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PROCESSES AND ENVIRONMENTAL QUALITY IN THE YANGTZE RIVER SYSTEM

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

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Abstract The impounding of the Three Gorges Reservoir (TGR) at the Yangtze River caused large flooding of urban, industrial, and agricultural areas, and profound land use changes took place. Consequently, substantial amounts of organic and inorganic pollutants were released into the reservoir. Additionally, contaminants and nutrients are entering the reservoir by drift, drainage, and runoff from adjacent agricultural areas as well as from sewage of industry, aquacultures, and households. The main aim of the presented research project is a deeper understanding of the processes that determines the bioaccumulation and biomagnification of organic pollutants, i.e., mainly pesticides, in aquatic food webs under the newly developing conditions of the TGR. The project is part of the Yangtze-Hydro environmental program, financed by the German Ministry of Education and Science. In order to test combinations of environmental factors like nutrients and pollution, we use an integrated modeling approach to study the potential accumulation and biomagnification. We describe the integrative modeling approach and the consecutive adaption of the AQUATOX model, used as modeling framework for ecological risk assessment. As a starting point, pre-calibrated simulations were adapted to Yangtze-specific conditions (regionalization). Two exemplary food webs were developed by a thorough review of the pertinent literature. The first typical for the flowing conditions of the original Yangtze River and the Daning River near the city of Wushan, and the second for the stagnant reservoir characteristics of the aforementioned region that is marked by an intermediate between lake and large river communities of aquatic organisms. In close cooperation with German and Chinese partners of the Yangtze-Hydro Research Association, other site-specific parameters were estimated. The MINIBAT project contributed to the calibration of physicochemical and bathymetric parameters, and the TRANSMIC project delivered hydrodynamic models for water volume and flow velocity conditions. The research questions were firstly focused on the definition of scenarios that could depict representative situations regarding food webs, pollution, and flow conditions

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in the TGR. The food webs and the abiotic site conditions in the main study area near the city of Wushan that determine the environmental preconditions for the organisms were defined. In our conceptual approach, we used the pesticide propanil as a model substance.

Keywords Three Gorges Reservoir · Yangtze food webs · Bioaccumulation · Biomagnification · AQUATOX framework · Regionalization · Simulation · Environmental risk assessment · Integrated environmental modeling

Introduction

The Three Gorges Reservoir area at the Yangtze River

The Chinese people assign a significant portion of their cultural origins to the Yangtze River region nearby and along the Three Gorges Reservoir (TGR; Fig. 1). Since the region has been populated thousands of years ago, nowadays more than 400 million people live there (Müller et al. 2008). The TGR is of major importance for the economic development of the whole region between Chongqing city and the TGR dam site near the city of Yichang. The TGR serves for the generation of electrical power, the safeguarding of shipping, and the prevention of threatening flood events. The reservoir's appearance is characterized by 30-m water-level fluctuations due to seasonal variations of the discharge rates, natural precipitation, and designated reservoir management (China Three Gorges Corporation 2010). In general, the building of large dams impacts among many other factors the biodiversity of riverine species by altering the ancestral flow conditions, introducing exotic species, and reducing flood plains (McAllister et al. 2001). Caused by the intense resettlements in the area, there is a significant increase in soil surface nitrogen and phosphorous surplus since the time before the first impoundment of the TGR (Xu et al. 2011). In the TGR region, flowing waters became stagnant, periodical changes in water level caused flooding events, and thereby a relocation of contaminated water, particulate matter, and sediment onto agriculturally used areas along the reservoir's shore.

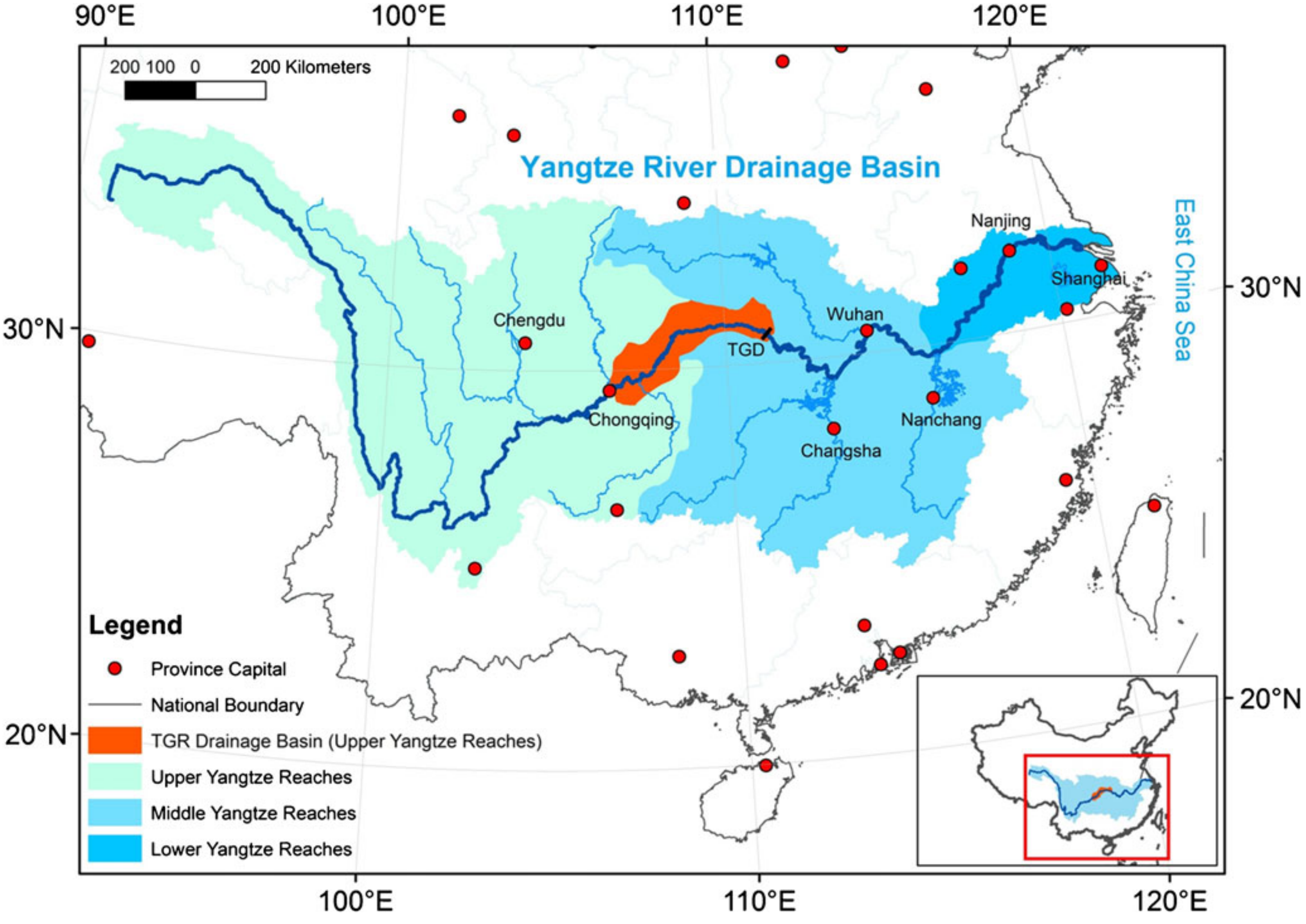

Fig. 1 Map of the Yangtze River Basin (*light to dark blue*) and the Three Gorges Reservoir (*TGR*; *red*). TGD *Three Gorges Dam*

Dynamics of TGR affect the bioaccumulation of pollutants within aquatic food webs

The loss of arable land after the impoundment of the river has caused an intensification of the agriculture on the remaining fields. In connection with high nonpoint pesticide loads by runoff, direct overspray, and drainage in the area, possible problems with the bioaccumulation along the aquatic food chains of the TGR could arise (Yong 2010). It is well known that an alteration of the flow regimen of a river from flowing to stagnant conditions entails manifold biotic alterations (Bunn and Arthington 2002). Organic pollutants pose a major threat to the ecosystems of the newly built reservoir, with many of them showing remarkable potential to accumulate in organisms. Among them, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides (OCP) have been detected in the water column of the TGR (measured, e.g., by Wang et al. 2009). From the group of OCP, the herbicide propanil has been identified as highly relevant because of its intense use in the TGR region (Zhang 2000).

Aims of the study

The main aim of our studies is a deeper understanding of the processes that determine the bioaccumulation of organic pollutants, mainly pesticides, within aquatic food chains under the newly developing conditions of the huge reservoir. For this purpose, we quantify the internal concentrations of chosen model pollutants in ecological and economical key species, i.e., mainly fish, under the influence of TGR-representative pollution scenarios. We analyze different agricultural land use patterns and nutrient loads under the fluctuating water level regimen caused by the mode of operation of the dam. The concept of this integrated modeling procedure requires input data from various scientific disciplines such as ecotoxicology, environmental analysis, ecology, and hydrology. Therefore, this paper describes in detail the approach to compare the environmental risks in an exemplified season under the new operating conditions of the dam and give recommendations for risk management procedures.

