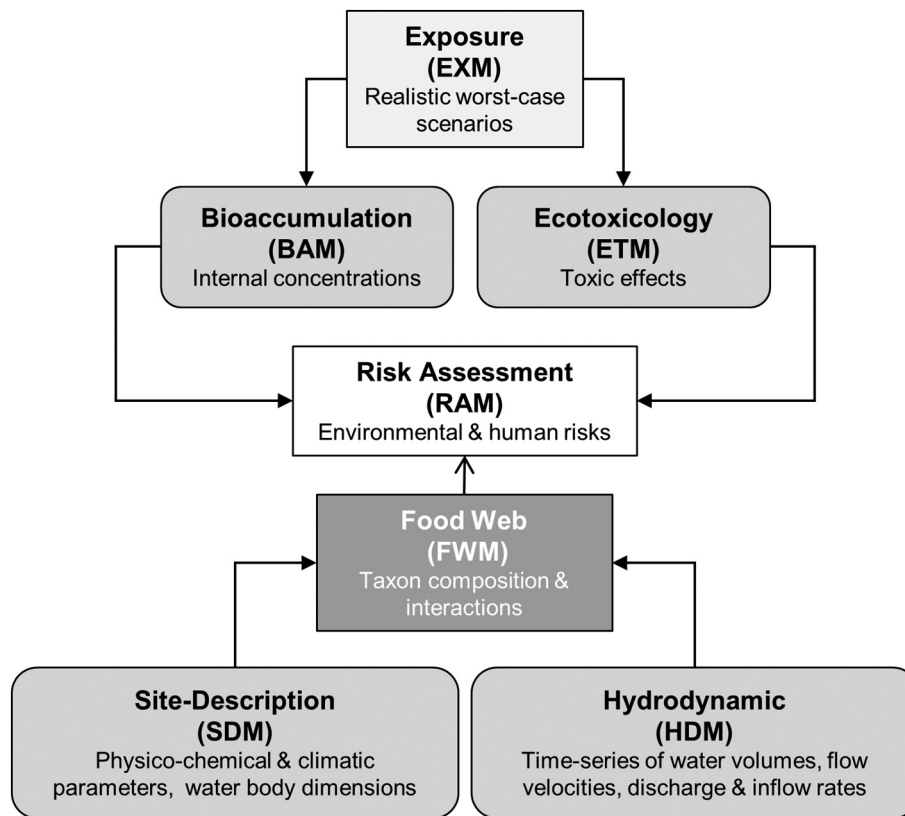
Fig. 1. Concept of the integrated modelling approach (adapted from Scholz-Starke et al., 2013) for simulation based impact assessment of pollutants. Exposure, bioaccumulation and ecotoxicity can be described for any model substances with sufficient calibration data available.

to fish, crustaceans and molluscs but relatively high toxicity towards algae and plants. The toxicity of the main metabolite 3,3′,4,4′-tetrachloroazobenzene (TCAB) was widely unknown and had to be estimated by QSAR models (UFZ, 2012) or interpolation estimates. Nevertheless, there was experimental work available that confirmed the higher toxicity of TCAB compared to the parent compound propanil (Xiao et al., 2016) as we found by QSAR modelling for the fish species Fathead Minnow (*Pimephales promelas*), we could not use these data because it was derived by sub-organismic screening bioassays only and could not extrapolated to adults. We derived a factor of 140-times lower acute LC_{50} after 96 hour exposure for *P. promelas* than for propanil

by the CHEMPROP model (29.2 vs. 4360 μg a.i./L). We applied this factor to all other endpoints for the 14 trophic guilds of our model. Bioaccumulation was estimated from the $logK_{OW}$ of the compounds (*modules ETM + BAM*). Two food webs that represented specialist flowing and stagnating water communities were set-up based on a surrogate species for each of the most important guilds of lakes and rivers in China, according to reports from the literature (*module FWM*, Scholz-Starke et al., 2013).

The AQUATOX simulation environment allows for the representation of simple beaker situations just like of very complex ecosystems. As we decided to make our simulations representative for a tributary
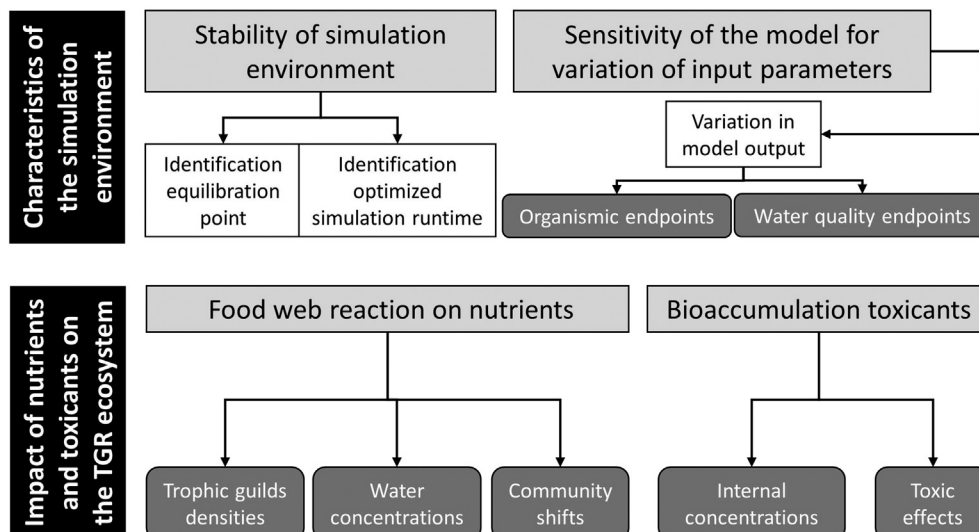

Fig. 2. Flow-chart of the data analysis of the simulation output. Refer to SI for analyses of stability and sensitivity of the simulation environment.
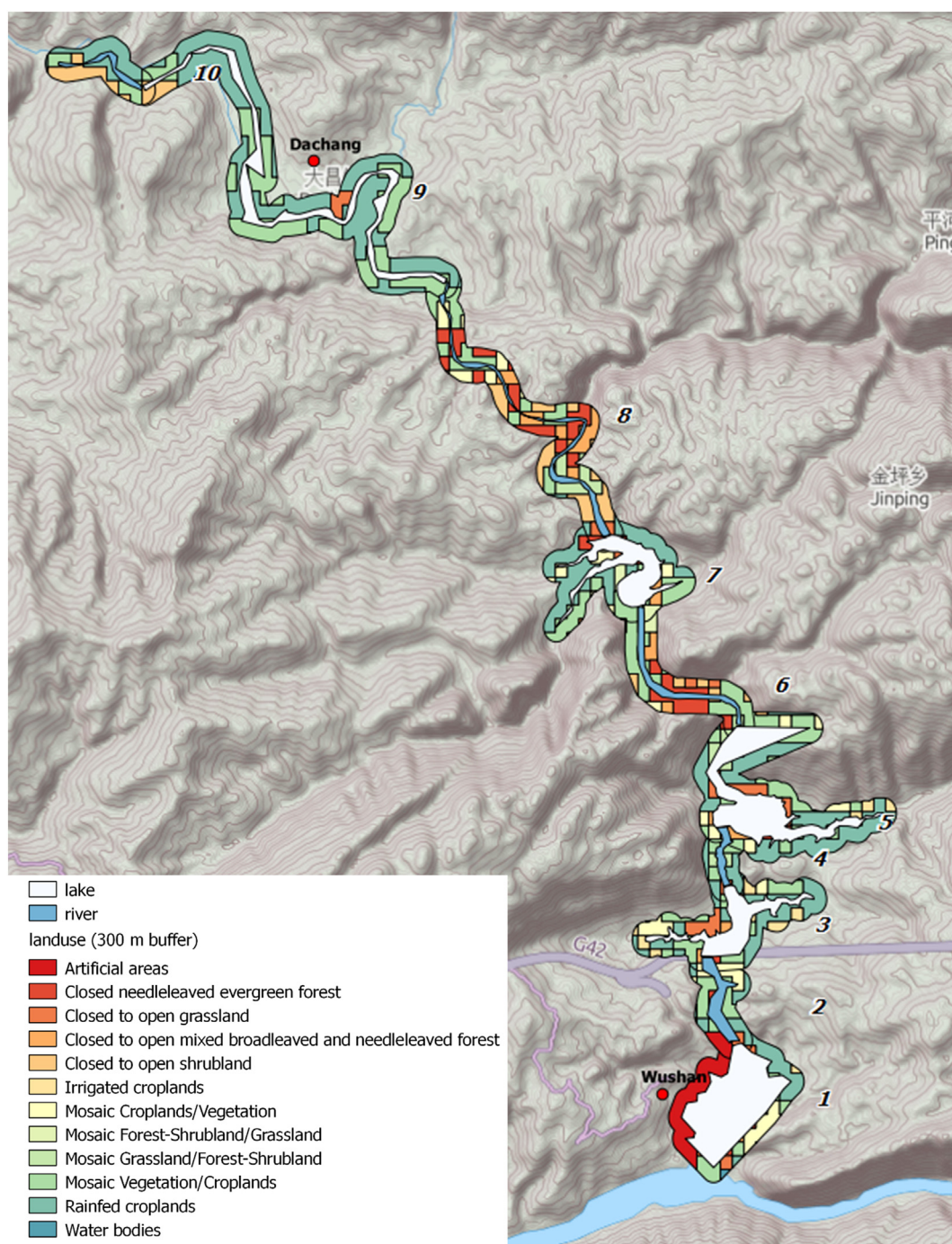
Fig. 3. Land-use in the fluctuation zone of the downstream Daning River in a 300 m-buffer around 10 numbered river and lake segments (calculation with QGIS software, source of land-use information Global land Cover Map (Arino et al., 2012)). The area is located at 31°6′N, 109°5′W.

stretch of the Yangtze River that was longer than 40 km, a large amount of information had to be queried, weighed and compiled. The sources of information, the rationales behind the decisions taken during the calibration processes and the parameter values used, are described in particular detail in the following. However, if information was not considered indispensable for the traceability of our rationales, it was filed in the Supplementary information (SI).

1.4. The simulation studies for an prospective environmental risk assessment

Simulation studies after calibration and check for plausibility and stability of the model were conducted for mainly two superior reasons:

Firstly, it was tested if very high dosages of nutrients would affect the food webs of the considered stream sections. This was investigated because algal blooms were identified by Chinese scientists as one of the most urging problems after the impounding of the TGD (Zhang and Lou, 2011). Secondly, the bioaccumulation potential of the parent model substance propanil and its metabolites were analysed. Long-term simulation runs gave information about stability and the optimum compromise between the equilibration and run-time of the program (upper part of Fig. 2). The hydrodynamic situation, i.e. water volume and flow velocity, alternated according to a fixed yearly pattern as described by Section 3.1. Organism densities varied over time depending on the changing environmental conditions originating in the initial densities that were chosen following the rationales described by Section 2.4.

It was shown that simulation results stabilized after an initial equilibrium period. For reasons of equilibration, the simulations run for 25 years and stable patterns only were interpreted (analyses shown in SI).

In our simulation studies, it was assumed that at least one of the essential nutrients, either nitrogen or phosphate would be the growth limiting factor for the primary producers, such as green, blue-green algae, as well as diatoms and macrophytes (as implemented in the AQUATOX model by Park and Clough, 2010 or compiled from ecology textbooks, e.g. Lampert and Sommer, 2007). Clear differences of water concentrations and guild densities were expected from effects of systematic N- and P-variation from basic ecological and physiological reasoning. For the primary producers direct effects were assumed, whereas the succeeding trophic levels were expected to show indirect effects of varying nutrient supply.

We focused on the suspected bioaccumulative secondary metabolite TCAB, but the bioaccumulation behaviour of propanil was modelled as well. The mechanism of downstream transport was assumed to be similar for propanil and TCAB; however only TCAB was expected to accumulate until internal concentrations would be toxic indeed. To check that the model assumptions worked out, the behaviour of the three substances (propanil, DCA, TCAB) was simulated and the resulting concentrations were compared.

Two questions arose from the perspective of an environmental risk assessment that could be addressed by simulation exercises using the model herbicide propanil and especially its secondary metabolite 3,3′,4,4′-tetrachloroazobenzene.

Firstly, was the accumulative potential of TCAB compared to propanil reflected by the simulations? A large difference was assumed from the differing log K_{OW}-values of the two substances that were used to determine the bioaccumulation factors by way of calculation. Propanil was known to be not accumulative due to log K_{OW}-values and fast degradation in the water phase (Ministry of Health of Italy, 2006). The primary metabolite 3,4-DCA was taken as a reference substance in separate simulations to check for the plausibility of the analyses compared to literature data (results not shown). For propanil and especially TCAB, no literature data was available.

Secondly, did the water concentrations and the internal concentrations within the modelled organisms resemble a realistic range compared to literature data? It was assumed that species-specific differences regarding the position along the aquatic food chain and the food source should determine the internal concentrations.

2. Methods

2.1. Characteristics of modelled water bodies - site descriptor and hydrodynamics modules

The water bodies from the upper reaches at Dachang Lake down to the Wushan Bay had to be represented with sufficient accuracy regarding the geometry of the sites, as well as the physico-chemical parameters used for the calibration of the simulation environment.

2.1.1. Physico-chemical parameters, remineralisation and climate

The nutrient contents (segment-internal state or driving variable) and loadings (segment-external state or driving variable) were leant against the measurements of the MINIBAT sampling campaigns (Holbach et al., 2012). Loadings were chosen very high at each simulation time-step to maintain the nutrient status in the single segments, despite the relatively fast streaming conditions. This was done to counteract the dilution effect. The amount of organic matter was not primarily assigned by loadings or other external resources in the model settings. We left it to be solely formed by partitioning processes of the internal biomass. Table 1 lists the initial variable values of the physico-chemical parameters. Remineralisation rates were set to default.

Table 1

Initial values and loadings of physico-chemical parameters for the base simulation of the model region at Daning River. -/-: no loadings from upstream segment.

Variable	Initial condition	Daily loadings (from upstream segment)	Unit
NO_3^- [a]	5	5	mg/L
P [b]	0.35	0.3	mg/L
CO_2 [c]	0.5	-/-	mg/L
O_2 [d]	7.2	-/-	mg/L
TSS [e]	0	-/-	mg/L
R detr sed [f]	0	-/-	g dry weight/m^2
L detr sed [g]	0	-/-	g dry weight/m^3
R detr diss [h]	2.94	-/-	mg dry weight/L
L detr diss [h]	0.48	-/-	mg dry weight/L
R detr part [h]	0.52	-/-	mg dry weight/L
L detr part [h]	0.08	-/-	mg dry weight/L
Temp$_{const.}$ [i]	14.8		deg. C
Wind$_{const.}$ [j]	2		m/s
Light$_{const.}$ [k]	300		Ly/day
pH$_{const.}$ [l]	8		pH

[a] Equals total nitrogen; initial MINIBAT measurements 3–25 NO_3^-/L, mostly 4–6 mg nitrate/L, final data published by Holbach et al. (2012).

[b] Equals total soluble phosphorous; initial manyfolds of dissolved phosphorous leant against measurements of Holbach et al. (2012) at Wushan Lake.

[c] Initial arbitrarily chosen, no loading, formation up to remineralisation, assimilation, atmospheric exchange processes.

[d] Measured at own sampling campaign, 2011-09-25 at 25 °C water temperature.

[e] Total suspended solids, build by generic processes in the model from biomass.

[f] Refractory detritus sediment.

[g] Labile detritus sediment.

[h] Detrimental (detr) organic matter in the water phase, converted by the AQUATOX model originating from 2.12 mg organic carbon/L dry weight according to standard in the technical documentation (Park and Clough, 2010); dissolved (diss) ↔ particulate (part) = suspended percentages 85% ↔ 15%, labile (L) ↔ refractory (R) percentages 14% ↔ 86%; not considered: buried organic matter.

[i] MINIBAT measurements at starting day of the simulation (1st of January), then modelled regression time series using climate diagrams of Wushan City.

[j] Constant, estimated to assure surface mixis.

[k] Langleys/day; average light intensity in kWh/m^2 day was estimated from the map: http://www.wrsc.org/attach_paper/china-global-horizontal-solar-radiation-annual and converted.

[l] Lower values of MINIBAT measurements (Holbach et al., 2012).

Zhang et al. (2010) saw statistically significant differences between dry, flood and normal seasons, before the complete impounding of the TGR. They reported long-time measurement series (2004–2007) of TP, TN and Chlorophyll-a in the Daning River at three sampling sites from the bridge before the confluence with the Wushan Lake up to the middle of Dachang lake. Values of TN ranged between 0.62 and 1.35 mg/L, TP from 0.005 to 0.06 mg/L and Chlorophyll-a from 1 to 24 mg/L. In our studies, we referenced this publication for comparisons if the simulation results met the range of desired output values.

A monthly time-series of epilimnic water temperatures was introduced to the AQUATOX program, which was deduced by linear regression of long-term climate data of Wushan versus surface water temperatures measured by the MINIBAT project (Holbach et al., 2012).

2.1.2. Morphometry of and linkages between the water bodies

In general, two types of water bodies were defined that differ fundamentally in water flow conditions and food-web composition. There are five reservoir-like 'lake' segments, with slow flowing waters and specific stagnant aquatic communities. Further, five faster flowing 'stream' segments hosted specialized stream organisms (Fig. 3, refer to Figs. 1 and 2 in SI for representations of the sequence of water flows in the model environment). Chinese ecologists confirmed this rationale as appropriate (personal communication Junli Huo, East China Sea Fisheries Research Institute, Shanghai, PR China).

Generally, reservoirs and rivers in AQUATOX were modelled as extreme elliptic sinusoids (Neumann, 1959), while bathymetry equations were set active. We assumed that the cuboid system had vertical walls and thus a constant area applied as a function of depth. Consequently, water depth was calculated using the coefficient of volume and surface

Table 2
Dimensions of ten stream and lake segments of the model region at Daning River.

Site name	Volume [m³ * 100] (annual mean)	Area = [m² * 1000]	Maximum depth [m]	Width[a] [m]	Maximum reach length [m]	Mean depth [m]
Segment_01_reservoir	1,446,800	3200	95	6	3	84
Segment_02_stream	136,100	530	91	1	2	81
Segment_03_reservoir	611,700	1400	84	5	2	73
Segment_04_stream	44,743	240	82	0	1	72
Segment_05_reservoir	1,411,300	2900	78	5	4	68
Segment_06_stream	313,840	580	72	1	4	61
Segment_07_reservoir	576,130	1600	61	5	2	51
Segment_08_stream	250,860	794	58	1	9	48
Segment_09_reservoir	1,956,000	2000	46	4	14	35
Segment_10_stream	38,310	225	32	1	2	22

[a] (Calculated by volume / (length * width)).

area. The dimensions of the water bodies of the ten segments were taken from the hydrodynamic model (HEC-RAS) of the NUMOS project within the joint Yangtze project. Areas and lengths were measured by means of QGIS functionality (Quantum GIS Development Team, 2013, more information in SI) (Table 2).

2.1.3. Flow conditions and water volume changes

The HEC-RAS model was calibrated to the boundary conditions defined by a water level time-series at the level of the city of Wuxi (upstream the Dachang Lake, not influenced by the dynamics and outside of the fluctuation zone of the TGR) and by the time-series at the level of the City of Wushan downstream before the confluence of the Daning River with the Yangtze River, which is strongly influenced by the water fluctuation zone (details in SI).

2.2. Setup of simulation studies

2.2.1. Nutrient variation

The daily loads of each of the ten segments were varied simultaneously with factors of 0.5, 1, 5, 10, 50-fold loadings for nitrogen, phosphate and the combination of nitrogen and phosphate, compared to the base-run (0.3 mg P/L, 5 mg N/L daily loads from feeder, mainly upstream) segments. I.e. the total amount of nutrients that entered the water bodies strongly depended on the size and transport capacity of the upstream segments. Here, concentrations of ammonia and phosphate, as well as the densities of one guild of primary producers (green algae), primary consumers (daphnids), plant feeding fish (grass carp) and predatory fish (black carps) were analysed.

The simulation run for 25 years from 2012 to 2036 was analysed to answer these questions. The following results show the representative middle period of 5 years (2020–2024) after the system has levelled off at stable repeating patterns.

Results of the tenth year after simulation start were chosen because this period lies well within the stable phase after levelling (for demonstration of stabilization of the simulated fluctuating population patterns refer to SI – section 'Stability of the simulation environment and time to equilibration'). We decided to mainly analyse results of the simulation runtime between five and ten years.

2.2.2. Realization of pollution scenarios - exposure module

The main scenarios of pollution were derived in an incremental procedure. Firstly, a study area near Wushan city was chosen because of its exemplary pattern of landscape features and pollution sources (Fig. 3). Secondly, the hydrodynamic situation in the designated study area was estimated by simulating the yearly patterns of flow conditions and water volumes of Daning River sections. Thirdly, based on the patterns of agricultural practice and land use, segments with high and low pesticide loads were determined. The assumptions and predictions of a standard environmental risk assessment were used to define maximum loads of pesticides accordingly the expectable application procedures and additional massive overuse. The segment definition procedure included that neighboured lake and stream segments were linked.

Feedback links were incorporated in cases where the hydrodynamic model predicted backflow to upstream segments or where the respective segment was directly connected to stagnant waters. The supposed area-of-exposition was marked by agriculture (rice or maize crops) on terraces. Hence, intense nutrient and pesticide use could be expected.

Not each of the stream and lake segments 1–10 of Fig. 3 had the same exposure probability to plant protection products, especially to the designated model substance propanil. In order to define segments that received high, medium, or zero application rates of the herbicide propanil, the land-use of the adjacent areas was analysed. The analysis was based on the global land use map 'Globcover' of the European Space Agency (Leroy et al., 2006). All of the land-use types within a 300 m buffer zone around the segments were analysed for percentage area coverage of the total buffered fluctuation zone (Fig. 3). It was assumed that the category 'irrigated cropland' was most likely to be cropped with rice (or maize) cultures and the adjacent areas with high relative areas thus received high amounts of herbicides by drift or runoff events. The highest exposure class was assigned to the segments three and five (bold segment numbers in Fig. 3). The herbicide in this case was represented by our model compound propanil. Further three categories of 'croplands' were found in the region ('mosaic vegetation/croplands', 'rain fed croplands', 'mosaic croplands/vegetation') and considered to receive medium amounts of pesticides (italic segment numbers four, seven, eight and nine in Table 3). Six of the land-use types around lake and stream segments in the model region were combinations of shrubland, forests, grassland or artificial areas that with no indication of intensive pesticide use. The adjacent segments with high relative areas of non-exposed land-uses were set to zero exposure (segments one, two, six, ten).

The exposure regime was applied at two two-week periods per year. There was evidence that in sub-tropical regions two growing periods per year would be possible (in the lower reaches, even three harvests were reported (Encyclopaedia Britannica, 2014). Application and run-off to the water bodies were set from 1st to 14th of April in spring and

Table 3
Analysis of land-use cover in a 300 m buffer zone around the segments of the model region 'Daning River'. Bold segment numbers: Segments surrounded by irrigated croplands with high probability of propanil exposure; Italic segment numbers: medium exposed segments surrounded by 'other croplands'. Segments 1, 2, 6, 10 were considered to have low probabilities of propanil exposure.

Segment no.	1	2	**3**	*4*	**5**	6	*7*	*8*	*9*	10
Irrigated croplands		3	**15**		**1**					
Rainfed croplands	12	35	**22**	*21*	**34**	1	*12*	*2*	*52*	43
Mosaic vegetation/croplands	2	11	**16**	*33*	**16**	18	*41*	*22*	*44*	22
Mosaic croplands/vegetation	35	13	**21**	*31*	**27**	4	*3*	*15*		
Closed needleleaved evergreen forest	3	12	2		2	24	23	27		
Closed to open mixed broadleaved and needleleaved forest	2	3	4	*11*	6	11	4	13		
Mosaic grassland/forest-shrubland				*2*	5	1		4		
Mosaic forest-shrubland/grassland						5	5			
Closed to open grassland	19	11	**20**	*1*	**9**	2	*12*	*8*	*2*	
Closed to open shrubland						34	*1*	*8*	*2*	35
Artificial areas	26	12								

from 1st to 14th of September in autumn. The mode of application in Chinese rice cultures was assumed similar to the intended uses underlying the application for re-inclusion of the substance in European countries that was finally not granted by the EU member state Italy (Ministry of Health Italy, 2006). Propanil should be applied twice a year in a 15 day interval to drained paddy fields at maximum rates of 4000 g a.s./ha to control *Echinochloa crus-galli*, sedges and further species of water plantain family originating from seeds.

The question of how much of the substance reached the water bodies was deduced from regulatory risk assessment data of propanil (Ministry of Health of Italy, 2006) as rule-of-thumb estimates. The worst case $PEC_{initial}$ given by MED-rice simulations (scenario 1a, no degradation, no sorption) for application rates of propanil of 4 kg a.i./ha in surface waters was 191.9 μg/L. Adding some 10% to this $PEC_{initial}$ gave 220 μg propanil/L, and correspondingly to the proposed standard degradation scheme of propanil (refer to SI), 10% of parent 3,4-DCA (22 μg/L), and finally out of that 5% TCAB (0.5% of parent equals 1.1 μg/L) for the medium exposed segments were applied. The exposure was realized by a daily loading of propanil and TCAB from very small 'creek' tributaries of 1000 m^3 constant volume and 1000 m^3 loaded inflow. For the highly exposed segments 3 and 5, the basic loadings were assumed 10-fold higher than for medium exposed segments. Resulting peak concentrations in the actual lake and stream segments were much lower (refer to the results).