Model structure—conceptual approach

Integrated modeling

In this study, we follow an integrated modeling approach to gain a comprehensive overview on factors and mechanisms that trigger the bioaccumulation of organic pollutants in aquatic ecosystems. *Integrated Environmental Modeling* (IEM; Argent 2004) is of increasing importance in environmental management, decision-making, and risk assessment. This interdisciplinary approach allows for a gainful aggregation of knowledge and data from different disciplines and the handling of the complexity of environmental systems (Jopp et al. 2011). It is based on the idea of an integrated assessment (Hisschemöller et al. 2001). To account for the complexity of the TGR situation concerning hydrological, biological, and ecotoxicological factors, we combine and couple several specialized modules to focus on TGR-specific environmental and ecological conditions (Fig. 2). The AQUATOX model suite (Park et al. 2008) is used as an interconnected modeling framework. It links the eight modules exposition module (EXM), food-web module (FWM), hydrodynamic module (HDM), particle transport module (PTM), site-descriptor module (SDM), bioaccumulation module (BAM), ecotoxicological module (ETM), and risk-assessment module (RAM) of our approach seamlessly. The modules are implemented either as integrated submodels within the AQUATOX modeling environment or as external models. Adequate input values are provided by literature data, expert knowledge, or available empirical data (e.g., in the case of FWM). In some cases, e.g., for HDM, results of external models have been used. Thereby, this modular approach fulfills the requirements for an aquatic environmental risk assessment, as evaluated by Echeverría et al. (2003) for AQUATOX.

Exposition module The exposition module estimates environmental concentrations of xenobiotics under different pollution scenarios specifically for the TGR region. Here, we rely on the standard assumptions from the EU environmental risk assessment (ERA) which is based on realistic worst-case scenarios. Spatial aspects of exposition are considered by the distribution of relevant model substances. In particular, the rice herbicide propanil, which is a widely used crop protection substance in Asia (Labrada 2003) and its main metabolites 3,4-dichloroaniline (3,4-DCA) and 3,4,3′,4′-tetrachloro-azobenzene (TCAB) will be modeled by the HDM and the PTM. Estimated concentrations of these model substances are handed over to the chemical fate module of AQUATOX.

Food-web module The food web module describes the composition, interactions and dynamics of the communities of aquatic organisms in the TGR. This module is integrated within the AQUATOX environment. The AQUATOX model provides validated surrogate simulations with all biotic and abiotic properties. These simulations are subsequently modified to regionalize the standard site (river scenarios) or are compiled from the scratch (reservoir scenarios) if necessary.

Hydrodynamic module The hydrodynamic module is used to generate flow conditions of the given water bodies according to the normal operation mode of the Three Gorges Dam (TGD). The module describes changes in water

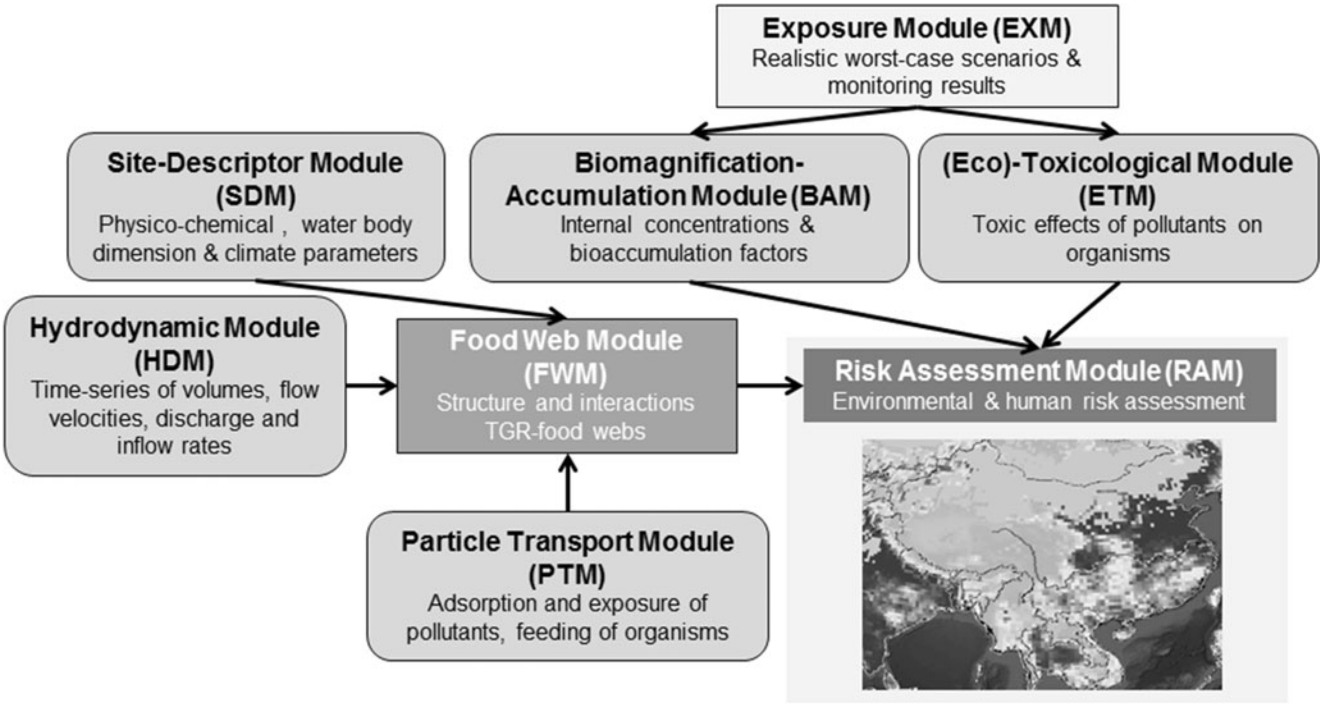

Fig. 2 Integrated environmental modeling approach of the bioaccumulation module within the MICROTOX project. TGR-specific scenarios are adapted to describe the potential bioaccumulation under the altered land use and water-level regimen in the TGR region by linking specialized submodules

volume, flow velocity, discharge and inflow rates delivered by the external 1D model HEC-RAS (U.S. Army Corps of Engineers 2001). These flow conditions are provided to the AQUATOX environment as time series data in the water volume module.

Particle transport module The particle transport module simulates the distribution of contaminated particles within the TGR water bodies (TELEMAC 2-D, Hervouet 2007). These particles are of particular importance in the TGR as they absorb the pollutants, feed the organisms, expose the organisms to the pollutants and distribute the pollutants over the water body. Detritus particles as well as algae can act in such a way. The simulations provide spatially explicit time series of pollutant concentrations, which are provided to the AQUATOX environment via the toxicity module to define site-specific expositions. The sampling sites are defined according to the general pollution scenarios that correspond to specific sites at the TGR where samples for sediment toxicity characterization within the MICROTOX project have been taken.

Site-descriptor module The site descriptor module provides the site-specific environmental conditions, such as water temperatures, nutrients and radiation energy. These variables have been measured in the field, taken from literature or provided by external models. They are used as fixed site-specific state variables for the internal module in AQUATOX.

Bioaccumulation module The bioaccumulation module describes the adsorption of the model pollutants (e.g., TCAB) to detritus particles by chemical characteristics. An adsorption coefficient can be modeled via adsorption isotherms (Foo and Hameed 2010). In case of substances with unknown chemical properties, the adsorption characteristics have been estimated by external QSAR-based chemical properties estimation software (CHEMPROP; Schüürmann et al. 1997). In case of algae as transporting particles, the accumulation of model substances within the algae is modeled via uptake factors in the AQUATOX environment and exported as bioconcentration factors. Based on the loading of pollutants on the surfaces of detritus particles or concentrations within the algae, the BAM models the accumulation of these substances in the higher aquatic surrogate species of the TGR food web (especially fish) also via uptake factors.

Ecotoxicological module Based on the estimated internal pollutant concentrations provided by BAM, ecotoxicological effects of the model substances are estimated in the ETM using literature data on toxic effects to aquatic organisms, sediment toxicity information generated in the MICROTOX project and interpolation by inter-species correlation estimates (Web ICE) within AQUATOX (Raimondo et al. 2010). Due to the outstanding importance of fish as humans' food resource in the TGR region, the adaptation of the food webs focuses on carps that pose the main target species for our environmental risk assessment.

Risk-assessment module We assess the risk for the environment by comparing the effects of different doses of pollutants that are predicted by the AQUATOX model on the level of individuals, populations and aquatic communities. For the estimate of risks to humans, we compare the internal pollutant concentrations of important food source fishes with acceptable daily intake rates (ADI).