2.3. Accumulation of propanil within aquatic food webs - bioaccumulation module

2.3.1. Toxicant bioconcentration and bioaccumulation in plants and animals

Standard equations of AQUATOX were used to model toxicant uptake and egestion by plants and animals. For algae and macrophytes, as well as for invertebrates and fish, the bioconcentration factors (partitioning between organism and water) were calculated mainly depending on the octanol-water-coefficient of the respective compound and the lipid content of the organism. The time to reach equilibrium between the exposure events was taken into account, if necessary non-equilibrium kinetics was applied (Park and Clough, 2010). The uptake rate K1 for animals depended on both uptake via water phase and by feeding, thus the bioconcentration factor became a bioaccumulation factor accounting for food chain effects.

2.3.2. Biotransformation and biodegradation of propanil and TCAB

Most of the information on degradation of propanil was gained from EFSAs draft assessment report (DAR). 3,4-DCA and TCAB are just by- or intermediate products of pesticide production or degradation. Basic knowledge on the microbial degradation half times under aerobic and

anaerobic conditions as well as photolysis rates was necessary for the calibration of the model (Ministry of Health Italy, 2006).

Hydrolytic processes were considered irrelevant at pH between 7 and 8 as observed at the Daning River. Therefore, propanil (and arbitrarily TCAB also) catalysed and uncatalysed hydrolysis constants have been set to zero. The rate of anaerobic microbial degradation was unknown and therefore set to zero. The maximum rates of aerobic microbial degradation in water were calculated with $DT_{50} = 2$ days, equals 0.25/day (taken from DAR propanil, Ministry of Health Italy, 2006, assuming constant loss rates). The photolysis rate was estimated from an environmental DT_{50} by direct photolysis at the water surface with 52.1 days (Ministry of Health Italy, 2006). The rate was calculated with 50%/52.1 days = 0.01/day (assuming constant loss rates).

2.4. Biotic components of TGR ecosystems - food web module

2.4.1. Trophic guilds and interactions

Fourteen trophic guilds were defined based on literature research on the most common and representative species in the TGR-region. The food web consisted of five fish guilds (derived from the species *Mylopharyngodon piceus*, *Hypophthalmichthys molitrix*, *Ctenopharyngodon idella*, *Hypophthalmichthys nobilis*, *Tachysurus fulvidraco*), three zooplankton organisms (*Daphnia magna*, *Bosmina fatalis*, *Mesocyclops leuckarti*), one macro-invertebrate (*Chironomus* spec.), one mollusc (*Corbicula fluminea*), three algae (depending on whether found in lake or stream segments *Microcystis* spec., *Melosira granulata*, *Scenedesmus arcuatus*, *Cyclotella comta*, *Chroococcus* spec.) and one macrophyte (*Myriophyllum spicatum*). The physiological characteristics of the species were leant against standard species implemented in the internal AQUATOX databases and modified by traits of sub-tropical plankton and fish species (Rings, 2013, food web structure with trophic interactions between guilds in SI, SI_figure 6).

2.4.2. Initial densities, organism loadings and striven equilibria

It was expected that the undisturbed conditions of the AQUATOX simulation changed to an equilibrium ('levelling phase'), providing realistic densities of organisms after sufficient time. In the long term, a stable system would be established. Loadings of organisms and nutrients were added at each time-step. This led to well-maintained populations in case of approaching complete extinctions, which could occur due to very high flow rates (emigration) and dilution factors, and due to mortality after adding toxic substances.

At the beginning of the levelling phase of 5 years, primary producers were initially added with densities of 100 mg dry weight/L, zooplankton organisms were introduced with densities of 10 mg dry weight/L. Fish were added in densities of 10 g dry weight/m^2 (differences between lake and stream segments lists Table 4). At each of the next time-

Table 4
Initial densities and daily loadings in lake and stream segments.

Test item	Test species	AQUATOX toxicity entry	Test system	Duration of exposure	Results
Propanil technical	*Cyprinodon variegatus*	Cyp var	Acute	96 h	LC$_{50}$: 4.6 mg/L[a]
	Daphnia magna	Dap mag	Acute	48 h	LC$_{50}$: 6.7 mg/L[b]
	Lemna gibba	Lem gib	Acute	14d	EC$_{50}$: 0.11 mg/L[c]
	Navicula pelliculosa	Nav pel	Acute	72 h	EC$_{50}$: 0.025 mg/L[d]
	Physella acuta	Phy acu	Not known	48 h	LC$_{50}$: 8.8 mg/L[e]
TCAB	*Pimephales promelas*	Cyp var	Acute	96 h	LC$_{50}$: 0.029 mg/L[f]
	Daphnia magna	Dap mag	Acute	72 h	LC$_{50}$: 0.048 mg/L[g]
	Lemna gibba	Lem gib	Acute	72 h	LC$_{50}$: 0.00079 mg/L[g]
	Navicula pelliculosa	Nav pel	Acute	72 h	LC$_{50}$: 0.00017 mg/L[g]
	Physella acuta	Phy acu	Acute	48 h	LC$_{50}$: 0.063 mg/L[g]

[a] Sousa (1990).
[b] Graney (1982).
[c] Giddings et al. (1990a), used as LC50 in AQUATOX.
[d] Giddings et al. (1990b), used as LC50 in AQUATOX.
[e] Kegley et al. (2014).
[f] Chemprop QSAR model (Scholz-Starke et al., 2013).
[g] Own estimate by using the proportion of 140 fold higher toxicity between fish toxicity of propanil and TCAB derived from Chemprop model, supported by Xiao et al. (2016).

steps, populations were increased by 10% of the initial density to balance losses for all reasons implemented in the model (differentiated mortalities, washout from upstream segments, which means immigration). It depends on whether a segment has stream or lake character, and on the period of the season, if immigration or emigration processes predominate in regarded segment.

Averaged over a simulation year, we aimed to consider realistic densities of organisms. Literature on Chinese rivers and lakes as well as experiences from temperate regions served as guidelines for plausibility checks. Chlorophyll-*a* contents at the Daning River in the period just before the impoundment of TGR 2004–2007, varied with season between 1 and 23 μg Chlorophyll-*a*/L (Zhang et al., 2010). *Copepods*, in particular the species *Mesocyclops leuckarti*, occurred in the main river area of the TGD in densities of 0.046, 0.372, 0.062, 0.006 individuals/L (Yao et al., 2008). A portion of 10% of the populations of all five fish species actively migrate once a year to the connected upstream and downstream segment. All other state variables (nutrients, pollutants, plankton organisms, detritus) are subjected to passive drift in stream direction (wash-in- and wash-out mechanisms).

2.5. Multivariate statistics

For the multivariate analysis of the impact of varying nutrient loads, a Principal Response Curve Analysis (PRC, Van den Brink and Ter Braak, 1999) was conducted. The method was derived from a redundancy analysis and developed for the ease of interpretation of temporal changes in species composition of a community after the impact of a toxic substance. The PRC-diagram displays on left-hand side the relative mean deviation of each treatment community from control level on the y-axis (c_{dt}), the time course of effects can be tracked on the x-axis. On the right, the diagram shows the relative affinity (correlation) of each species to the overall response (species weights b_k). The summary table of the test statistics helps with the interpretation and gives the statistical significance of the most important canonical axis (after Monte-Carlo permutation test) and the partitioning of the total variance that was captured by treatment, time or between-replicates variability.

2.6. Toxic action of model substances - ecotoxicity module

The realistic representation of the effects of the model substances propanil and TCAB required to include toxicity data for the 14 feeding guilds. Therefore, the literature was searched for standard toxicity data to be appropriate for the multi-guild groups 'mussels', 'fish', 'zooplankton organisms', 'macrophytes' and 'algae'. Because the suspected bioaccumulative and toxic metabolite TCAB was scarcely investigated, a QSAR model was applied (UFZ, 2012) and own expert assumptions on the toxicity of the compounds were acquired (overview on chemical properties and degradation of propanil in SI) (Table 5).

3. Results

3.1. Shifts of food web structure due to varying amounts of growth limiting nutrients

3.1.1. Water concentrations of nutrients

Ammonia and total phosphate concentrations in water did not show clear dose-dependent differences as an effect of N-variation (Fig. 4). However, clear dose-dependent differences in phosphate water concentrations were detected after P-variation (Fig. 5). Patterns differ clearly between lake and stream segments for the concentrations of ammonia and not for phosphate. We had chosen segments one and six to be displayed, however similar results were obtained for other segments of the model region. Nonetheless, segment one as the last component of our ten segment stretch and the final 'trap' of upstream compounds was of outstanding importance for our analyses.

3.1.2. Densities of feeding guilds

Because of the differences in concentrations of total phosphate, densities of green algae varied dose-related in the lake segment 01 as well as in the stream segment 06.

The invertebrates, e.g. daphnids, that feed on the primary producers followed roughly the patterns predetermined by the phytoplankton organisms and thus reveal a relation to the nutrient contents in the water column as well (Fig. 7).

The simulation showed for fish, here exemplified by the herbivorous grass carp (Fig. 8) and the predatory black carp (Fig. 9, for feeding preferences refer to Section 2.4 and SI), that additionally to seasonal density changes nutrient-related shifts occurred. The grass carps did not occur in stream segments. For that reason a minimum number of individuals occurred in segment 06, supplied by the upstream migration rate from segment 07 of 1% per time-step and downstream migration from 05. However, no locally stable population could be maintained.

3.1.3. Alterations of communities

Shifts of the aquatic communities, represented by trophic guilds, were followed by the PRC over a representative season (Fig. 10). The reference load was taken as the control or baseline (1-fold concentration of nutrients, x-axis). Five lake segments 1, 3, 5, 7, and 9 served as replicates that were not independent of each other. The mean density of each trophic guild was sampled at each month of the simulation year 15, which was considered well after equilibration of the simulation run.

There was no statistically significant effect of the nutrient regimen on the composition of the 'guild community', neither over all sampling dates, nor at single dates out of the 12 sampled months of simulation year 15. Only slight differences compared to the base level were caused

Table 5
Plant and animal toxicity data for the herbicidal parent model substance propanil and its secondary metabolite TCAB.