The AQUATOX model and its adaptation

Since the analysis of organic traces in environmental samples and organisms tissues is very labor and cost intensive, we use deterministic modeling approaches for the prediction of the potential accumulation and biomagnification of model pollutants. The whole complexity and the basic mechanism of the unique hydrological, biological and ecotoxicological situation of the TGR can be best reflected by an ecological model for environmental risk assessment, as shown by the reviews cited in Lei et al. (2008). We use an AQUATOX-based simulation model that has been adapted to the local conditions at the TGR to predict the fate of pollutants, such as pesticides or nutrients, and to describe the potential accumulation within the food webs of the reservoir. The AQUATOX model has been developed for the US Environmental Protection Agency for the purpose of environmental risk assessment (Park and Clough 2010). It is a general, mechanistic model that can be used to predict the fate, behavior, and effects of various stressors, such as toxic chemicals, nutrients, or environmental variables in an environmental risk assessment context for aquatic ecosystems (Park et al. 2008). Lei et al. (2008) described a successful example of an adaptation of the AQUATOX simulation environment to the situation of a Chinese river. In our study, already existing simulations are adapted to the specific requirements of the recent study by detailed knowledge on the structure of the river and the reservoir biocoenoses. We describe the consecutive adaptation steps that are necessary to change the pre-defined simulations of AQUATOX to “Yangtze-specific” conditions (“regionalization”). A scenario-based procedure is preferred over the best possible representation of real sites because an understanding of the underlying processes that determine the effects and the bio-accumulation of pollutants is desired. The definition of scenarios includes the status of agricultural and industrial pollution, the hydrology, the mode of operation of the TGD and further aspects. Our research is focused on the influence of high concentrations of nutrients on food web structures. Two different types of simulations, “reservoir” and “river,” have been adapted in AQUATOX based on the “Cheney reservoir” data that are marked by lake species (USGS 2008) and the predefined “Rum River” scenario (Park et al. 2005) marked by flowing water specialists, respectively.

Definition of scenarios

The main scenarios of pollution (compare step 1 “definition of scenarios” in the flow chart of Fig. 3) have been derived in an incremental procedure. Firstly, a study area near Wushan city has been chosen because of its exemplary pattern of landscape features and pollution sources. Secondly, the hydrodynamic situation in the designated study area has been 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

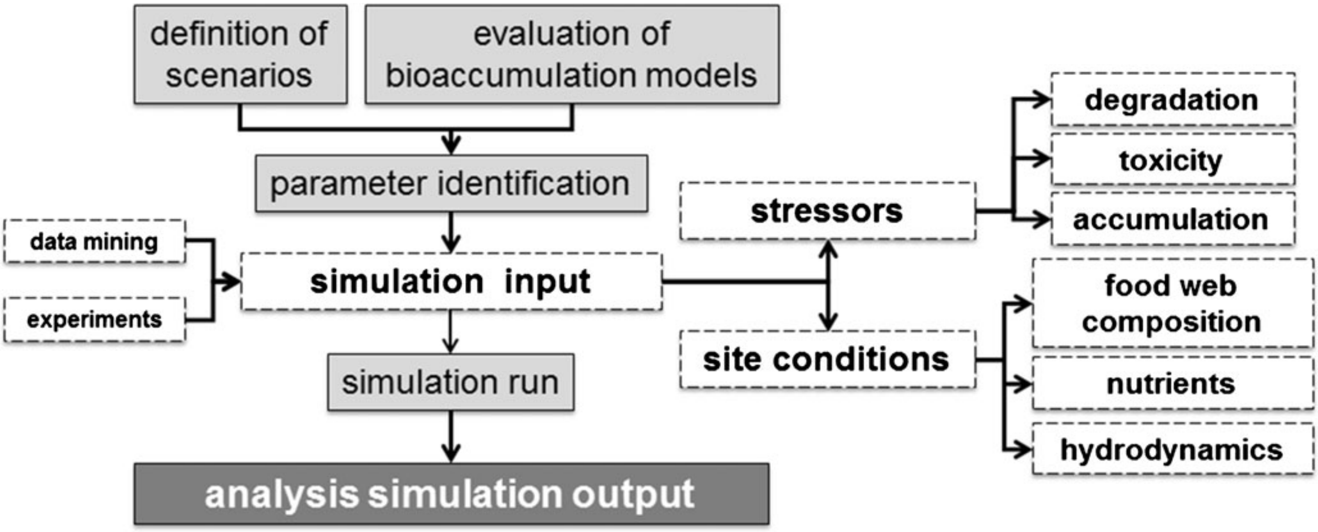

Fig. 3 Set up of the adapted simulations. Workflow of bioaccumulation studies. A step-wise procedure for the definition of necessary input data to conduct sound simulation experiments is established

high and low pesticide loads have been determined. The assumptions and predictions of a standard environmental risk assessment are used to define maximum loads of pesticides according to expectable application procedures and additional massive overuse. The study area is marked by a "unique" hydrodynamic situation at the mouth of the Daning River where a huge whirlpool with high-residence time of Wushan Lake water is located. The segment definition procedure in the MICROTOX project includes that "reservoir" and "river" segments are linked. Feedback links are incorporated in case the hydrodynamic model predicts a backflow of water to upstream or the respective segment is directly connected to stagnant waters. The supposed "area-of-exposition" is marked by rice cultures on terraces. Hence, intense nutrient and pesticide use can be expected. The main branch of the Yangtze River is assumed to contribute minor pollution loads and is hence a "diluting agent." Segments have been defined and their characteristics of the area studied have been implemented into the simulation environment of AQUATOX. The segments are linked in a feed-back and feed-forward way to adjacent ones according to requirements of the AQUATOX simulation environment (Park and Clough 2010). The linkages between segments may be unidirectional or bidirectional. (1) All of the linked segments have an identical set of state variables; (2) each segment is assumed to be well mixed. Hence, a dynamic stratification of water layers does not apply. The stratified pairs of segments must be specified by the user. In a simulation, nutrients, biota, and other state variables "pass" from segment to segment through active migration, passive drift, diffusion, or bed-load. Four segments representing different pollution scenarios have been defined.

HDM—hydrological characteristics of the study area water bodies

The study area near the city of Wushan includes the Daning River up to Dachang Lake, as well as adjacent upstream and downstream parts of the Yangtze River in western and eastern direction. It has been chosen as the model region to show basic patterns of bioaccumulation under unique hydrodynamic conditions in the confluence of the Yangtze River and the Daning River into the Wushan Lake. The Wushan district is located at the eastern boarder of the Chongqing municipality in a subtropical area in central China. Depending on the water level of the TGR and the actual flood conditions, a massive backflow of water from the Yangtze into the Daning River is often observed. This leads to the rare situation that a large mixing zone alters the normal exchange rates in the huge "whirlpool" in front of Wushan city. The area is divided in several sections according to the basic river geometry. "Fast-flowing gorges" are assumed equipped with a typical river food web and "slow-flowing basins" with reservoir food webs. Several segments of significantly differing flow conditions and probable pollution patterns are intended to be modeled (as schematically shown by Fig. 4). The predefined segments have been refined and re-defined by the results of the one-dimensional HDM HEC-RAS (U.S. Army Corps of Engineers 2001) considering the water level alterations, realistic flow conditions in an annual cycle and the volumes of the different water bodies. The model HEC-RAS has been developed by the Hydrologic Engineering Center as a River Analysis System. It models the one-dimensional flow disregarding the shape of a river cross-section. It has a graphical user interface integrated in ArcGIS for the pre- and post-processing for the modeling and models the hydrodynamic situation based on available spatial data. The water channels of the Daning River between the Dachang Lake and the bridge near Wushan, and the Wushan Lake are first divided in sectors by drawing 125 cutlines (Fig. 5). The model has been calibrated to the specific conditions in the regarded region; the geometry of the river system has been built by the worldwide digital elevation model (DEM) and water depth measurement of the MINIBAT project. Data for water level fluctuations have been taken from the gauging station Wushan in the mainstream of the Yangtze River as the downstream boundary condition. Discharge data have been taken from the Wuxi gauging station in the Daning River mainstream. Inflows have been estimated from smaller tributaries as the upstream boundary condition. The DEM data are available in the public domain (DLR-German Aerospace Center 2000). After calibration, the HDM models the volume, inflow, and discharge rates as well as the actual water levels of each of the sections in a daily time-step. The data delivered by the HEC-RAS model have been used to define homogenous segments within the study area that show flowing or stagnant characteristics and to calculate relevant input values for the AQUATOX *site descriptors*. Seasonal changes in the water level and the operation mode of TGD take effect in the AQUATOX model through water volume and inflow and/or discharge rates in a given cross-section of the river.