| State variable name (unit)	STREAM segment			LAKE segment		
	Init. cond.	Daily load	Multiple loading factor	Init. cond.	Daily load	Multiple loading factor
Y_Diatom (mg dry weight/L)	100	10	1	0	0	0
Y_Phyto Greens (mg dry weight/L)	100	10	1	100	10	1
Y_Blue-Greens (mg dry weight/L)	100	10	1	100	10	1
Y_Myriophyllum (g dry weight/m²)	0	0	0	1	1	100
Y_Chironomid (g dry weight/m²)	1	0	1	0	0	0
Y_Bosmina (mg dry weight/L)	0	0	0	1	0	1
Y_Copepod (mg dry weight/L)	0	0	0	1	0.1	1
Y_Daphnia (mg dry weight/L)	1	0.1	1	0	0	0
Y_Mussel (g dry weight/m²)	10	1	1	0	0	0
Y_Catfish (g dry weight/m²)	10	1	1	0	0	0
Y_GrassCarp (g dry weight/m²)	0	0	0	10	1	1
Y_BlackCarp (g dry weight/m²)	10	1	1	10	1	1
Y_SilverCarp (g dry weight/m²)	10	1	1	10	1	1
Y_BigheadCarp (g dry weight/m²)	10	1	1	0	0	0
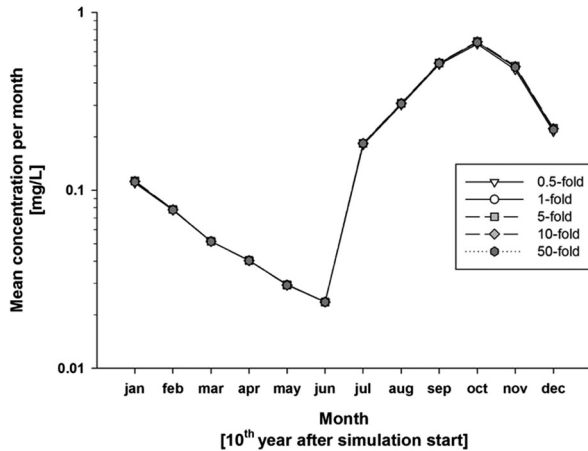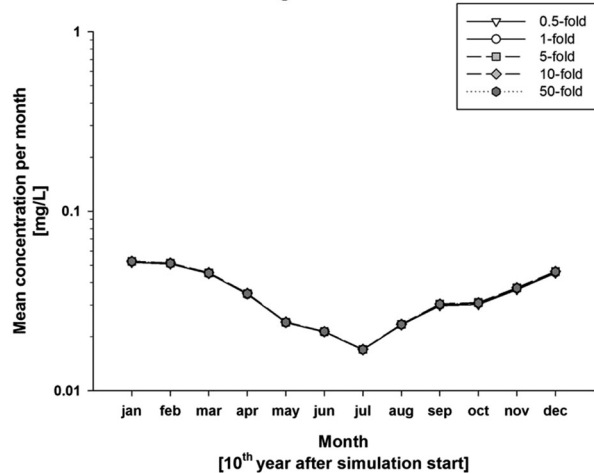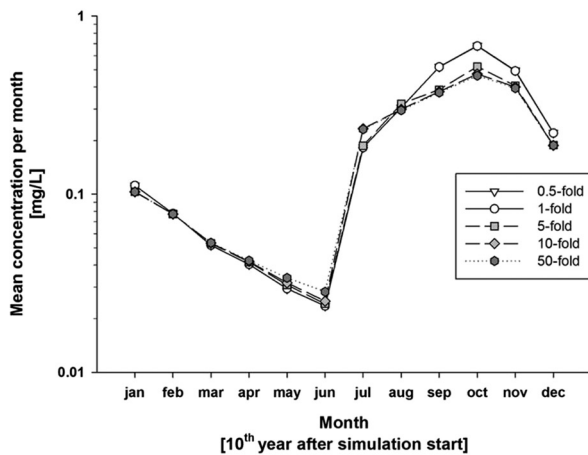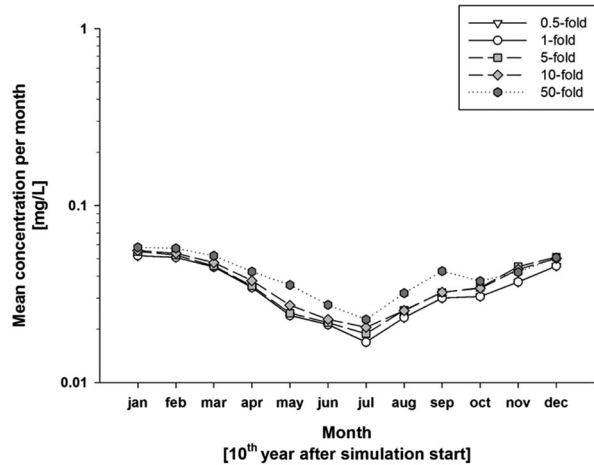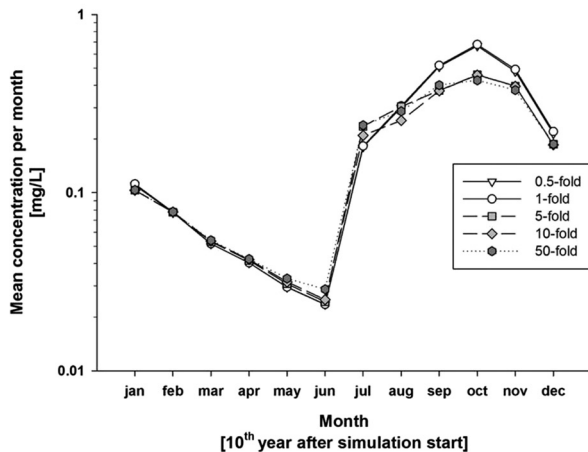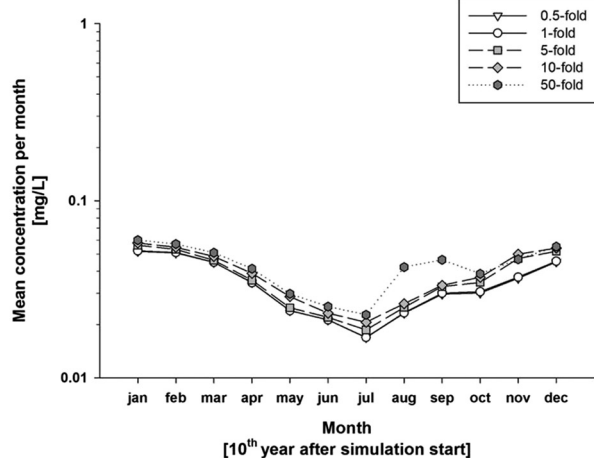
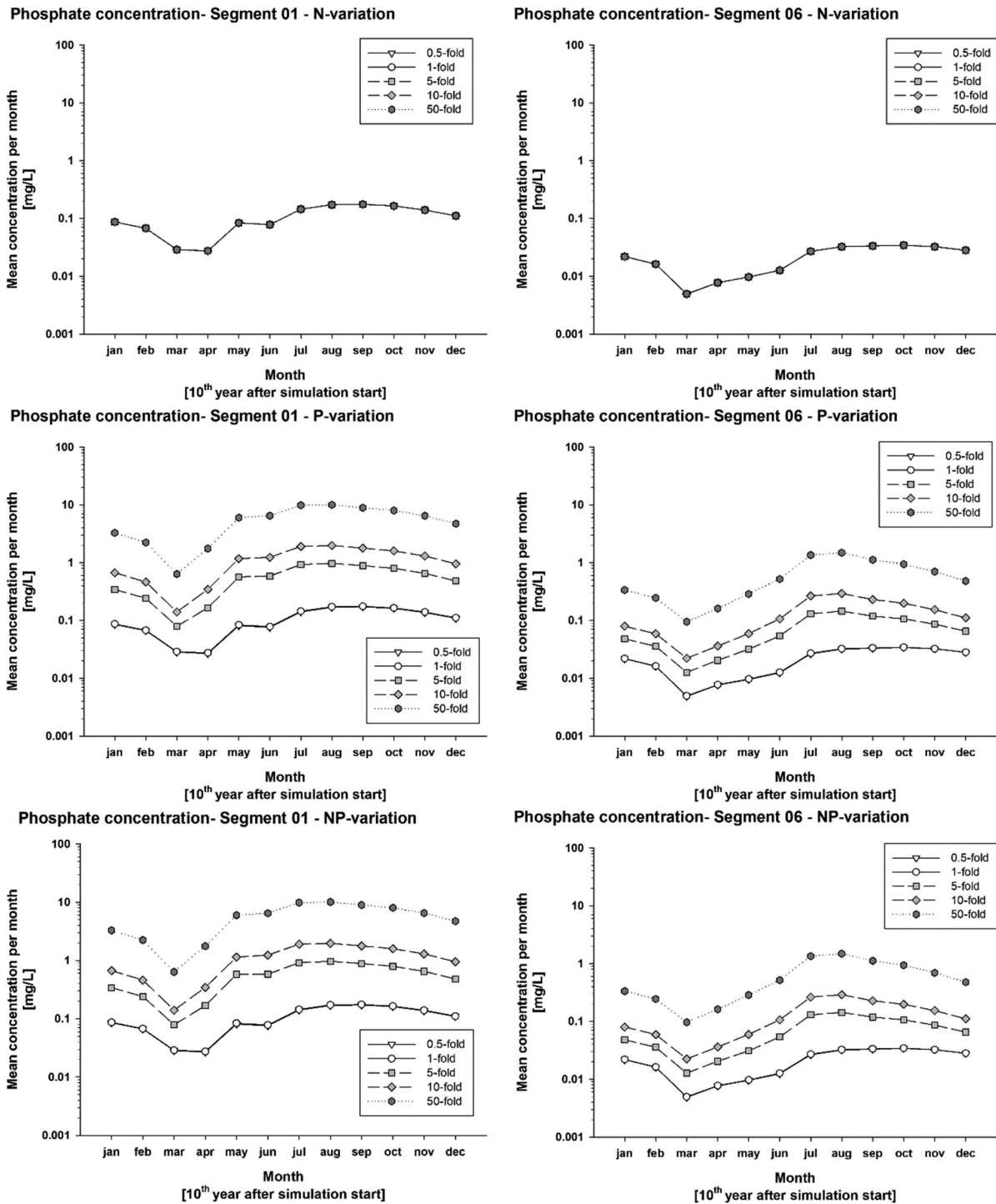**Fig. 4.** Ammonia concentrations after variation of phosphate, nitrate and phosphate + nitrate loads from 0.5 to 50 fold of 0.3 mg P/L constant loading from upstream segments.

by the nutrient regimes with 5–50 fold loads, with highest deviation by the highest nutrient level.

3.2. Bioaccumulation of model pollutants within the aquatic food webs

3.2.1. Water concentrations

The highest water concentrations of both dissolved propanil and TCAB were modelled to occur after the second application period in mid-September for propanil in the downstream Wushan Lake segment

with water concentrations between 0.009 and 0.010 μg/L and most of the times 5 weeks later for TCAB with concentrations in water between 0.007 and 0.017 μg/L.

3.2.2. Internal concentrations

All of the modelled organisms (trophic guilds) accumulated TCAB within their tissues. Amongst the guilds occurring in the lake segments of the simulations, catfish showed the highest mean concentrations of 40,000 μg TCAB/kg wet weight within the five-year period evaluated

Fig. 5. Phosphate concentrations after variation of phosphate, nitrate and phosphate + nitrate loads from 0.5 to 50 fold of 5 mg nitrate/L for segments 01 (lake) and 06 (stream).

(2020–2024). The primary producers showed mean concentrations of 300 μg TCAB/kg wet weight. Zooplankton organisms and other fish like the carps showed internal concentrations between 650 and 22,000 μg TCAB/kg wet weight.

3.2.3. Toxic effects

Treatments by TCAB led to 30% increase of biomass (daphnids) on the one hand, and to complete extinction of fish species in periods of very high exposure (e.g. grass carps). Peak burdens caused high mortality rates of up to 100% of the populations, which recovered very fast from upstream resources and daily loads (Fig. 11).

4. Discussion & conclusions

4.1. Bioaccumulation of pesticides

As we had shown by the analysis of land-use patterns from publicly available data (Fig. 3), exposure to plant protection products, in particular rice herbicides, could be plausibly expected for the model region at the confluence of Daning and Yangtze rivers due to intense agricultural use of the riverbanks. This prerequisite of our study is not supported by GIS data as well as by field investigations confirming the traditional use of the littoral zone (Chen et al., 2017).
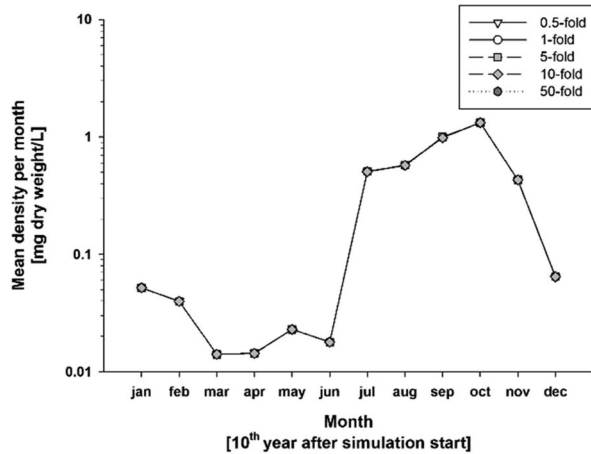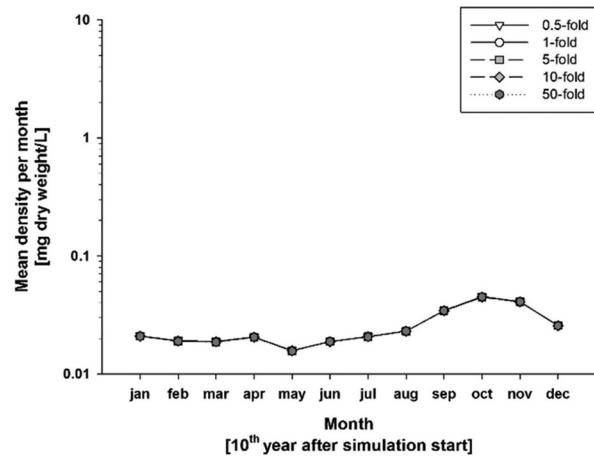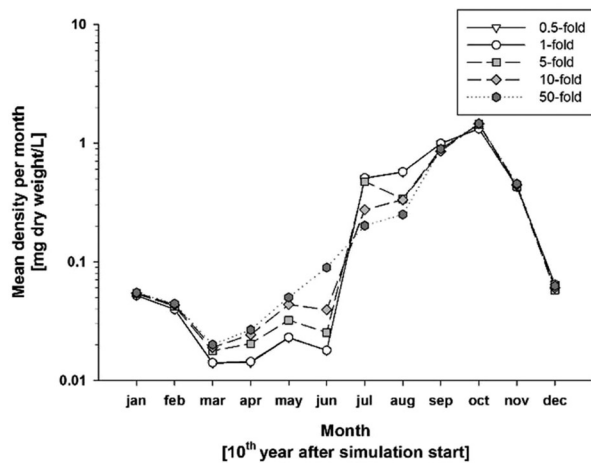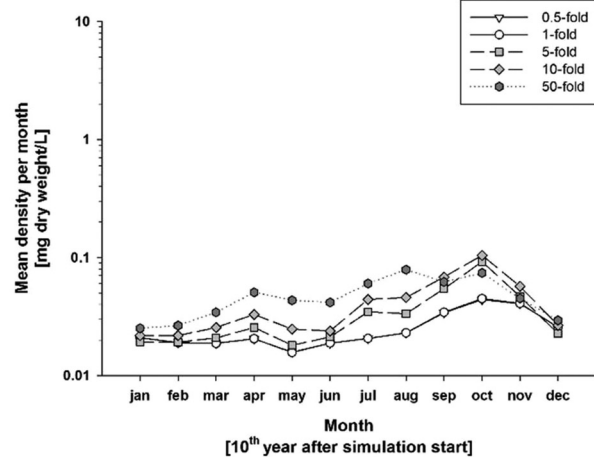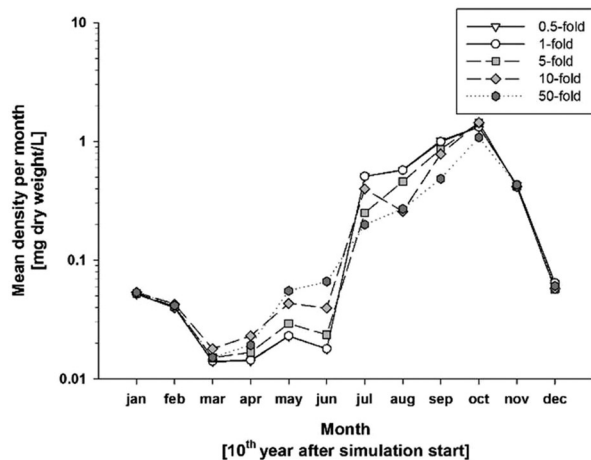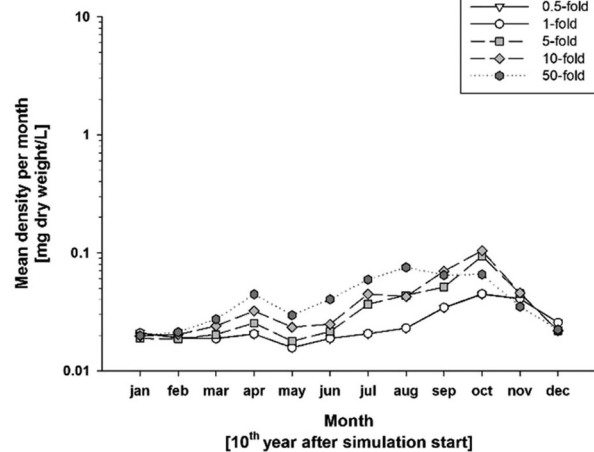
Fig. 6. Average densities of green algae (mg dry weight/L) per month, 10 years after start of the simulations.

Since the model substances propanil and TCAB were transported fast to the last downstream segment of the model region before the confluence with Yangtze River, highest water concentrations accumulated in Wushan lake. This was mainly because the yearly periods of contamination were short and the transport via water flow was mainly directed downstream. Focusing on the worst case for the environmental and human risk assessment, the results of the simulation studies in which the model substances were applied were shown for the Wushan Lake segment no. 01.

An earlier application of the AQUATOX model showed for the 'Coralville reservoir' standard study, that a peak concentration of 0.465 μg a.i./L after (resulting from 10 kg of the pesticide dieldrin applied in a terrorist attack), resulted in maximum internal concentration of about 1000 μg dieldrin/kg wet weight in shad fish (Rashleigh, 2007). Dieldrin has comparably to TCAB a very high octanol-water partition coefficient of 5 (TCAB 5.84). The variable values of water concentrations after short-time application and the internal concentrations within the organisms in our simulations were plausible for very bioaccumulative
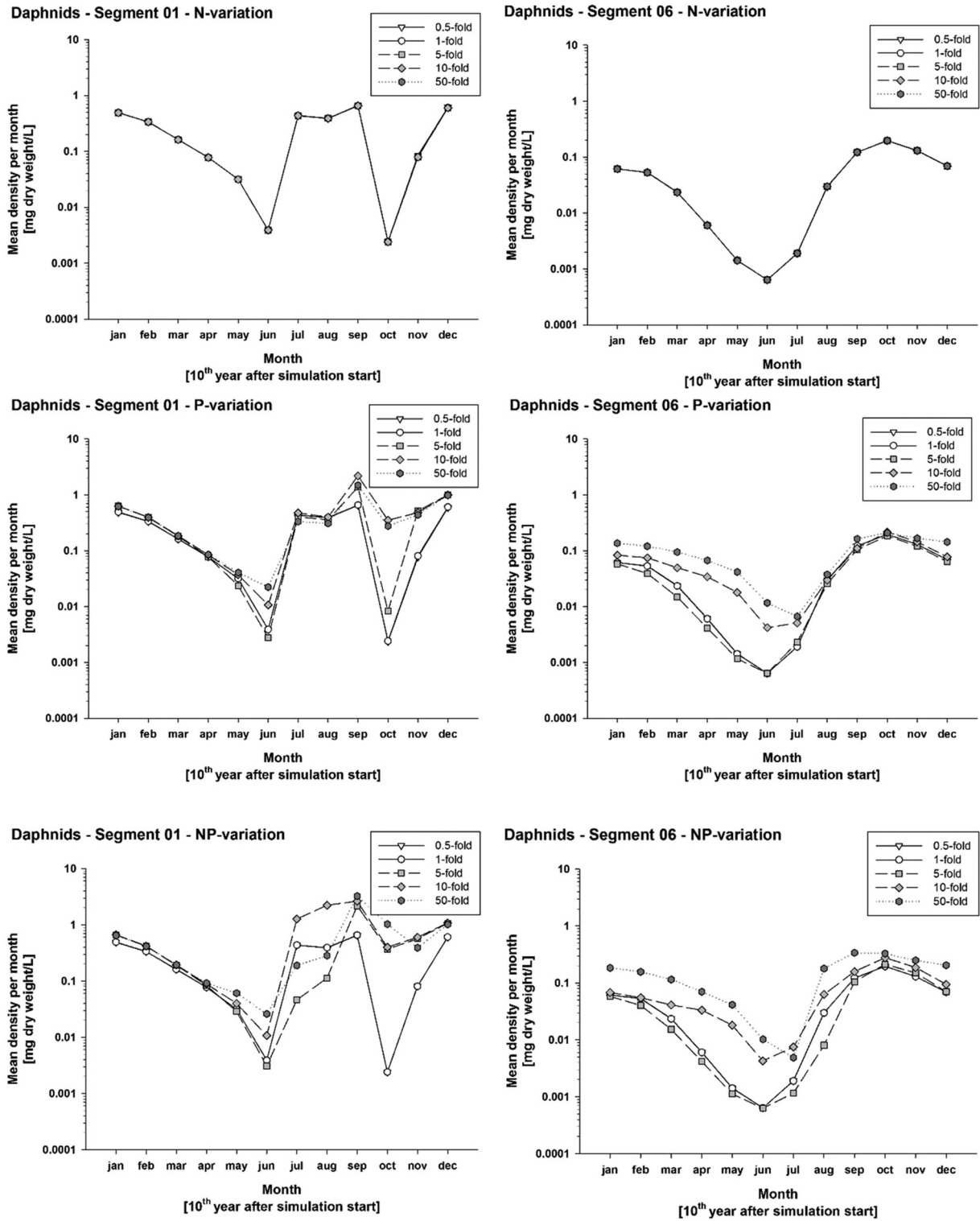
Fig. 7. Average densities of daphnids (mg dry weight/L)per month 10 years, after start of the simulations.

chemicals. It was seen that a considerable amount of TCAB was fixed for a certain time in refractory and labile detritus, in particular in particulate and sediment fractions (e.g. for the refractory detritus in sediment). All of the fish guilds fed partly on detritus, and thus an additional uptake path was given beyond direct uptake via the water phase or biomagnification via other organisms.

However, concerning a risk assessment for the consumption of fish would necessitate acceptable daily intake rates (ADI) for the considered

substance. Such values were available for propanil from the DAR (Ministry of Health of Italy, 2006). The rapporteur came to the conclusion that a consumption rate of 0.03 mg propanil/kg body weight/day would have no harmful long-term impact on human health. Assuming that an average resident has a weight of 60 kg, one could consume 1.8 mg propanil per day. The range of catfish internal concentrations within one year was approx. between 0.0001 and 10,000 μg a.i./kg wet weight. If someone would subsist on 200 g of catfish at every day of a
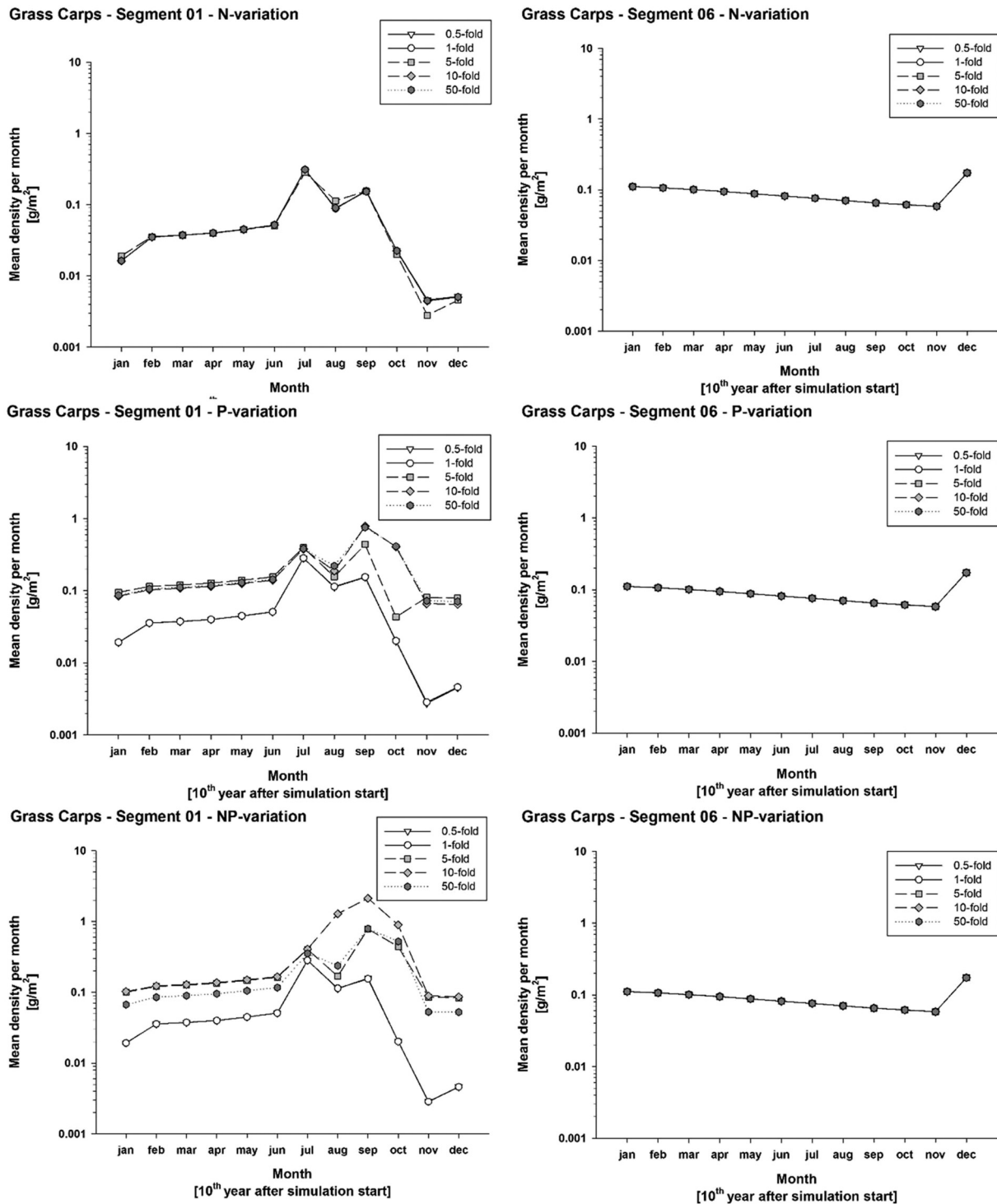
Fig. 8. Average densities of grass carps (g dry weight/m²) per month, 10 years after start of the simulations.

year, this would result for the worst-case to 2 mg propanil/kg body weight/day and thus exceedance of the ADI.