EXM—exposure

Estimation of pollution loads

The next step in setting up pollution scenarios is the estimation of the most probable exposition to the organisms of the Yangtze food webs. Several Yangtze-Hydro sub-projects occasionally identified increased pesticide concentrations in the past, particularly in TGR tributary water bodies (Wolf et al. 2012). However, the exposition has been assessed mainly by using the standard environmental risk assessment procedures for the registration of plant protection products within the European Union. Scenarios for example applications of

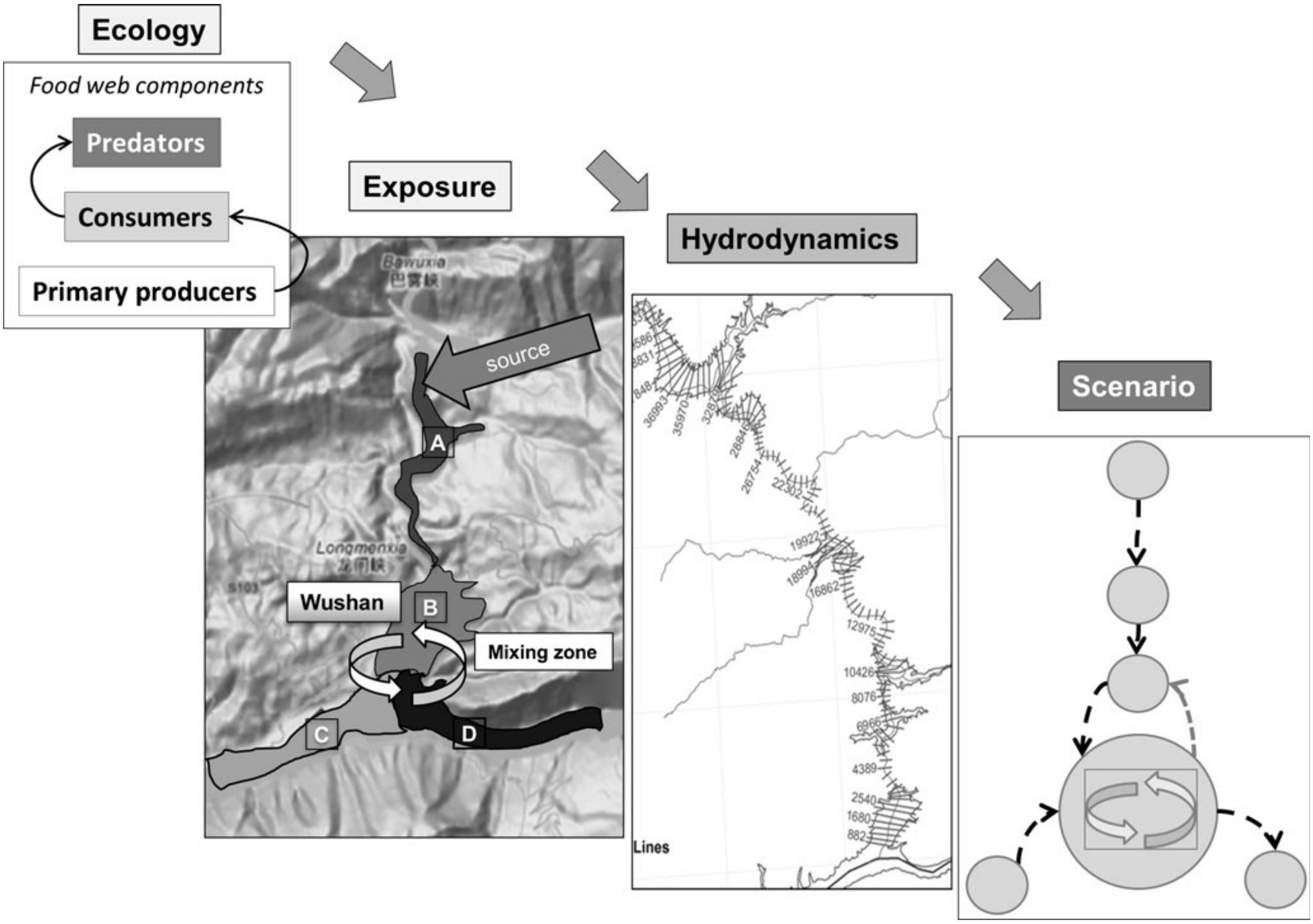

Fig. 4 The derivation of relevant scenarios (i.e., segments of the Yangtze River or its tributaries) for simulation experiments in the MICROTOX project combining the ecological, exposure, and hydrodynamic situation at the TGR. Four schematic pollution scenarios near the city of Wushan, Hubei province. Ecological assumptions on typical biocoenoses led to the definition of TGR food webs, separately for "rivers" and "reservoir" intercepts. The exposure situation is characterized by *A* a high risk of agricultural pollution due to adjacent fields, by *B* pollution from urban waste water and a water body mixing zone with high residence times, by *C* highly diluted urban and agricultural pollution, and by *D* an intermediate burden of contamination after confluence. Flow conditions are modeled by the HEC-RAS model

the model substances proposed by Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS (2001)) and Med-Rice (2003) helped to identify the worst-case surface water concentrations, mainly caused by drift events. In our studies, we concentrate on fate, effects, bioaccumulation and biomagnification of the parent compound propanil, its main and primary metabolite 3,4-DCA within the components of the aquatic food webs, and a supposedly lipophilic and thus accumulative secondary metabolite TCAB. The surface water concentrations of propanil and 3,4-DCA are taken from the literature, particularly from the draft assessment report (DAR) of propanil that has been written by the rapporteur member state Italy, which is again the most important rice producer within the European Union (Ministry of Health of Italy 2006). The DAR has been written for the environmental risk assessment prior the decision to list propanil in Annex I of Commission Directive 91/414/EEC as a post-emergence, foliar-applied rice herbicide and is thus relevant for Chinese use patterns. Propanil is intended to be used on drained paddy fields with a maximum of two sequencing spray applications within a 14-day interval. In the DAR of propanil, a single application of 4-kg active ingredient (a.i.)/ha has been assumed, because of its very short degradation half-time (DT_{50}) of 0.5–3 days. For 3,4-DCA, the $DT_{50}>26$ days leads to the assumption of a 2-fold application with 14 days time lag. The Predicted Environmental Concentrations in surface waters (PEC_{SW}) of propanil from realistic worst-case standard scenarios are calculated by the MED-RICE model Standard scenario 1b (degradation, no sorption). The PEC has been assumed to appear and affect the communities directly after application as initial concentrations (PEC_{SWini}). Thus, the PEC_{SWini} for propanil is then 0.0022 mg a.i./L, the PEC_{SWini} for 3,4-DCA has been 0.094 mg a.i./L, respectively.

The formation rate of TCAB from the parent substance is about 0.5 %. However, no PEC-calculations for TCAB are

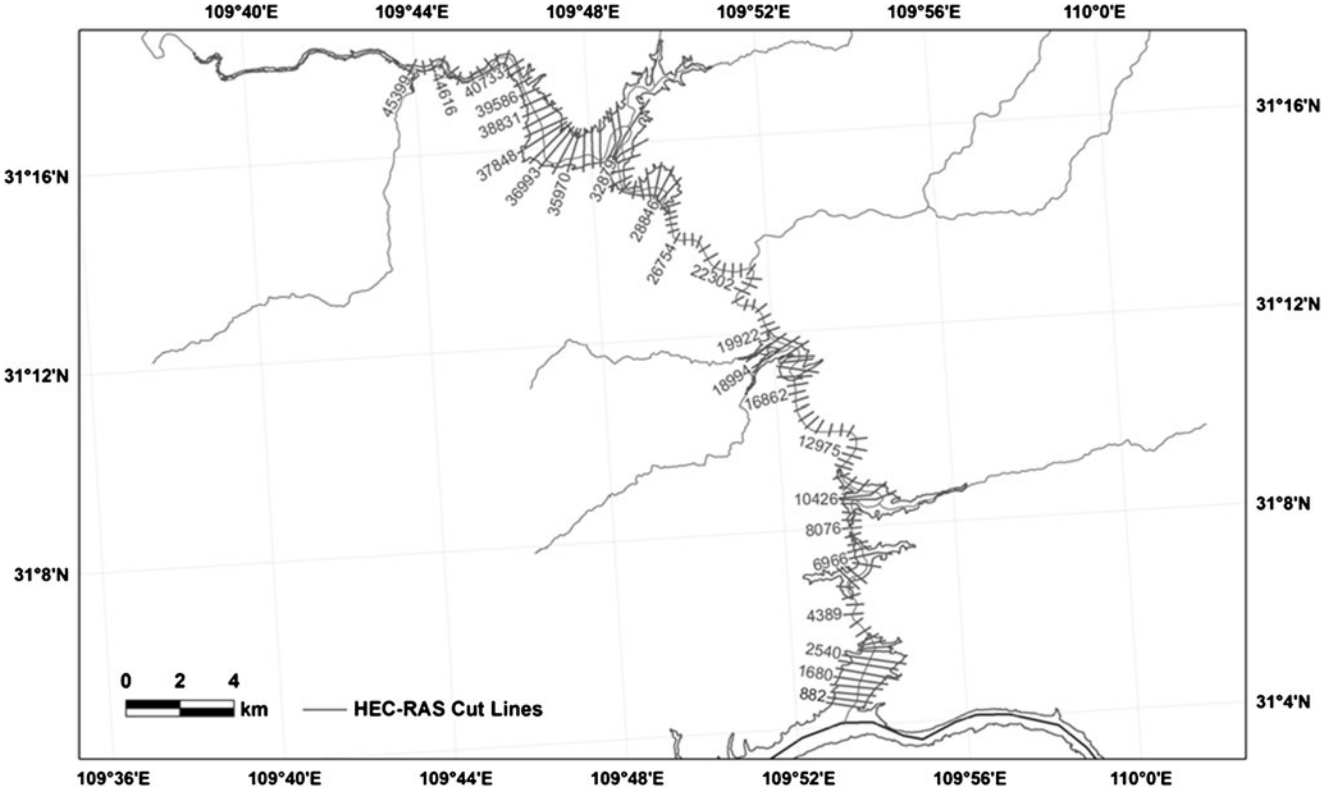

Fig. 5 Map of the Daning River including the Dachang Lake divided by 125 cutlines that are interconnected but modeled separately