The patterns of water and internal concentrations followed very well the application patterns. In autumn, the effect of an application was resulting in much higher water concentrations than in spring. This was neither due to differing water volumes in segment 01, nor to differing temperatures, which were very similar in the respective periods.

The aquatic food web of the TGR-model contained several interconnected trophic levels. Together with the high log K_{OW} of the suspect metabolite TCAB, a significant biomagnification of this secondary metabolite was expected and confirmed by the simulation studies. In

particular, stagnant downstream sections of tributaries like the Daning River exhibited comparably high risks of accumulating pesticides from upstream sources.

Altogether, it was seen that TCAB accumulated along the food chains in the TGR environment. No clear food chain effect and thus no strong biomagnification were deduced from the results for silver carps that had a broad spectrum of food items (according to Kolar et al., 2005). Silver carps are known from stable isotope analyses to have lower trophic positions in aquatic food webs than closely related species, e.g. Bighead carps (Rogowski et al., 2009). For the interpretation of the results, it was important to know that the bioaccumulation within the AQUATOX
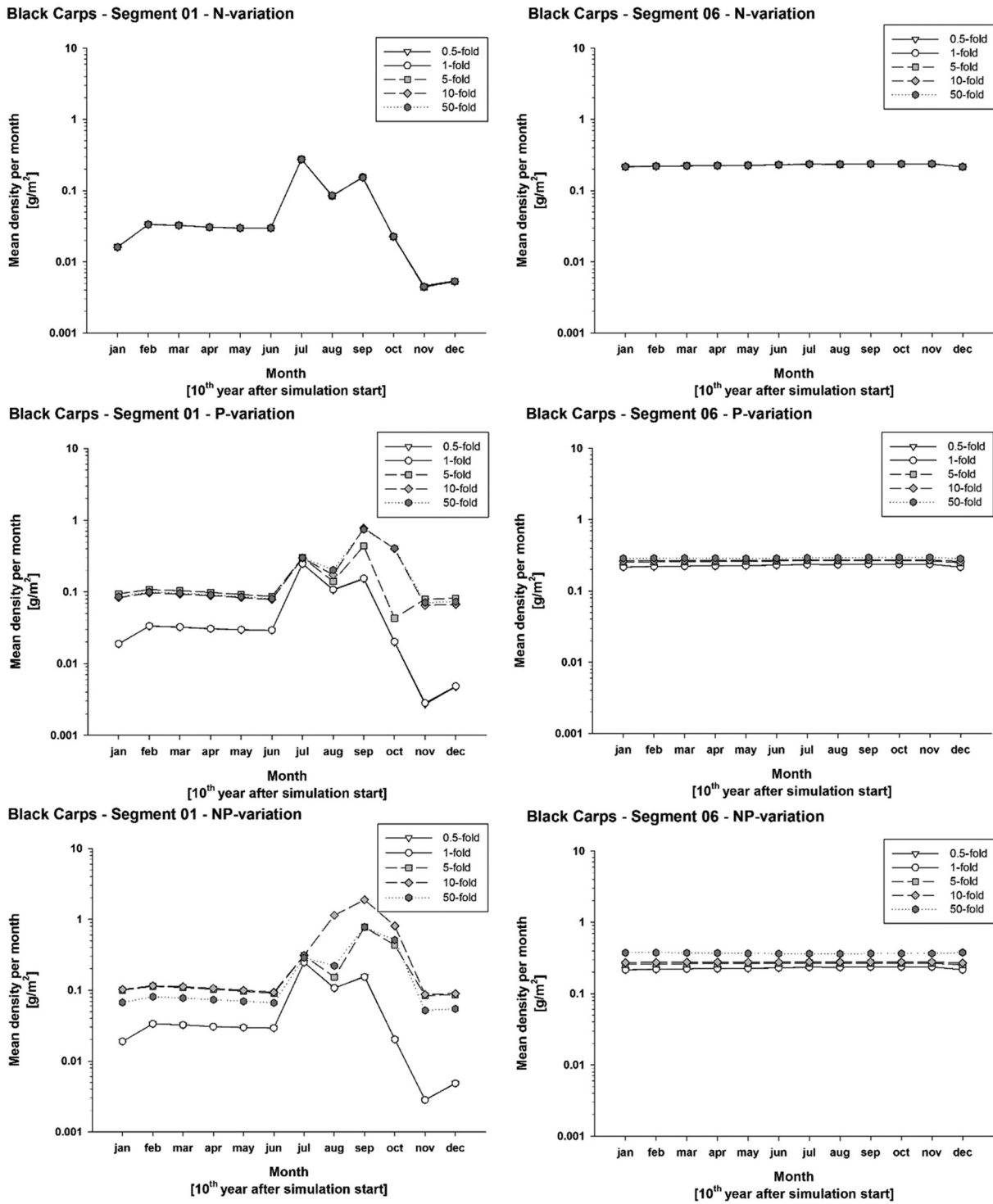
Fig. 9. Average densities of black carps (g dry weight/m^2)per month 10 years after start of the simulations.

model in large fish was determined by gill uptake and dietary uptake, while the elimination from the organisms' tissues were expressed as functions of excretion and biotransformation processes (Park and Clough, 2010). We recommend to manage the upstream catchment area regarding sustainable pesticide use, e.g. by the introduction of the principles of Integrated Pest Management (Furlan and Kreutzweiser, 2015), that has been already applied in a high number of industrialised and developing countries. The model can now be further adapted and applied to a variety of different compounds and exposure patterns. It is planned to integrate some of the most important polychlorinated

biphenyls that have been found relevant in the water of Yangtze River and in the tissues of fish (Ge et al., 2014) often exceeding the water quality standards of 20 ng/L (according to the Ministry of Environmental Protection of the People's Republic of China as per Floehr et al., 2013).

4.2. Nutrient impact on limnic communities

Besides the impact of pesticidal compounds on the aquatic ecosystems, it was identified as a common problem that high amounts of nutrients entered the aquatic systems of the region. Especially adverse site
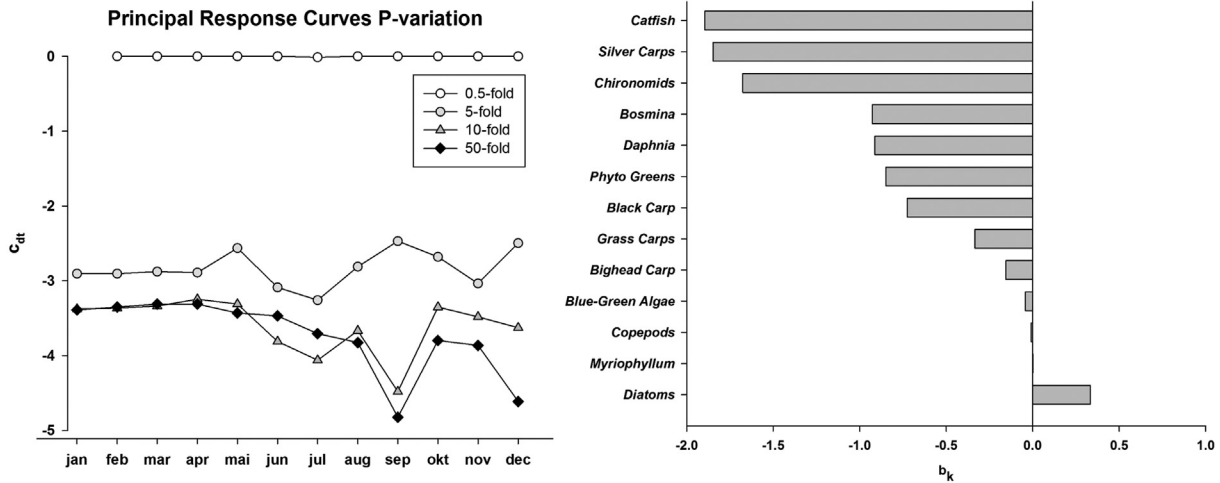
Fig. 10. Principal Response Curves (PRC) Analysis of the simulation experiment introducing varying daily phosphate loads into all lake segments at the Daning River. No significant influence of the treatment (RDA on single dates) and no statistical differences (PCA sample scores) between any treatment and control at any time point.

conditions, like stagnating flowing-sections, had shown a profound influence on the results of the simulation studies. We demonstrated this influence on populations (and on communities) of feeding guilds in virtual dose-response simulation experiments.

The results of the combined concordant variation of N and P loads per time step of the simulation did not show any emergent effects on the water concentrations that were not explainable as from the variation (i.e. concentration) of one nutritional component alone. We are therefore allowed to interpret the impacts of nutrient variation on the feeding guilds without additional confounding factors. The patterns of feeding guild densities, exemplified by the population dynamics of green algae in Fig. 6, could not completely be explained by the fraction of the total populations that were limited by the respective nutrients. This was because the growth of e.g. green algae and diatoms in the reference system (1-fold = normal nutrient loadings per time step of the simulation, all segments considered) was predominantly limited by the nitrogen concentrations (approx. 80% and 50% fraction limited on average over all segments, respectively) and not by phosphate concentrations (approx. 30% fraction limited for both groups).

The growth of most trophic guilds highly depended on the phosphate contents whereas the variation in nitrogen contents influenced the densities to minor extent. For blue-green algae, the limitation was similar with 70% nitrogen limitation and about 40% phosphate limitation (AQUATOX output not shown). This is because the system was severely P-oversaturated.

Blue-greens usually compete better than other algae in N-limitation or O_2 deficiency situations. Accordingly, the blue-green algae revealed a P-half saturation rate of 0.03 mg/L and N-half saturation rate of 0.4 mg/L, whereas green algae had half saturation rates of 0.05 mg N/L and 0.006 mg P/L.

Nutrient limitation was not suited as the main explaining factor for population dynamics that depended on nutrient variations. The patterns of primary producer's densities over a representative year (15 years after simulation start) emerged partially from complex interactions within the model that could not be ascribed to monocausal origins. Since the daphnids, abstracted as the algae feeding guild, fed on green, blue-green and diatom algae and detritus to the same extent, the resulting pattern was influenced by complex biotic and abiotic factors.

However, even high nutrient loads resulted in only slight changes of densities of organisms of all trophic levels. The system was saturated and contained quite high nutrient concentrations, so that e.g. phosphate was not considered the limiting factor for the growth of primary producers. It was concluded that the state of the Daning River at the site investigated was eutrophic anyway. Nevertheless, the probability of emerging large-scale algal blooms affecting the drinking water quality in the Wushan Lake was small because of the high flow velocities and discharge rates towards the Yangtze River.

Summing up the impact of different nutrient loads on the trophic guilds, the system reached a new trophic status only after adding large amounts of nutrients. Due to high flow rates of river sections, resulting in fast dilution, the system is well buffered towards massive introduction of nutrients. A significant increase of agricultural activity in the upstream areas of the Daning River impacted the aquatic communities only slightly. However, the longer the free-flowing section, the less turbulent the water towards stagnant conditions and the longer the residence time of the water was, the more apparent was the impact of nutrients. It was shown by other authors that large scale algal blooms under the hydrodynamic preconditions of a relatively fast flowing tributary of the Yangtze River, like the Jialing River in the city of Chongqing are expected to be rarely occurring (Long et al., 2011). Zeng et al. (2007) found no correlation between phytoplankton densities and nutrient concentrations in the TGR water. In temperate European lakes, maxima of diatom algae usually occurred in spring, followed by a period of dominance of green algae in summer. In late summer, the possibility of blue-green algae blooms was given (Schaumburg, 1992). In the simulated ecosystem at the Daning River under sub-tropical conditions, the peaks of guilds of diatoms, green algae and blue-green algae occurred in the rainy season between mid of July to end of September. Zeng et al. (2006) found also the highest densities of algae from August samples in the rainy season. In April, during the dry season, densities were relatively lower. They concluded from their results that decreased flow velocity led to the occurrence of algal blooms rather than a higher nutritional status.

A trophic classification of stagnant waters of large flooded gravel pits in the 'German system' (LAWA, 2003) took several abiotic and biotic factors into account. A classification into five classes, oligotrophic, mesotrophic, eutrophic, polytrophic and hypertrophic was done by the criteria Chlorophyll-a content, Secchi depth, total phosphate (TP) in spring and summer. The AQUATOX program provided trophic state indices based on the classification by the US Environmental Protection Agency (see USEPA, 2000), which included the water concentration of nitrogen instead of distinguishing between spring and summer TP. It was assumed applicable to lakes and reservoirs and should be used with care for the stream sections of the simulations. It is therefore used for section 01 only. The analysis showed that the trophic state of the model region's last segment was eutrophic to hyper-eutrophic in the reference simulation anyway, even without increased loadings.
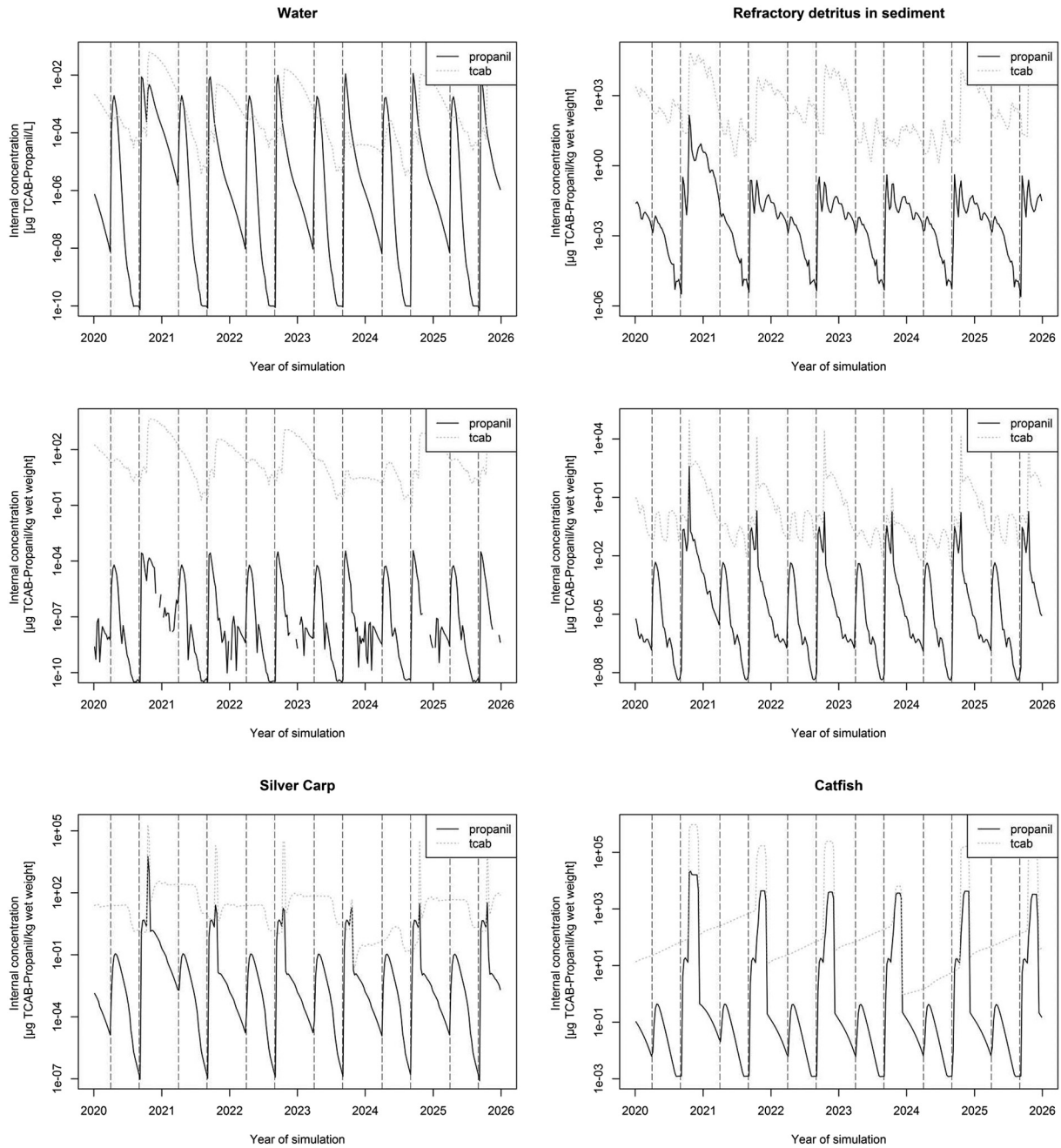
Fig. 11. Water and internal concentrations of propanil and its metabolite TCAB at segment 01 of the Daning River within a simulated five-year period.

This was the case for all segments up to the Dachang Lake. In 2009, up to 43% of the primary tributaries of the TGD were found eutrophic by the Chinese monitoring program accompanying the construction of the TGD (MEP, 2010). It could be concluded that even massive extension of agriculture, which was unlikely because of the morphology of the adjacent hills of the catchment area would not cause further deterioration of the trophic state. The hypertrophic state of the river system under the influence of TGD could indeed lead to mass developments of single algal species in periods of low water level and slow flowing water (as indicated by Long et al., 2011 for the Jialing River, for trophic state indices Table 6). The Secchi depth was the only measure that indicated an oligotrophic state of the reservoir, which seemed to be very unlikely. The AQUATOX algorithms calculated the Secchi depth from the overall extinction, composed from phytoplankton, water and from particulate and dissolved organic matter (POM, DOM). In our simulation, very small amounts of organic matter were added. It was up to the genesis

from biomass and thus stayed very small during the whole simulation period. Own measurements, admittedly in a period of serious flooding with high particle transport, had shown that at least in extreme situations average Secchi depths of about 40 cm had to be expected. Consequently, the Secchi measures were not considered for further interpretation.

Even loadings (mostly from upstream) of 250 mg nitrate/L (50-fold of normal rate) per simulation time-step of one day that resulted in average nitrate concentrations of 35 mg/L caused toxic concentrations of nitrate for fish. Only toxicity via ammonia was implemented in the model. While nitrogen was added via nitrate loadings, the formation of ammonia was up to nitrification processes determined in the remineralisation variables (not further described here, refer to the technical Documentation of AQUATOX (Park and Clough, 2010)). Consequently, total ammonia concentrations were well below toxic thresholds.

Table 6
Trophic state indices TSI (USEPA, 2000) for the last section 01 – Wushan Lake of the Daning River before the confluence with the Yangtze River. Results averaged for the 5-year period between 2020-01-01 and 2014-12-31. The nutrient loadings varied systematically to look for dose-related shifts of the trophic level. NP-scenario: nitrogen & phosphorous loads varied, P-scenario: phosphorous loads varied, nitrogen constant at default, N-scenario: nitrogen loads varied, phosphorous constant at default. TSI < 40 → oligotrophic state, TSI 40–50 → meso-trophic state, TSI 50–60 → eutrophic, TSI > 60 → hypereutrophic. TN: total nitrogen [µg/L]; SD: Secchi depth [m]; CHLA: Chlorophyll a-content in water [µg/L]; TP: total phosphorous [µg/L].

Scenario	0.5-Fold NP	1-Fold NP	5-Fold NP	10-Fold NP	50-Fold NP
TSI (TN)	51.18(0.7971)	56.56 (1.157)	78.27 (5.211)	88.34 (10.47)	111.4 (51.77)
TSI (SD)	13.77 (24.73)	13.79 (24.7)	13.91 (24.5)	14.12 (24.13)	13.63 (24.97)
TSI (CHL)	60.17 (20.38)	60.19 (20.41)	59.06 (18.2)	59.15 (18.37)	56.97 (14.71)
TSI (TP)	73.55 (123.1)	73.8 (125.3)	95.72 (572.8)	105.6 (1136)	128.9 (5698)
Scenario	0.5-Fold N	1-Fold N	5-Fold N	10-Fold N	50-Fold N
TSI (TN)	51.18 (0.7975)	56.56 (1.157)	74.49 (4.009)	83.67 (7.574)	106.2 (36.12)
TSI (SD)	13.78 (24.71)	13.79 (24.7)	13.8 (24.68)	13.8 (24.69)	13.79 (24.69)
TSI (CHL)	60.19 (20.41)	60.19 (20.41)	60.16 (20.35)	60.19 (20.42)	60.19 (20.41)
TSI (TP)	73.81 (125.3)	73.8 (125.3)	73.83 (125.4)	73.8 (125.3)	73.8 (125.3)
Scenario	0.5-Fold P	1-Fold P	5-Fold P	10-Fold P	50-Fold P
TSI (TN)	56.54 (1.156)	56.56 (1.157)	58.14 (1.292)	58.28 (1.304)	58.56 (1.329)
TSI (SD)	13.78 (24.71)	13.79 (24.7)	14.52 (23.48)	14.72 (23.15)	14.85 (22.96)
TSI (CHL)	60.18 (20.4)	60.19 (20.41)	59.79 (19.6)	59.08 (18.22)	58.71 (17.55)
TSI (TP)	73.55 (123)	73.8 (125.3)	95.76 (574.3)	105.7 (1142)	128.8 (5693)

4.3. Potential of simulation-based risk-assessment

The simulation environment provided by the AQUATOX software is a powerful tool and an excellent starting point for the adaptation to the specific situation at a tributary reach of the Yangtze River. Many parameters needed for the calibration of the model could be taken from the literature or formulated as generic assumptions. The general usefulness of our modelling approach for the understanding of basic principles that underlies tributary systems under large level fluctuations was demonstrated. It was difficult to gain original and long-term monitoring data on the ecology and water chemistry of the TGR from Chinese experts, because the region is of great national interest and raw data was considered sensitive. However, the calibration of the simulation environment led to widely plausible results, in terms of orders of magnitude of organism densities and the dynamics of the system. The simulation of the situation at the downstream Daning River allowed for the deduction of internal concentrations within fish as the main animal protein source of the local population. In case of knowledge of the maximum residue levels in food items and the maximum daily intake rates of the respective model substances propanil and TCAB, a risk assessment for humans would be possible. At the present, we think a further adjustment of model assumptions would be necessary before realistic human risk assessment can be carried out. This is unless we gave an example for the worst-case internal concentration of propanil in catfish expanded to acceptable daily intake rates (Section 4.1). Propanil was not approved for the use in the European Union for a lack of substantial information to do a proper risk assessment, as stated by the review report of the European Commission (European Commission, 2011; EFSA, 2013). The scenarios and assumptions on the exposure to pesticides due to altered land-use patterns, the accumulation behaviour of the model substances and the most adverse flow conditions marked by less dilution and long-term stagnating conditions led to worst-case results. Those could be turned into realistic scenarios by the simple assumptions of multiple exposures to a variety of pesticides and industrial pollutants in the region to end up with conservative recommendations for health and food safety of the people of this region.

An integrated approach could be used for a huge variety of research questions in the future. This was beyond the questions of stability, sensitivity towards increasing nutrients and the potential for bioaccumulation of pesticidal substances along the food chains or within the specific food webs as addressed at this point. We see a high potential of simulation-based assessments like ours that provide information for risk managers dealing with whole catchment areas. They will be put in the position to differentiate the magnitude of impacts of various factors and decide about the most effective measures and remediation actions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.057.

References

Arino, O., Ramos, P., Jose, J., Kalogirou, V., Bontemps, S., Defourny, P., Van Bogaert, E., 2012. Global Land Cover Map for 2009 (GlobCover 2009). European Space Agency (ESA) & Université catholique de Louvain (UCL) https://doi.org/10.1594/PANGAEA.787668.

Bergmann, A., Bi, Y., Chen, L., Floehr, T., Henkelmann, B., Holbach, A., Hollert, H., Hu, W., Kranzioch, I., Klumpp, E., Küppers, S., Norra, S., Ottermanns, R., Pfister, G., Roß-Nickoll, M., Schäffer, A., Schleicher, N., Schmidt, B., Scholz-Starke, B., Schramm, K.W., Subklew, G., Tiehm, A., Temoka, C., Wang, J., Westrich, B., Wilken, R.D., Wolf, A., Xiang, X., Yuan, Y., 2012. The Yangtze-Hydro Project: a Chinese-German environmental program. Environ. Sci. Pollut. Res. 19, 1341–1344.

Chen, J., Chen, Z., Xu, K., Wei, T., Li, M., Wang, Z., Watanabe, M., 2005. ADP-flow velocity profile to interpret hydromorphological features of China's Yangtze Three-Gorges valley. Chin. Sci. Bull. 50, 679–684.

Chen, Z., Li, J., Shen, H., Zhanghua, W., 2010. Yangtze River of China: historical analysis of discharge variability and sediment flux. Geomorphology 41, 77–91.

Chen, Z., Schmidt, B., Schaeffer, A., 2017. Uptake and decomposition of the herbicide propanil in the plant Bidens pilosa L. dominating in the Yangtze Three Gorges Reservoir (TGR). Environ. Sci. Pollut. Res. 24, 11141–11153.

Large dams: learning from the past, looking at the future. In: Dorcey, A.H. (Ed.), Workshop Proceedings. Workshop Proceedings, Gland, Switzerland, April 11–12, 1997. World Bank Publications, p. 145.

EFSA - European Food Safety Authority, 2013. Reasoned opinion on the review of the existing maximum residue levels (MRLs) for propanil according to Article 12 of Regulation (EC) No 396/2005. EFSA J. 11 (6), 3280–3302.