available; the maximum formation rates are known to reach approximately 26 % of the concentration of the parent substance in rice paddy soils (Chisaka and Kearney 1970). Having fixed the initial surface water concentration of the three model substances, the concentrations have been multiplied by a factor of 100 to reflect heavy overuse. Overuse of pesticides is known to be a common problem in rural areas of China (Yang et al. 2008).

Chemical properties of the parent pollutant and its metabolites

Like other dichloropropionanilide pesticides, propanil is readily cleaved to release 3,4-DCA which subsequently, catalyzed by oxidative enzymes, such as lignin peroxidase in soils, forms TCAB (Pieper et al. 1992). 3,4-DCA is also formed by degradation of phenyl-carbamates, phenylureas, and other acylanilides and represents a "priority pollutant" (Ashauer et al. 2010). Although the formation rate of TCAB in soils varies greatly, probably due to different oxidation states of the soils, many studies revealed quite high TCAB concentrations in soils. Chisaka and Kearney (1970) reported the percent conversion of propanil to TCAB in five soils with similar physico-chemical properties varied between 1.3 and 26.2 %. This was if propanil has been applied at 850 ppm. At lower application rates of propanil (85 ppm), the TCAB conversion rate varied between 1.0 and 18.6 %. TCAB seems to be persistent in the environment. During the incubation period of 105 days in the latter experiment, TCAB was not degraded. However, specific information of the fate of TCAB in soils and sediment is not available. TCAB in nutrient solution is absorbed by rice plants (5–6 % of the amount applied to soil of which less than 10 % is transported to the shoots). From rice treated with propanil and with 3,4-DCA, however, no TCAB can be isolated (Still 1969). Soya beans resorb TCAB from soils. Roots of plants grown in a soil with 1.7 % organic matter and treated with 10 mg/kg TCAB reach levels above 50 mg/kg, while in the shoots TCAB concentrations are lower (<1 mg/kg) (Worobey 1984). Trans-TCAB is taken up from soils by carrots (Worobey 1988) that has been incubated with 0.02 and 10 mg/kg a.i. Residues in the plants are highest in the carrot peels (1.9 and 375 μg/kg, respectively). Many reports are available that prove the high mutagenic, cancerogenic and toxic activity of TCAB for which a reactive arene oxide intermediate mediated by oxidative enzymes has been proposed as responsible mediator (Witt et al. 2000; Van Birgelen et al. 1999; Allison and Morita 1995; Hsia and Kreamer 1981). Polychlorinated trans-azobenzenes in their stereo configuration and toxicity resemble some of highly toxic planar polychlorinated dibenzo-*p*-dioxins. It is interesting to note that the chemical stability and toxicity of the chlorinated trans-azobenzenes are considered more relevant than that of the corresponding *cis*-analogues (Wilczynska et al. 2006). Our own experiments in synthesizing TCAB by both enzymatic reaction (horseradish peroxidase) and chemical oxidation (MnO_2) reveal that both isomers are formed in various ratios, most often in favor of the trans-product (Fig. 6).

3,4-DCA is quite well water soluble (0.58 g/L at 20 °C; log P_{OW}=2.7, European Chemicals Bureau 2006). The compound has a low Henry's law constant (0.05 $Pa \times m^3 \times mol^{-1}$), a low potential for abiotic hydrolysis but is prone to be degraded by photolysis in surface waters. The biodegradation rate of 3,4-DCA is low but the reactivity to form covalent bonds in humic matter is high. Thus, the concentration of 3,4-DCA residues in soil and sediment is expected to be high (e.g., in milligrams per kilogram quantities as calculated from typical application and production rates of 3,4-DCA and corresponding pesticides). 3,4-DCA releasing pesticides therefore form high amounts of nonextractable residues (NER), probably due to the binding of chloroaniline to humic matter. However, there is no experimental proof for this hypothesis. Neither is it known whether NER in soils and sediments contain incorporated TCAB. In Table 1, the physicochemical properties of propanil, 3,4-DCA and TCAB are summarized as calculated by the structure activity model ChemProp (Schüürmann et al. 1997, 2007). It is obvious, that bioaccumulation of the final metabolite TCAB is most relevant while that of propanil and 3,4-DCA is low. However, bioaccumulation data for aquatic and terrestrial organisms, the ecotoxicological profile and the fate of TCAB in the environment are largely unknown.

Data input for simulation setup (localization)

SDM—localized site properties

Site-specific variables as surface water temperatures have been measured in time-series during the MINIBAT (Stüben et al. 1998; Casagrande 1995) sampling campaigns combined with point estimates of own sampling campaigns. The data serve as input for the modified AQUATOX model (Table 2). The joint MINIBAT project contributed nutrient measures also (NO^{3-}, total phosphorus). For each of the pollution scenarios in the Wushan region, the parameters have been calculated separately. For each scenario segment, the corresponding MINIBAT measurements are averaged for the upper 1-m water layer. The data are partly imported into the AQUATOX simulation as fixed site-specific state variables directly, and partly converted into compatible units (i.e., chlorophyll *a* concentration is converted to primary producer's biomass (Desortova 1981)). State variables like annual mean radiation and the limits of air and water temperature variation determine the maximum rates of photosynthesis in the AQUATOX model. The annual radiation has been taken from Chen et al. (2001).

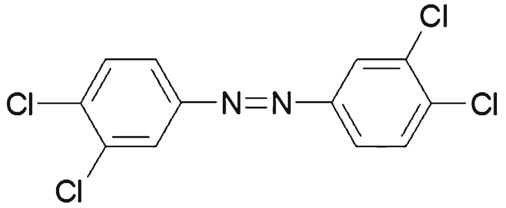

Fig. 6 Isomers of TCAB formed by enzymatic and chemical dimerization of 3,4-DCA

FWM—food web

The food-related interactions within a community can be represented by a simple food chain. The energy fixed by primary producers is transferred to the highest trophic level in distinct steps. All organisms of a "trophic level" in a food web share the same number of transfer processes their diet passed through (Schwoerbel 1999). In our approach, for each of the trophic levels only one species or guild is listed (Figs. 7 and 8). In our studies, we use a food web with four trophic levels. The composition of the TGR biocoenoses is expected to be a mixture of the typical coenoses of flowing and stagnant waters. According to a time scale for the succession of communities of aquatic organisms with relatively short generation times, the recently impounded reservoir is assumed to be in a steady state already. Clear changes of, e.g., the nutrient status and the algal communities have been recorded immediately after impounding within a period of one year (Dai et al. 2010). For this reason *two basic simulations*, one representative for a "reservoir" and one for "river," including different food webs and flow conditions have been set up. A food web consists of a typical structure marked by hierarchical guilds. The energy flows from the primary producers (algae and macrophytes) to the primary consumers (invertebrate feeders and planktivorous fishes), and then to the first order predators (predatory or omnivorous fishes). The arrows in Figs. 7 and 8 point from predator to prey, as indicated. Second order predatory fishes or mammals are not included in our sketches of the TGR food webs, because it is not expected that typical predators like the Chinese Sturgeon (*Acipenser sinensis*) or the Yangtze Dolphin (*Lipotes vexillifer*) have a significant influence on the Yangtze ecosystems. These species are critically endangered and close to extinction since a long time (Xie 2003; IUCN 2012). In our system, secondary predator-like effects are represented by human fishing and piscivorous birds. Species names are meant to be common representatives of a trophic guild, combined with a distinct taxonomical group. The trophic group of primary producers is represented in Fig. 8 by the green algae *Scenedesmus arctuatus*. The predefined food web has thus been simplified in the way that information has been reduced from "species level" to "guild level" and typical surrogate species for the TGR have been chosen.