Encyclopaedia Britannica, 2014. Yangtze River. Encyclopædia Britannica Online. 2014. Encyclopædia Britannica Inc.http://www.britannica.com/Ebchecked/topic/651857/Yangtze-River/48046/Agriculture, Accessed date: 27 June 2014.

European Commission (2011) Review report for the active substance propanil finalised in the Standing Committee on the Food Chain and Animal Health at its meeting on 27 September 2011 in view of the non approval of propanil as active substances in accordance with Regulation (EC) No 1107/2009. SANCO/11868/2011.

Floehr, T., Xiao, H., Scholz-Starke, B., Wu, L., Hou, J., Yin, D., Zhang, X., Ji, R., Yuan, X., Roß-Nickoll, M., Schäffer, A., Hollert, H., 2013. Solution by dilution? - a review on the pollution status of the Yangtze River. Environ. Sci. Pollut. Res. 20, 6934–6971.

Floehr, T., Scholz-Starke, B., Xiao, H., Koch, J., Wu, L., Hou, J., Wolf, A., Bergmann, B., Bluhm, K., Yuan, X., Roß-Nickoll, M., Schäffer, A., Hollert, H., 2015. Yangtze Three Gorges Reservoir, China: a holistic assessment of organic pollution, mutagenic effects of sediments and genotoxic impacts on fish. J. Environ. Sci. 38, 63–82.

Fu, B., Wu, B., Lue, Y., Xu, Z., Cao, J., Niu, D., Yang, G., Zhou, Y., 2010. Three Gorges Project: efforts and challenges for the environment. Prog. Phys. Geogr. 34, 741–754.

Furlan, L., Kreutzweiser, D., 2015. Worldwide integrated assessment on systemic pesticides - alternatives to neonicotinoid insecticides for pest control: case studies in agriculture and forestry. Environ. Sci. Pollut. Res. 22, 135–147.

Ge, J., Yun, X., Liu, M., Yang, Y., Zhang, M., Wang, J., 2014. Distribution, potential source and ecotoxicological risk of polychlorinated biphenyls and polybrominated diphenyl ethers in the surface water of the Three Gorges Dam region of the Yangtze River, China. Ecotoxicology 23, 978–987.

Giddings, J.M., DeCosta, C., Mao, J., Shepherd, S.P., 1990a. Propanil - Toxicity to Duckweed (*Lemna gibba* G3). SLI Report No. 90-3-3294. Performed by Springborn Laboratories, Inc., Wareham, Massachusetts. Submitted by the Propanil Task Force. EPA MRID No. 417772-01.

Giddings, J.M., Bayne, M.C.R., Mao, J., 1990b. Propanil - Toxicity to the Freshwater Diatom *Navicula pelliculosa*. SLI Report No. 90-3-3254. Performed by Springborn Laboratories, Inc., Wareham, Massachusetts. Submitted by the Propanil Task Force. EPA MRID No. 417775-01.

Graney, R.L., 1982. The Acute Toxicity of STAM Technical to the *Daphnia magna* Strauss. Biospherics Project No. 82_E_401B_DM; Rohm & Haas Protocol No. 82P_306. Final Rept. (Unpublished study received Jan. 21, 1983 under 707_75; prepared by Biospherics, Inc., submitted by Rohm & Haas Co., Philadelphia, Pa.; CDL:249347_B).

Holbach, A., Wang, L., Chen, H., Hu, W., Schleicher, N., Zheng, B., Norra, S., 2012. Water mass interaction in the confluence zone of the Daning River and the Yangtze River - a driving force for algal growth in the Three Gorges Reservoir. Environ. Sci. Pollut. Res. 20, 7027–7037.

Kegley, S.E., Hill, B.R., Orme, S., Choi, A.H., 2014. Toxicity of Propanil to Molluscs. PAN Pesticide Database, Pesticide Action Network, North America (Oakland, CA) http://www.pesticideinfo.org http://www.pesticideinfo.org/List_AquireAcuteSum.jsp?Rec_Id=PC34265&Taxa_Group=Molluscs (2014).

Kolar, C.S., Chapman, D.C., Courtenay, W.R., Housel, C.M., Williams, J.D., Jennings, D.P., 2005. Asian Carps of the Genus *Hypophthalmichthys* (Pisces, Cyprinidae) - A Biological Synopsis and Environmental Risk Assessment. Report to U.S. Fish and Wildlife Service per Interagency Agreement 94400-3-0128. p. 182.

Lampert, W., Sommer, U., 2007. Limnoecology: The Ecology of Lakes and Streams. Oxford University Press.

LAWA - Länderarbeitsgemeinschaft Wasser, 2003. Vorläufige Richtlinie für eine Erstbewertung von Baggerseen nach trophischen Kriterien - Preliminary guideline for initial assessments of quarry ponds by trophic criteria. Kulturbuch-Verlag Berlin, p. 25.

Leroy, M., Bicheron, P., Brockmann, C., Krämer, U., Miras, B., Huc, M., Ninô, F., Defourny, P., Vancutsem, C., Petit, D., Amberg, V., Berthelt, B., Arino, O., Ranera, F., 2006. GLOBCOVER: a 300 m global land cover product for 2005 using ENVISAT MERIS time series. ISPRS Commission VII Mid-Term Symposium: Remote Sensing: From Pixels to Processes, Enschede (NL).

Liang, X.Q., Chen, Y.X., Nie, Z.Y., Ye, Y.S., Liu, J., Tian, G.M., Wang, G.H., Tuong, T.P., 2013. Mitigation of nutrient losses via surface runoff from rice cropping systems with alternate wetting and drying irrigation and site-specific nutrient management practices. Environ. Sci. Pollut. Res. 20, 6980–6991.

Lombardo, A., Franco, A., Pivato, A., Barausse, A., 2015. Food web modeling of a river ecosystem for risk assessment of down-the-drain chemicals: a case study with AQUATOX. Sci. Total Environ. 508, 214–227.

Long, T.Y., Wu, L., Meng, G.H., Guo, W.H., 2011. Numerical simulation for impacts of hydrodynamic conditions on algae growth in Chongqing Section of Jialing River, China. Ecol. Model. 222, 112–119.

Megaproject: a case study of China's Three Gorges Project. In: Luk, S., Whitney, L.B. (Eds.), Chinese Studies on China, 1st edition ME Sharpe, p. 248.

McKnight, U.S., Rasmussen, J.J., Kronvang, B., Bjerg, P.L., Binning, P.J., 2012. Integrated assessment of the impact of chemical stressors on surface water ecosystems. Sci. Total Environ. 427-428, 319–331.

MEP - Ministry of Environmental Protection of the People's Republic of China, 2010. Bulletin on the ecological and environmental monitoring results of the Three Gorges Project. Online in the Internet. http://english.mep.gov.cn/down_load/Documents/, Accessed date: July 2014.

Ministry of Health of Italy, 2006. Propanil - Report and Proposed Decision of Italy Made to the European Commission Under 91/414/EEC. vol. 1–9. European Commission, Brussels.

NBS - National Bureau of Statistics of China, 2018. Resident population (year-end) of the greater region of Chongqing. Online in the Internet:. http://data.stats.gov.cn/english/easyquery.htm?cn=E0103, Accessed date: 26 February 2018.

Neumann, J., 1959. Maximum depth and average depth of lakes. J. Fish. Res. Board Can. 16 (6), 923–927.

Park, R.A., Clough, J.S., 2010. Aquatox (Release 3.1 Beta) Modeling Environmental Fate and Ecological Effects in Aquatic Ecosystems. Draft Volume 2: Technical Documentation. United States Environmental Protection Agency, Office of Water (4305) (EPA-823-R-09-004).

Park, R.A., Clough, J.S., Coombs Wellman, M., 2008. AQUATOX: modeling environmental fate and ecological effects in aquatic ecosystems. Ecol. Model. 213, 1–15.

Quantum GIS Development Team, 2013. Quantum GIS Version 2.2.0 'Dufour' GNU General Public License. http://qgis.osgeo.org.

Rashleigh, B., 2007. Assessment of lake ecosystem response to toxic events with the Aquatox model. In: Gonenc, I.E., Koutitonsky, V.G., Rashleigh, B., Ambrose, R.B., Wolflin, J.P. (Eds.), Assessment of the Fate and Effects of Toxic Agents on Water Resources. NATO Security Through Science Series. Springer Netherlands, pp. 291–297.

Rings, U., 2013. Adaptation of the Complex Ecosystem Model AQUATOX for the Simulation of Aquatic Food Webs at the Three Gorges Reservoir in China. p. 106 (Master thesis at the Institute for Environmental Research of the RWTH Aachen University).

Rogowski, D.L., Soucek, D.J., Levengood, J.M., Johnson, S.R., Chick, J.H., Dettmers, J.M., Pegg, M.A., Epifanio, J.M., 2009. Contaminant concentrations in Asian carps, invasive species in the Mississippi and Illinois Rivers. Environ. Monit. Assess. 157, 211–222.

Schaumburg, J., 1992. To the limnology of the Chiemsee. Informationsberichte des Bayerischen Landesamtes für Wasserwirtschaft.

Scholz-Starke, B., Ottermanns, R., Rings, U., Floehr, T., Hollert, H., Hou, J., Li, B., Wu, L.L., Yuan, X., Strauch, K., Wei, H., Norra, S., Holbach, A., Westrich, B., Schäffer, A., Roß-Nickoll, M., 2013. An integrated approach to model the biomagnification of organic pollutants in aquatic food webs of the Yangtze Three Gorges Reservoir ecosystem using adapted pollution scenarios. Environ. Sci. Pollut. Res. 20, 7009–7026.

Sousa, J.V., 1990. Propanil - Acute Toxicity to Sheepshead Minnow (*Cyprinodon variegatus*) Under Flow-through Conditions. SLI Report No. 90-02-3227. Prepared by Springborn Laboratories, Inc., Warham, Massachusetts. Submitted by the Propanil Task Force. EPA MRID No. 417760-01.

Sun, C., Shen, Z., Liu, R., Xiong, M., Ma, F., Zhang, O., Li, Y., Chen, L., 2013. Historical trend of nitrogen and phosphorus loads from the upper Yangtze River basin and their responses to the Three Gorges Dam. Environ. Sci. Pollut. Res. 20, 8871–8880.

UFZ – Helmholtz Centre for Environmental Research, 2012. ChemProp 5.2.8. http://www.ufz.de/index.php?en=673.

USEPA - United States Environmental Protection Agency, 2000. Nutrient Criteria Technical Guidance Manual, Rivers and Streams. EPA 822-B-00-002.

Van den Brink, P.J., Ter Braak, C.J.F., 1999. Principal Response Curves: analysis of time-dependent multivariate responses of biological community to stress. Environ. Toxicol. Chem. 18, 138–148.

Wang, J., Bi, Y., Pfister, G., Henkelmann, B., Zhu, K., Schramm, K.W., 2009. Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75, 1119–1127.

Xiao, H., Kuckelkorn, J., Nüßer, L.K., Floehr, T., Hennig, M.P., Roß-Nickoll, M., Schäffer, A., Hollert, H., 2016. The metabolite 3,4,3′,4′-tetrachloroazoxybenzene (TCAB) exerts a higher ecotoxicity than the parent compounds 3,4-dichloroaniline (3,4-DCA) and propanil. Sci. Total Environ. 551-552, 304–316.

Xie, P., 2003. Three-Gorges Dam: risk to ancient fish. Science 302, 1149.

Yao, J., Xue, J., Wang, D., Cai, Q., Huang, X., Liu, J., 2008. Seasonal variation and longitudinal distribution of copepods in the main river area of the Three Gorges Reservoir. Front. Biol. China 3, 525–529.

Zeng, H., Song, L., Yu, Z., Chen, H., 2006. Distribution of phytoplankton in the Three-Gorge Reservoir during rainy and dry seasons. Sci. Total Environ. 367, 999–1009.

Zeng, H., Song, L., Yu, Z., Chen, H.T., 2007. Post-impoundment biomass and composition of phytoplankton in the Yangtze River. Int. Rev. Hydrobiol. 92, 267–280.

Zhang, Z.P., 2003. Development of chemical weed control and integrated weed management in China. Weed Biol. Manag. 3, 197–203.

Zhang, Q., Lou, Z., 2011. The environmental changes and mitigation actions in the Three Gorges Reservoir region, China. Environ. Sci. Pol. 14, 1132–1138.

Zhang, J.L., Zheng, B.H., Liu, L.S., Wang, L.P., Huang, M.S., Wu, G.Y., 2010. Seasonal variation of phytoplankton in the DaNing River and its relationships with environmental factors after impounding of the Three Gorges Reservoir: a four-year study. Procedia Environ Sci 2, 1479–1490.