Table 1 Chemical properties of model substances

Property	Propanil	3,4-DCA	TCAB
CAS No.	709-98-8^{e}	95-76-1^{e}	14047-09-7
Molecular weight (g/mol)	218.1	162.02	320
Octanol (oc)–water partitioning coefficient log K_{ow} (mol/mol)	2.29^{e}	2.69^{e}	5.84^{a}
Henry law constant log K_{aw} (dimensionless)	−7.53^{j}	−4.47^{j}	−3.74^{k}
Soil sorption log K_{OC} (L (water)/kg (oc))	2.17^{c}	2.68^{c}	4.47^{b}
Water solubility (mg/L) at 20°C	95^{e}	580^{e}	0.04^{d}
Bioconcentration factor (log BCF)	1.75 (uncertainty 0.25)^{f}	1.37 (uncertainty 0.2)^{f}	4.52 (uncertainty 0.5)^{f}
Bioaccumulation factor (log BAF)	1.66^{g}	1.56^{g}	5.74^{g}
Fish toxicity fathead minnow (log LC_{50}mol^{-1}l^{-1})	−4.60^{c}	−4.57^{c}	−7.04^{h}
Mutagenicity	No^{c}	No^{c}	Yes^{i}

Values set in italics are estimated by ChemProp Ver. 5.2.8, UFZ Department of Ecological Chemistry (2012), basically described by Schüürmann et al. (1997, 2007)

[a] Estimated by class-based model selection, selected model: Hou and Xu (2003)

[b] Estimated as mean value via decision tree by Sabljic et al. and according to LSER Poole and Poole (1999)

[c] Read across from ACF (UFZ set, ACF similarity=1)

[d] Estimated by ACF-based model selection, selected model: Klopman and Zhu (2001)

[e] Source: PPDB (2009)

[f] Estimated for fish from K_{ow} according to Mackay (1982)

[g] Estimated according to Arnot and Gobas (2003)

[h] Estimated from ECOSAR type model: 96-h log LC_{50} for fish according to Nabholz and Mayo-Bean (2009)

[i] Predicted according to Kazius et al. (2005) and Benigni and Bossa (2008)

[j] Read across from ACF (UFZ set, chemical domain=in)

[k] Estimated according to Meylan and Howard (1991) (bond 2.6)

Fishes

The fish surrogate species are chosen according to the number of relevant literature entries and their economic importance. Many references mention the four main "Asian carp" species (Wanner and Klumb 2009; Kocovsky et al. 2012), which shows the particular commercial meaning of those species in the TGR region (Zhang et al. 2012; Duan et al. 2009; Yi et al. 2010). Namely, these are *Ctenopharyngodon idella* (grass carp), *Mylopharyngodon piceus* (black carp), *Hypophthalmichtys molitrix* (silver carp), and *Hypophthalmichtys nobilis* (bighead carp). Although the four species belong to the family of cyprinids (order cypriniformes), they show different behaviors and body masses (Table 3). While the grass carp is herbivorous and prefers to live near the river bank, silver and bighead carp stay in deeper waters where they feed on plankton. The black carp lives near the bottom and its diet mainly consists of molluscs (Yi et al. 2010; Duan et al. 2009). Additionally, two further common non-cyprinid fish species are chosen, namely *Tachysurus fulvidraco* (yellowhead catfish) and *Monopterus albus* (Asian swamp or rice field eel). The two latter species have been integrated in the simulations for having at least one bottom dwelling fish species with close contact to the sediment and thus connected to the resuspension of toxicants from the sediment. Secondary predatory fishes have been substituted by fishing pressure (approximately 100 kg fish/fisherman in the Kaixian area) and by piscivorous birds as mentioned above.

Table 2 Physicochemical variables measured by the MINIBAT

Endpoint	Unit
Water level	Meter
Water temperature	°C
Water depth	Meter
Conductivity	µS/cm
Turbidity	% base saturation
Chlorophyll *a*	µg/L
pH	Unitless
Oxygen	Backscatter %

Units have been converted to AQUATOX-compatible values where necessary

Algae and macrophytes

The feeding preferences of fishes and invertebrates have been analyzed for the identification of the most important groups of algae and macrophytes as primary producers. The occurrence of the above species in the study area, the

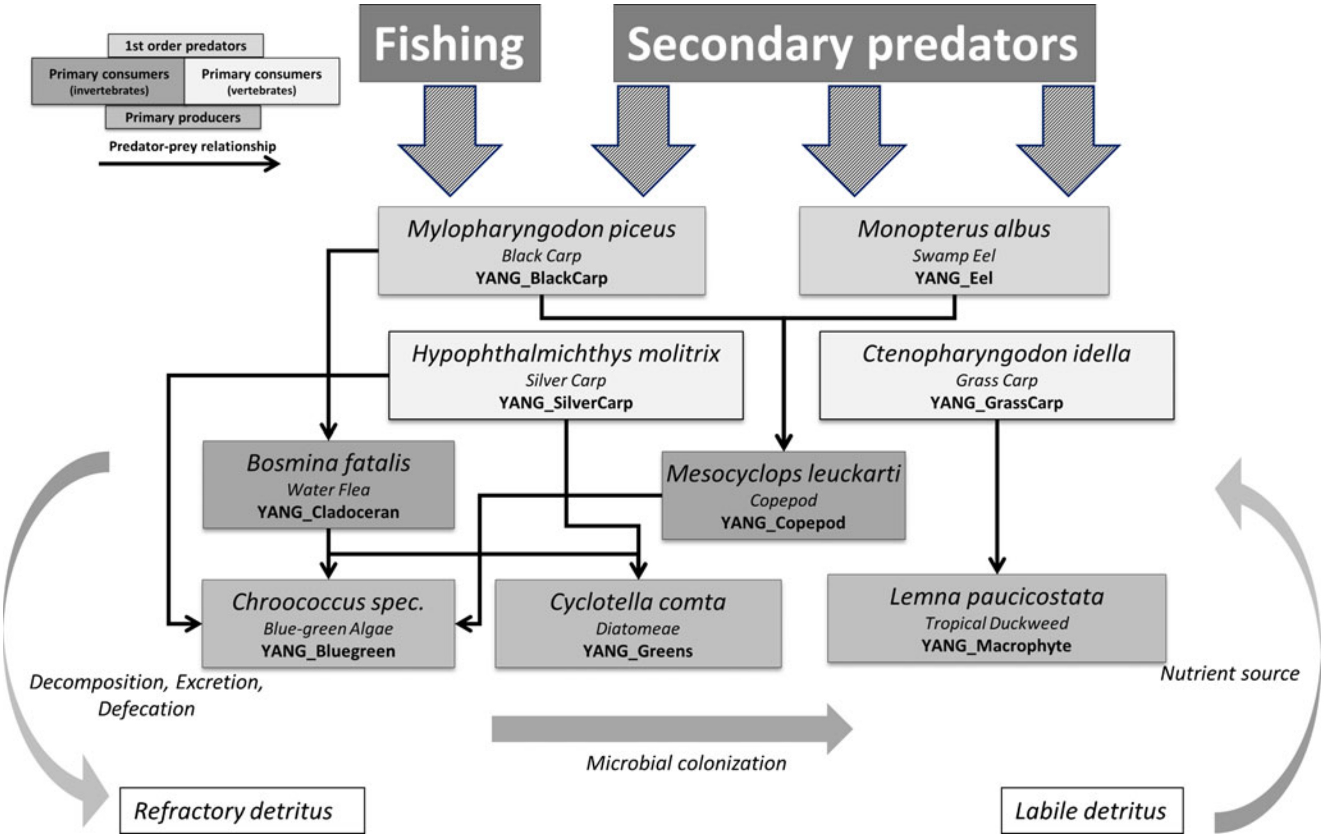

Fig. 7 The simplified "connectedness" food web of the reservoir simulation as implemented in the AQUATOX model. *Arrows* point from predators to prey

Yangtze River and its tributaries has been acquired. For each of the taxonomic groups and for each of the pollution scenarios, one representative has been chosen and implemented into the AQUATOX simulations. The green algae are represented by *S. arctuatus*, the diatoms by *Cyclotella comta* (reservoir scenario) and *Melosira granulata* (river scenario). The surrogate species for the group of cyanobacteria that cause particular problems in the region associated with progressing eutrophication are *Microcystis* sp. (river scenario) and *Chroococcus* sp. (reservoir scenario) (Kawanabe 1996). In the food web, the algae are fed upon by phyto-planktivorous fishes, e.g., silver carp and by invertebrates (Liu and Wang 2008; Calkins et al. 2012). The macro-herbivorous grass carp needs macrophytes, in this case *Lemna paucicostata* in its diet.

Zooplankton and molluscs

Zooplankton organisms are chosen by their occurrence in the lakes and rivers of the study area as well as by the food preferences of the fishes. One surrogate species that can stand for the focused taxonomic groups has been integrated in the model food webs. The cladocerans *Daphnia magna* (river scenario) and *Bosmina fatalis* (reservoir scenario) serve as food for the zooplanktivorous fishes (Kawanabe 1996). *Corbicula fluminea* is a common mollusc species in the study area (Xia et al. 2006). Additionally, insect larvae (*Chironomus* sp.) and copepodes (*Mesocyclops leuckarti*) are introduced as food, e.g., the swamp eel (Yang et al. 1997).

Interactions

After identifying surrogate species for the set up of the specific food webs "river" and "reservoir," predator–prey relationships and food intake rates have been estimated from literature (e.g., Cui et al. 1992). The grass carp has been artificially introduced in the past into Chinese surface waters to reduce the densities of macrophytes (Kirkağac and Demir 2006; Krupska et al. 2012). For this reason, in our approach it is assigned to feed exclusively on the macrophyte *L. paucicostata*. Several studies have shown that silver carps feed on more than one trophic level and the species has already been deployed to control algal growth in experimental ponds (Kocovsky et al. 2012; Calkins et al. 2012). This information is used to connect the silver carp to the trophic levels of primary producers and

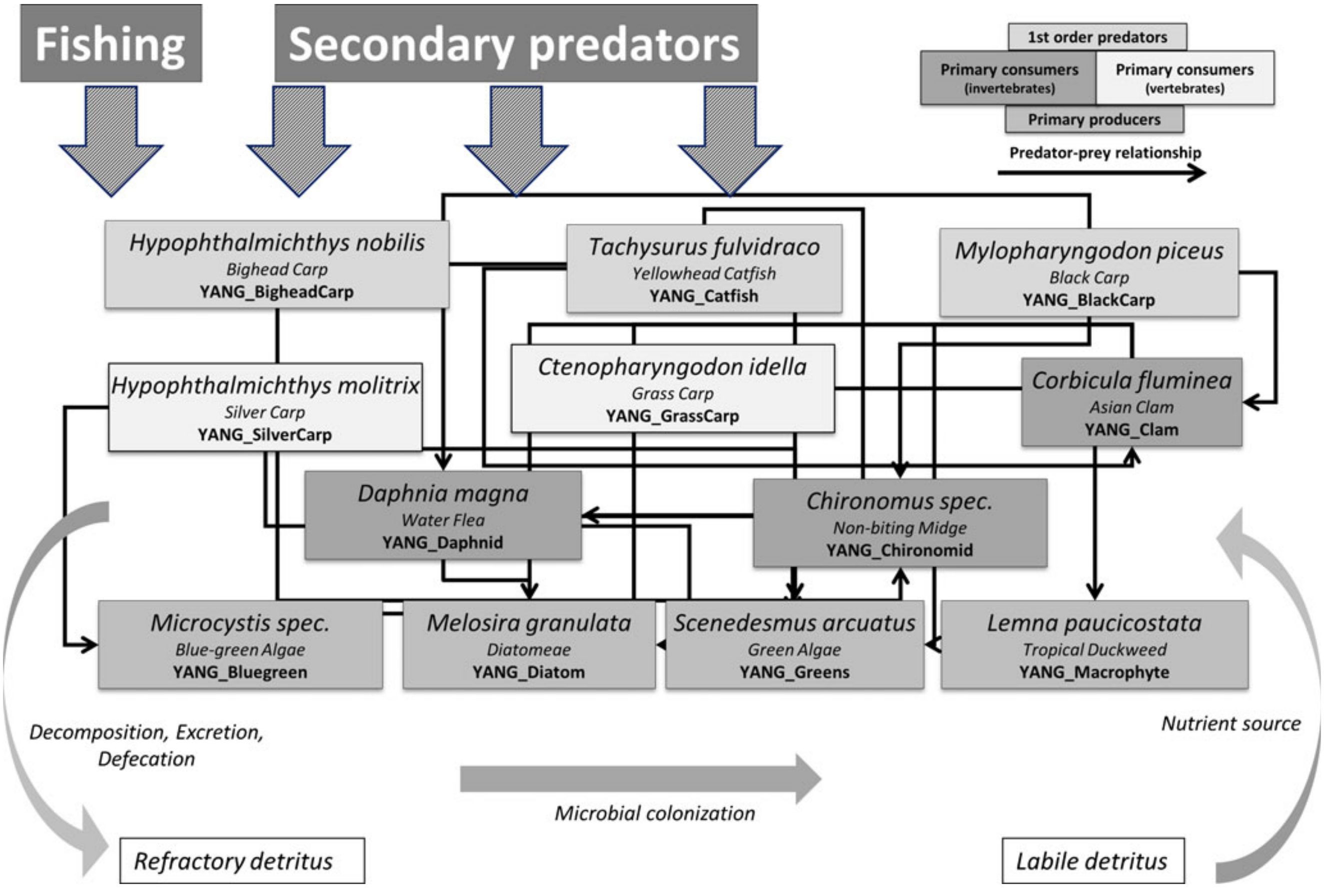

Fig. 8 The simplified “connectedness” food web of the river simulation as implemented in the AQUATOX model. *Arrows* point from predators to prey

primary consumers within the food webs. The bighead carp shows a similar behavior as it is feeds on zooplankton organisms also. However, alternatively it can use phytoplankton and cyanobacteria as food sources in case of zooplankton deficiency (Kocovsky et al. 2012; Zhou et al. 2009). The black carp mainly feeds on mussels and molluscs. At some places, it is used as a pest control against molluscs (Wui and Engle 2007). *T. fulvidraco* feeds mainly on mussels and bottom-bound insect larvae (trichopterans, chironomids, referred to Froese and Pauly 2012). The carnivorous swamp eel feeds on worms and crustaceans, in our model represented by the copepod *M. leuckarti* (Yang et al. 1997). A complex detrital side chain is implemented in the model. Physiological parameters that could not be estimated from literature data are taken from the original AQUATOX model environment for similar closely related species.

Bioaccumulation and ecotoxicity

The chemical properties of the model substance, as well as the (initial) concentrations of the pollutants (propanil and its metabolites) have been described according to the procedures of module EXM. The way how pollutants enter the (species) components of food webs, how they distribute

Table 3 Characteristics of fish species represented in the food webs of the river and reservoir simulation scenarios

Species	Habitat	Food preferences
Ctenopharyngodon idella (grass carp)	Litoral zone	Herbivorous (macrophytes)
Hypophthalmichtys molitrix (silver carp)	Upper water layer	Phyto- and zooplanktivorous
Hypophthalmichtys nobilis (bighead carp)	Upper water layer	Phyto- and zooplanktivorous
Mylopharyngodon piceus (black carp)	Deeper water layer	Molluscs
Tachysurus fulvidraco (yellowhead catfish)	Bottom layer	Molluscs and insects
Monopterus albus (Asian swamp eel)	Bottom layer	Worms and crustaceans

within the organisms and how they are eliminated from the tissues, crucially affects the biomagnification on the organism level in the module Toxic effects from the ETM module can veil the bioaccumulation procedures of BAM and reduce the individual fitness of the focused species.

BAM—bioaccumulation

The bioaccumulation mainly depends on the chemical properties of the model substances, mainly the octanol–water coefficient (log K_{OW}) and the organism-specific routes of exposure and uptake. Park and Clough (2010) estimated the bioaccumulation by empirical regressions, which highly depends on the lipid content of an organism and varies greatly between algae, detritus, macrophytes, invertebrates, and fish. Under *steady-state conditions*, the AQUATOX model uses bioconcentration factors BCF (synonym: bioaccumulation factor BAF) to describe the partition between the organism tissues and the surrounding water. These factors are in particular used here to describe the internal toxicity of pollutants in aquatic organisms. Empirical regression equations and the log K_{OW} serve as the predictors of bioaccumulation. The coefficients are taken from literature, or they are calculated by the AQUATOX model based on the chemical properties of the model substances. The partition coefficients for detritus are estimated based on assumptions by Abbott et al. (1995) and Schwarzenbach et al. (1993). The partition coefficients used in AQUATOX for macrophytes and algae are taken from Gobas et al. (1991) and Koelmans and Heugens (1998), respectively. Coefficients for invertebrates are derived from Southworth et al. (1978) and Lyman et al. (1982). In the case of short exposure times, no equilibrium can be assumed and thus no steady-state partition coefficients are used but the kinetic processes are modeled. In our studies, we focus on the bioaccumulation in fish. Uptake pathways via gills and diet are considered by the model, using respiration and ingestion rates. The basic equations for fishes are taken from Park and Clough (2010).

ETM—ecotoxicity

The MICROTOX project focuses on the herbicidal model substance propanil. The ecotoxicological properties of the parent and its metabolites 3,4-DCA and TCAB are evaluated because of their relevance for the environmental risk assessment (propanil and 3,4-DCA) and the assumptive persistence (TCAB). While 3,4-DCA is very well described and a number of data are available in the public domain, studies on propanil have been mainly filed in the context of the Annex-I inclusion during the registration process of propanil for the use as a herbicidal substance in the European Union. For the estimation of toxic effects from exposure to propanil, 3,4-DCA and TCAB, the most sensitive endpoints have been taken from the DAR of propanil (Ministry of Health of Italy 2006; Table 4). The rationale behind the choice is not to find the most relevant effect concentration regarding taxonomical or distributional characteristics of the species that are found to fit our Yangtze food web but to depict a worst-case threshold. In case the pollution scenarios deliver very high concentrations, it is assumed that complete extinctions of sensitive species could occur. As propanil inhibits the photosynthesis of higher plants and algae (disruption of Hill's reaction as herbicidal mode of action, Corbett et al. 1984), it is expected that aquatic plants, algae or macrophytes are the most sensitive species. Some different modes of action of 3,4-DCA are known from human risk assessments, referring to in vitro and in vivo experiments with mammals other than humans. Beyond its unspecific polar narcotical mechanism of action, it acts as an antagonist of the androgynous receptor of rats, thus being an endocrine disruptor (Cook et al. 1993). A further specific mechanism of action of 3,4-DCA is the formation of methaemoglobin based on hydroxylated compounds (compare, e.g., Lenk and Sterzl 1984).

Outlook

Improvement of scenarios

The simulation environment will be improved in the future for all modules of the integrative modeling approach. Further regionalization, e.g., by using real initial biomasses other than the default assumptions (validated scenarios of "Cheney Reservoir" and "Rum River"), will be achieved in cooperation with sub-projects of the German Yangtze environmental program and the Chinese project partners. Up to now, initial algal biomasses are derived from measured chlorophyll *a* concentrations using the empirical relationships described by Desortova (1981). Nevertheless, consultations with Chinese experts at a project related workshop in Shanghai 2012 already revealed the high degree of accuracy and relevance of the abstracted food webs, which contain surrogate species for trophic guilds.

In the course of further studies, we will also broaden the sub-model implementation beyond the scope of the data included in the manuscript at hand. For example, the spatial distribution of tracer particles, predicted by the particle transport module (PTM), will be used to provide spatially explicit information about the distribution of pollutants within the water bodies. Tracer particles thereby represent detritus particles or plankton organisms that are subjected to passive drift even under the new and reduced TGR flow conditions and thus constantly loaded with organic (model) substances. Using this approach, we are able to describe the

Table 4 Toxicity endpoints for aquatic species relevant for the toxicity of individual surrogate species of the "river" and "reservoir" scenarios and for ERA of the model substances propanil, 3,4-DCA and TCAB

Test species	Endpoint	Effect measure (exposure period)	Effect concentration	Unit
Propanil				
Acute				
Cyprinodon variegatus (sheepshead minnow)	Mortality	LC_{50} (96 h)	4.6	mg/L
Navicula pelliculosa	Growth rate	EC_{50} (72 h)	0.025	mg/L
Anabaena flos-aquae	Growth rate	EC_{50} (96 h)	0.070	mg/L
Lemna gibba	Growth rate	EC_{50} (14 days)	0.11	mg/L
Daphnia magna	Immobilization	LC_{50} (48 h)	6.7	mg/L
Long term				
Pimephales promelas (fathead minnow)	Weight and length of fry	NOEC (35 days; early life stage)	0.019	mg/L
Daphnia magna	Immobilization	NOEC (21 days)	0.086	mg/L
Chironomus riparius	Emergence	NOEC (28 days; full life cycle (spiked sediment))	16	mg as/kg dw sediment
C. riparius	Emergence	NOEC (28 days; full life cycle (spiked water))	1.9	mg/L
3,4-DCA				
Acute				
Oncorhynchus mykiss (rainbow trout)	Mortality	LC_{50} (96 h)	1.9	mg/L
D. magna (water flea)	Immobilization	LC_{50} (48 h; acute)	0.012	mg/L
Pristina longiseta	Mortality	LC_{50} (96 h)	2.5	mg/L
Phaeodactylum tricornutum	Growth rate	E_rC_{50} (96 h)	0.45	mg/L
C. riparius	Growth and mortality	LC_{50} (10 days)	450	mg/kg dw sediment
Long term				
Peocilia reticulata (guppy)	Number of offspring in F1	NOEC (42 days)	<0.002	mg/L
Ceriodaphnia quadrangula	Reproduction	NOEC (21 days)	0.002	mg/L

Data taken from Ministry of Health of Italy (2006). For results of QSAR estimations for the propanil metabolite TCAB, refer to Table 1

toxic effects of model pollutants on populations and aquatic communities. The realistic worst-case exposition is estimated in the EXM and can flexibly be used to conduct dose–response experiments using simulation output data. First numerical experiments reveal that the surface water concentrations vary between very low loads, in particular at sites where the pollutants are suspected to be diluted, to very high concentrations in scenarios where heavy overuse is assumed and the water is stagnant.

Statistical analysis of simulation outputs

After completion of scenarios and running the final simulations (according to Fig. 3), the output of simulations will be analyzed statistically (Fig. 9). The effects on populations will be described by univariate test statistics, e.g., by fitting dose response curves and deriving EC_{50} effect concentrations. Multivariate statistics will be used to calculate community-based effect thresholds from the time series, e.g., by principal

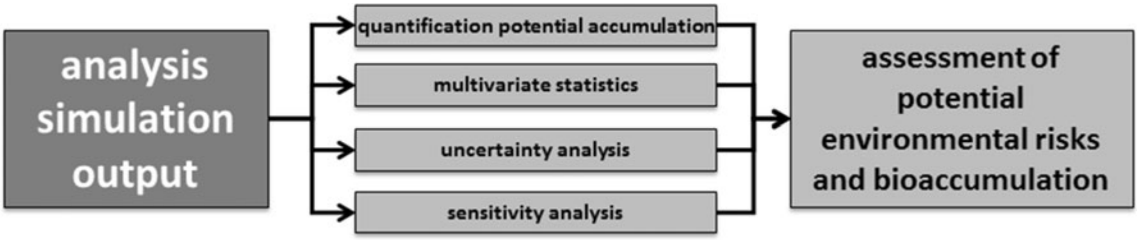

Fig. 9 Analysis of the model output. Workflow of bioaccumulation studies. A step-wise procedure for the definition of necessary input data to conduct sound simulation experiments is established

response curve analysis (Van den Brink and Ter Braak 1999). Furthermore, the AQUATOX model provides the opportunity to estimate uncertainties of simulation outputs and to quantify the most sensitive variables within the model. Using sensitivity analysis, the hypothesis that altered nutrient regimes or flow conditions of the newly built TGR severely and significantly affect the composition of the aquatic communities and the bioaccumulative processes will be tested. The food web will be further analyzed according to the proposal of Preziosi and Pastorok (2008).

Specification of ecological and human risk assessment

The indicators of environmental and consumer risks from the model pollutants will be further defined in RAM. This includes the definition of risk management measures, suitable for the overall aims of the Yangtze-Hydro environmental program, i.e., giving purposeful recommendations for the melioration of the TGR's water quality where appropriate. At this stage of our studies, it can already be stated that the criteria and parameters used in the model are suitable to distinguish between realistic ecological, toxicological and hydrological scenarios for the TGR situation possibly posing risks to communities of aquatic organisms as well as to consumers. Having finally identified the most critical scenarios, our approach can be used to recommend specific management actions to reduce the pollution loads in sensitive areas, e.g., by the prevention of pesticide overuse and establishment of waste water treatment plants. Furthermore, the emphasis of the risk assessment procedures is on concrete recommendations for consumers, e.g., to give advice how to avoid excess exposure by high pollutant burdens of food, especially fish.

In case of exceeded triggers, appropriate risk management measures will be subjected. In the above context, the use of internal concentrations in the AQUATOX program enables to calculate probabilities of toxic effects and risk.

The potential bioaccumulation of important food sources (e.g., the "Chinese carps") will be compared with ADI for chronic exposure as deduced from the ERA of the model substance propanil and its metabolites under the different pollution scenarios and under the regulation 91/414/EEC regarding the registration of plant protection products in the European Union. Finally, risk maps of a regarded region will be drawn based on time series data from the PTM.

Integrated environmental modeling

The integrated modeling approach can be described as a hybrid model as it combines and couples several methodologies under the AQUATOX framework. The modules are either of general static nature and defined by expert knowledge to provide suitable input values for existing submodel structures (e.g., species composition and interaction matrices within the food web model), spatially explicit and dynamical (like the hydrodynamic model providing time-variant flow conditions as simulation input) or theory-based and mechanistic (e.g., the bioaccumulation model to calculate the uptake). They are also statistical and probabilistic (like the regression or classification-based QSAR models within the ecotoxicological model to estimate chemical properties of metabolites) or synthetic (like the risk assessment module).

As this modeling approach combines theoretical models, empirical data, and expert knowledge to describe the TGR ecosystem, it is in accordance with the concept of IEM, which is of increasing importance in modern environmental management and decision-making (Jopp et al. 2011). It allows for the interpolation of information on ecosystem behavior on a local level, as well as for the extrapolation and transfer of results to other locations, to different scenarios and into the future.

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